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Impurity paramagnetic centers in a single crystal of zinc tungstate doped with thulium

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A thulium-doped ZnWO₄ crystal grown by the Czochralski method was studied by using the EPR method at room temperature. Accidental impurities of paramagnetic ions Fe³⁺, Mn²⁺, Cr³⁺, and Gd³⁺ were found in the crystal. Trivalent ions are represented by both single monoclinic centers and triclinic dimeric associates. Spin Hamiltonians of all observed centers were constructed, providing a reasonably good description of the experimental results. The concentration ratios of these centers were also estimated.

Keywords: zinc tungstate, impurity ions, iron group, REE, paramagnetic resonance.

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Introduction

Interest in zinc tungstate (ZnWO₄) is driven by its unique properties such as high scintillation efficiency [1–3], thermal and radiation stability, fairly good heat conductivity [4] and mechanical strength properties [5], possibility of growing from melt by the Czochralski method [2–6], and high moisture resistance. Due to these properties it is widely used in high-energy physics, space research, industry and medicine as an ionizing radiation detector [7,8]. Study of the ZnWO₄ crystal is also associated with prospects of its future use as a cryogenic scintillation rare-event detector [1,9].

Moreover, ZnWO₄ crystals doped with various rare-earth ions (REI) are extensively investigated as promising laser crystals [6,10–13]. They are characterized by high Stark splitting of the REIs ground state, high peak cross-sections and considerable inhomogeneous broadening of spectral bands [6,10]. This is very convenient for semiconductor diode pumping of lasers based on these crystals and for ultrashort mode-locked lasing and achievement of smoothly frequency tunable lasing. For Tm³⁺ ions, large Stark splitting also allows lasing in a range beyond 2 μm [10,12], which is especially relevant for applications in medicine and gas analysis.

To achieve all the above-mentioned goals, large, high-quality and optically homogeneous zinc tungstate crystals with high light yield and low intrinsic radiation background as well as high concentrations of dopants and uniform

dopant distribution throughout the sample volume are required.

At the same time, heterovalent introduction of large rare-earth ions into the structure of this crystal presents significant challenges. First, the substantial difference in sizes, formal charge and chemical nature between substituting and substituted ions negatively affects the distribution coefficient of the dopant ion between the crystal and the melt [5,6,10,13–15] and potential achievement of highly doped crystals with desired optical quality. The second difficulty lies in the fact that introducing REI activators without charge compensators leads to a sharp deterioration in the mechanical strength of the crystals [5]. This can be easily explained by the formation of a significant number of zinc vacancies in the absence of intentionally introduced compensators [13], which weakens the crystal lattice. Investigation of defects formation behavior in the ZnWO₄ crystal with introduction of rare-earth activators opens the way for the targeted development of techniques facilitating the introduction of considerable concentrations of these activators into the crystal without loss of optical quality and reduction of sample strength.

Hypersensitivity of spectral and scintillation properties even to the smallest amounts of accidental 3d-ion impurities, in particular, Fe, is one more important feature of the ZnWO₄ crystal. Even small concentrations of impurities such as tenths of ppm give a significant parasitic optical absorption of the crystal in a spectral range from 600 nm to

Table 1. SH parameters of monoclinic FeI and Mn^{2+} centers in ZnWO_4 at room temperature (b_{2m} , b_{4m} and A_i in MHz)

Description	FeI in the principal axes of tensor D [19]	Mn^{2+} in the principal axes of tensor D [20]*	Mn^{2+} in the principal axes of FeI center, this work*	Mn^{2+} in the principal axes of tensor D, this work*
g	2.0019	2.003	2.005	2.005
$b_{20} = D$	−20961	6288	5809	−6540
$b_{22} = 3E$	14805	4555	−7272	5077
b_{40}	196	28	−146	−97
b_{42}	−107	—	521	716
b_{44}	−1038	—	181	−160
A_x	—	250	−249	−245
A_y	—	248	−248	−248
A_z	—	243	−245	−249

Note. * Signs of b_{nm} are relative.

a short-wavelength edge of the material transparency window, significant shift of this edge toward longer wavelengths a reduction in luminescence intensity [16], and a decrease in scintillation light yield [17,18]. Therefore, it is of high importance to develop effective methods for controlling the concentrations of these ions in the ZnWO_4 crystal.

Electron paramagnetic resonance (EPR) is highly effective for investigating the structural localization of REI activators in crystals taking into account the defects that are formed during heterovalent introduction of the activators and compensate excess charge. Moreover, EPR is an effective method for detecting trace concentrations of accidental 3d-ion impurities in crystals. There are a number of works [19–27] addressing the investigation of EPR in zinc tungstate doped with Fe and REI group ions.

Thus, EPR measurements of the Fe-doped ZnWO_4 crystal in the frequency range of 8–70 GHz, reported in [19] showed that the sample contained monoclinic centers with spin $S = 5/2$ resulting from the substitution of Zn^{2+} sites by Fe^{3+} ions (electronic configuration $\text{Ar}3d^5$, ground state $^6S_{5/2}$) with non-local charge compensation. It was detected that the local (principal) magnetic z-axis of this center is rotated by 45.2° from the crystallographic $+a$ direction toward the $+c$ direction. Spin Hamiltonian (SH) parameters in the principal coordinate system (CS) at room temperature obtained in [19] are listed in Table 1.

EPR spectra of Mn-doped ZnWO_4 crystals at 10 and 40 GHz and room temperature were studied in [20]. Monoclinic centers of Mn^{2+} ions ($3d^5$, $^6S_{5/2}$) with electron and nuclear spins $S = 5/2$ and $I = 5/2$, respectively, were detected. Analysis of resonance positions of hyperfine structure (HFS) components in two extreme magnetic field orientations gave SH parameters, which are also shown in Table 1.

The authors of [21] measured the EPR spectra of $\text{ZnWO}_4\text{:Cr}$ crystals grown with lithium ions added to the melt to compensate the excess charge of trivalent chromium ions. The detected Cr^{3+} center ($3d^3$, 4F) was described by rhombic SH with parameters listed in Table 2. The principal magnetic z axis of this center is rotated from the crystallographic $+a$ direction of the crystal to the $+c$ axis

Table 2. SH parameters of paramagnetic Cr^{3+} centers in ZnWO_4 in the principal axes at room temperature (b_{2m} and ZFS are given in GHz)

Parameters	CrI-center [21]	CrI-center, this work	Cr2, Cr3-centers [23]	Cr2, Cr3-centers, this work
g_x	1.958	1.956	1.962	1.957
g_y	1.962	1.966	1.950	1.962
g_z	1.968	1.962	1.967	1.965
$b_{20} = D$	25.47	25.49	+42.8	29.1
$b_{22} = 3E$	−7.26	−7.23	13.5	9.0
ZFS	≈ 51	≈ 51	≈ 87.4	≈ 59.0

by 4.2° . These results agree well with the data of [22] obtained on samples grown from flux. The samples grown without lithium addition demonstrated a more complex spectrum of Cr^{3+} that is probably induced by the presence of dimer centers $\text{Cr}^{3+}-V_{\text{Zn}}$.

Investigation of $\text{ZnWO}_4\text{:Cr}$ crystals (nominal chromium concentration in the melt is 0.1–0.5%) at 9.4 GHz and room temperature in [23] detected, besides the primary monoclinic chromium center (Cr1), also low-intensity EPR spectra of two pairs of triclinic Cr^{3+} centers (Cr2, Cr3 and Cr4, Cr5). Centers in each pair are related by the crystal symmetry operation $C_2 \parallel b$. For a pair of triclinic Cr^{3+} centers (Cr2, Cr3) that gives a more intense spectrum rhombic SH parameters were defined in the principal axes (Table 2). The absence of interdoubtlet transitions in the spectrum hampers the evaluation of zero-field splitting (ZFS), results of the investigation of the temperature behavior of spin-lattice relaxation time were used for this purpose. The authors of [23] suggest that these centers correspond to $\text{Cr}^{3+}-V_{\text{Zn}}$ associates. ZnWO_4 crystals with monoclinic Cu^{2+} centers ($3d^9$, 2D) and Co^{2+} ($3d^7$, 4F) were studied in [24,25].

There are also two studies investigating ZnWO_4 crystals doped with REI: thulium and gadolinium. Authors of [26] recorded a spectrum of Tm^{2+} ion ($\text{Xe}4f^{13}$, $^2F_{7/2}$) associated with Zn vacancy in zinc tungstate at low temperature.

Intensity of this spectrum grows rapidly after exposure of the sample to ultraviolet light. Gd^{3+} centers ($4f^7$, $^8S_{7/2}$) were studied and SH parameters in a local CS were obtained in [27].

This work starts a series of our system investigations of paramagnetic centers formed in REI-doped $ZnWO_4$ crystals using various charge compensators aimed to identify their impurity composition, valent state and structural localization of paramagnetic impurity ions. This study investigated a crystal doped only with thulium ions without any charge compensators or other deliberately introduced dopants.

1. Sample and experiment procedure

$Tm:ZnWO_4$ single crystal was grown by the Czochralski method. ZnO (purity 99.999% Anhui Toplus Impex Co., LTD, PRC), WO_3 (99.999% CAS # 12036-22-5, Lanhit, Russia) and Tm_2O_3 (99.99% thulium oxide, TU 48-4-524-90, p/o 485, former USSR) were used as reagents for preparing the initial charge. Nominal concentration of thulium introduced into the charge for crystal growth was 4 at.% with respect to zinc. Reagents were annealed for 5 h at $700^\circ C$ to remove residual moisture. The annealed reagents were accurately weighed on the „Ohaus AX523“ (OHAUS Adventurer, Switzerland) analytical balance and then mixed in the „Multi RS-60“ programmable multirotator for 5 h. Then the prepared mixtures were annealed in a muffle furnace at $700^\circ C$ during 8 h for solid-phase synthesis.

Crystal growth from the prepared charge was carried out in a 40×40 mm (diameter/height) platinum crucible using the Kristall-2 system in air. An undoped $ZnWO_4$ single crystal bar cut along the $[001]$ crystallographic direction was used as seed. Pulling/rotation rates were 1 mm/h and 6 rpm, respectively. After completion of the growth and separation of the grown boule from the melt mirror, the crystal was cooled down slowly at a rate of $8^\circ C/h$ to room temperature to reduce the cracking risk. The grown crystal was annealed additionally in air at $900^\circ C$ for 2 weeks for thermomechanical stress relieve and oxygen stoichiometry recovery followed by cooling down to room temperature at a rate of $8^\circ C/h$.

Crystal orientation with respect to the optical indicatrix axes N_p , N_m and N_g was determined precisely by straight-light observation through crossed polarizers using the Biomed-5 (LOMO, Russia) optical polarization microscope.

Concentration of Tm^{3+} in the crystal was measured by the inductively coupled plasma mass spectrometry (ICP MS) method on the iCAP 6300 duo (Thermo Scientific, USA) spectrometer using a set of multi-element standards (high purity standards). To make a probe, crystal samples were ground and dissolved in orthophosphoric acid (Suprapur, Merck) at a temperature of upto $400^\circ C$. Measured actual concentration of thulium in the crystal was 0.62 ± 0.03 at.% with respect to zinc.

Concentrations of accidental impurities were not measured in this work. However they were measured in our

previous work [16] for undoped $ZnWO_4$ crystals. A sample studied in this work was grown from the same ZnO and WO_3 reagents as the „reference crystal“ examined in [16]. According to these measurements, the „reference crystal“ contained accidental impurities: 0.7 wt. ppm of Fe, 0.15 wt. ppm of Cr, and 0.1 wt. ppm of Ni.

The measurement record also contains an entry regarding detection of 1 wt. ppm of Cu impurity, however this entry shall be treated with care: the mass spectrometry might well have mistaken ions of a corresponding light isotope of double-charged zinc, being a matrix component, for double-charged copper ions. Other accidental impurities detected in the „reference crystal“ sample in [16] are either non-paramagnetic or were detected in the crystal in very negligible amounts, less than 0.01 ppm.

The main source of the Gd^{3+} impurity in the $Tm:ZnWO_4$ sample studied in this work was apparently the Tm_2O_3 reagent that was used for synthesizing this sample, but wasn't used before in [16]. Concentration of Gd^{3+} detected in the „reference crystal“ was just 0.002 wt. ppm. Concentration of Mn in the „reference crystal“ sample [16] appeared to be lower than the detection limit of this element, which was equal to 0.05 wt. ppm.

Space group of $ZnWO_4$ — $P2/c$ (C_{2h}^4) № 13, lattice cell parameters $a = 4.69 \text{ \AA}$, $b = 5.72 \text{ \AA}$, $c = 4.92 \text{ \AA}$, $\beta = 90.6^\circ$ [28]. Both cations in the crystal are surrounded by six oxygen ions forming monoclinically distorted octahedra, local symmetry group of the Zn^{2+} and W^{6+} -positions— $2(C_2)$.

The orientation behavior of positions of EPR transitions of the studied centers in the $Tm:ZnWO_4$ sample was measured with magnetic field rotation in the $c - a$ and $Z(\text{loc}) - Y \parallel b$ planes using the EMX Plus Bruker X-band spectrometer at room temperature in magnetic fields up to 1.4 T. $Z(\text{loc})$ — is the Z axis of a local coordinate system, in which the second-rank tensor of the spin Hamiltonian of the corresponding center (Fe1, Cr1) becomes diagonal. The sample in a spectrometer resonant cavity was attached to a holder that was secured on a standard automatic goniometer rod and was able to rotate around the axis perpendicular to the rod.

The $ZnWO_4$ test sample doped with 0.62 at.% Tm was made in the form of $5.18 \times 5.36 \times 7.61 \text{ mm}^3$ rectangular parallelepiped with faces perpendicular to the optical indicatrix axes. Relation between crystallographic axes and optical indicatrix axes for $ZnWO_4$ is shown in [6]. In this work, local coordinate systems of the paramagnetic centers are defined with respect to the crystal's crystallographic axes [19,21].

The above-mentioned crystal dimensions were too large for implementing some crystal orientations with respect to a magnetic field in the available microwave cavity. Therefore, the sample was cut into two unequal parts (large and small). Measurements were performed in the $Z(\text{Fe1}) - X(\text{Fe1})$ plane and $Z(\text{Cr1}) - Y \parallel b$ plane on the small and large parts, respectively.

2. Results and discussion

Reported monoclinic Cr^{3+} centers (Cr1) [21,22], Mn^{2+} [20], Fe^{3+} [19] and Gd^{3+} [27] were observed and identified in the EPR spectrum of the $\text{ZnWO}_4\text{:Tm}$ crystal (hereinafter referred to as Fe1 and Gd1, respectively). Moreover, the following triclinic centers were identified: previously reported Cr2 and Cr3 [23] and two types of iron and gadolinium centers each, information about which is absent in the available literature. They are denoted as Fe2, Fe3, and Gd2, Gd3. Intensity ratio of transitions of some above-mentioned centers is illustrated by the spectrum shown in Figure 1.

It is known [17,29,30] that iron in the ZnWO_4 crystal is present not only in the trivalent, but also in the divalent state, in comparable amounts. The incorporation of Fe^{2+} into zinc sites is isovalent, the FeWO_4 crystal is isostructural with ZnWO_4 and the expected distribution coefficient of Fe^{2+} ions between the crystal and melt is close to unity. However, the EPR spectrum of Fe^{2+} is observed only at low temperatures and at high frequencies [31]. Divalent iron was not investigated in this work. The EPR spectrum of Tm^{3+} and of most REI is not observed at room temperature.

The quality of the description of the angular dependencies of the Fe1 center transition positions by SH with parameters specified in [19] is demonstrated in Figures 2, 3. Orientation behavior of the triclinic Fe2, Fe3 centers which transform into each other under the symmetry operation $C_2 \parallel \mathbf{b}$ of the crystal is also shown in Figures 2 and 3. EPR spectra of the Fe2, Fe3 centers are degenerate in the $Z(\text{Fe1})-\text{X}(\text{Fe1})$ plane, but differ considerably in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane (Figures 2, 3) and degenerate at $B \parallel \text{Y}$ and $B \perp \text{Y}$.

Spin Hamiltonian is an adequate model that takes into account both the symmetry and spin state of a paramagnetic center. Optimization of the SH parameters is based on the minimization of rms deviation of the calculated transition frequencies obtained by means of SH matrix diagonalization for each magnetic field orientation from the experimental frequencies. Diagonalization of the optimized SH matrix provides the energies and wave functions of all $(2S+1)$ states of the paramagnetic ion.

Optimization of the Fe2, Fe3 fine structure parameters was performed within SH described in [32]

$$H_{sp} = \beta(\mathbf{BgS}) + \frac{1}{3}(b_{20}O_{20} + b_{22}O_{22}) + \frac{1}{60}(b_{40}O_{40} + b_{42}O_{42} + b_{44}O_{44}), \quad (1)$$

where $\mathbf{g}$ is the $\mathbf{g}$ -tensor, β is the Bohr magneton, $\mathbf{B}$ is the magnetic field induction, O_{nm} are the Stevens spin operators, b_{nm} are the fine structure parameters, with additional $b_{nm}O_{nm}$ and $c_{nm}\Omega_{nm}$ terms (including odd projections) [32].

Since intradoublet transitions of the Fe2, Fe3 centers are quite close to the corresponding Fe1 signals, corresponding parameters of the Fe1 center were taken as the initial set of SH parameters for the optimization procedure. Parameters

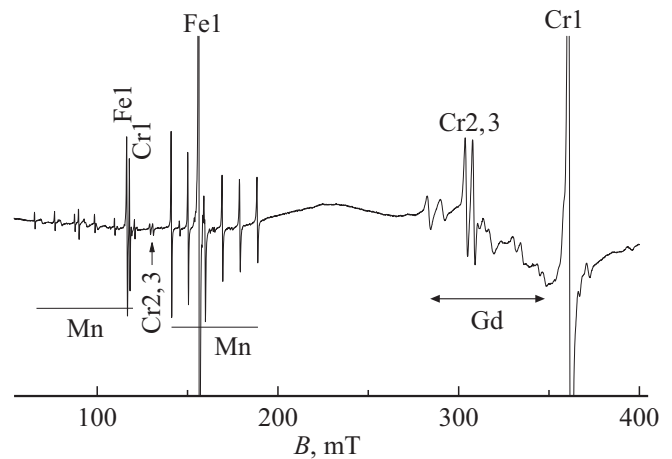


Figure 1. Fragment of the EPR spectrum (first derivative of the absorption spectrum) of the $\text{ZnWO}_4\text{:0.62\%Tm}$ crystal near $B \parallel Z(\text{Cr1})$ at 9650 MHz from the dependence in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane. Horizontal bars show the hyperfine structure fields of two electronic transitions of a monoclinic center of Mn^{2+} , and a segment with arrows shows the region where most of the transitions of the Gd1 center are observed.

optimized using the dependences in the $Z(\text{Fe1})-\text{X}(\text{Fe1})$ plane were converted into a local CS of the Cr1 center [21] for utilization of measurements in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane. Taking into account of the orientation behavior of the Fe2, Fe3 transition positions in two planes gave the following fine structure parameters in the Cr1 coordinate system (see the Introduction):

$$\begin{aligned} b_{20} &= -7030, b_{21} = 135930, b_{22} = 14090, \\ b_{40} &= 3160, b_{41} = 4960, b_{42} = 11320, \\ b_{43} &= -14020, b_{44} = 32380, c_{21} = \pm 9280, \\ c_{22} &= \pm 6640, c_{41} = \pm 86580, c_{42} = \pm 4260, \\ c_{43} &= \mp 113220, c_{44} = \pm 19140 \text{ MHz}, g = 2.000. \end{aligned} \quad (2)$$

Double signs of c_{nm} in (2) correspond to two sets of parameters for the Fe2 and Fe3 centers. Principal coordinate systems of tensor D of the triclinic Fe2 and Fe3 centers with $b_{20} = 37270$, $b_{22} = 29410$ MHz are linked to CS of the Cr1 center by the Euler angles $\alpha = \pm 7.1^\circ$, $\beta = 52.5^\circ$, $\gamma = \pm 85.3^\circ$.

Note that parameters (2) derived taking into account the orientation behavior of only intradoublet transitions 1-2, 3-4 and 5-6 are not intended for full description of the fine structure of these centers, including ZFS.

Azimuthal angular dependence of EPR positions of Mn^{2+} in the studied $\text{ZnWO}_4\text{:Tm}$ crystal is shown in Figure 4. Fine and hyperfine structural parameters of the Mn^{2+} centers were determined using SH (1) with an additional term

$$(\mathbf{SAI}), \quad (3)$$

where $\mathbf{A}$ is the hyperfine interaction tensor, $\mathbf{I}$ is the nuclear spin.

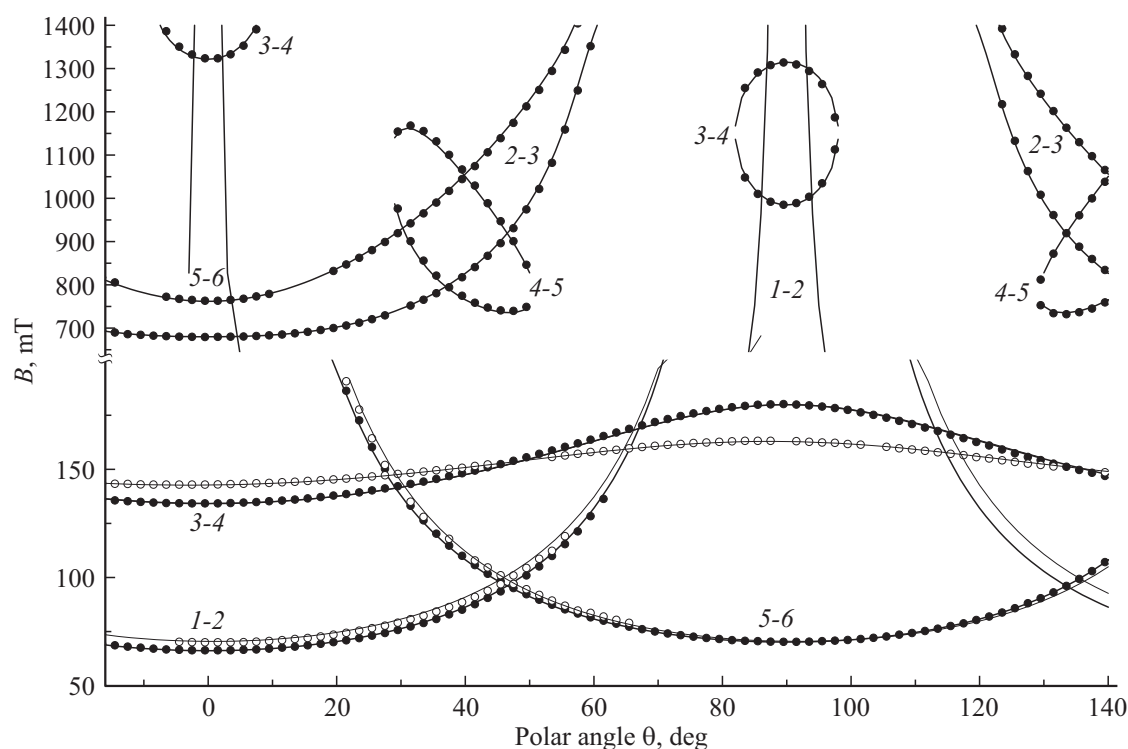


Figure 2. Orientation behavior of transition positions $i-j$ of the monoclinic Fe1 center (solid circles) and triclinic Fe2, Fe3 (open circles) in the $Z(\text{Fe1})-X(\text{Fe1})$ plane at 9126 MHz. Circles — our experiment, curves — calculation with parameters (2) and [19] in Table 1.

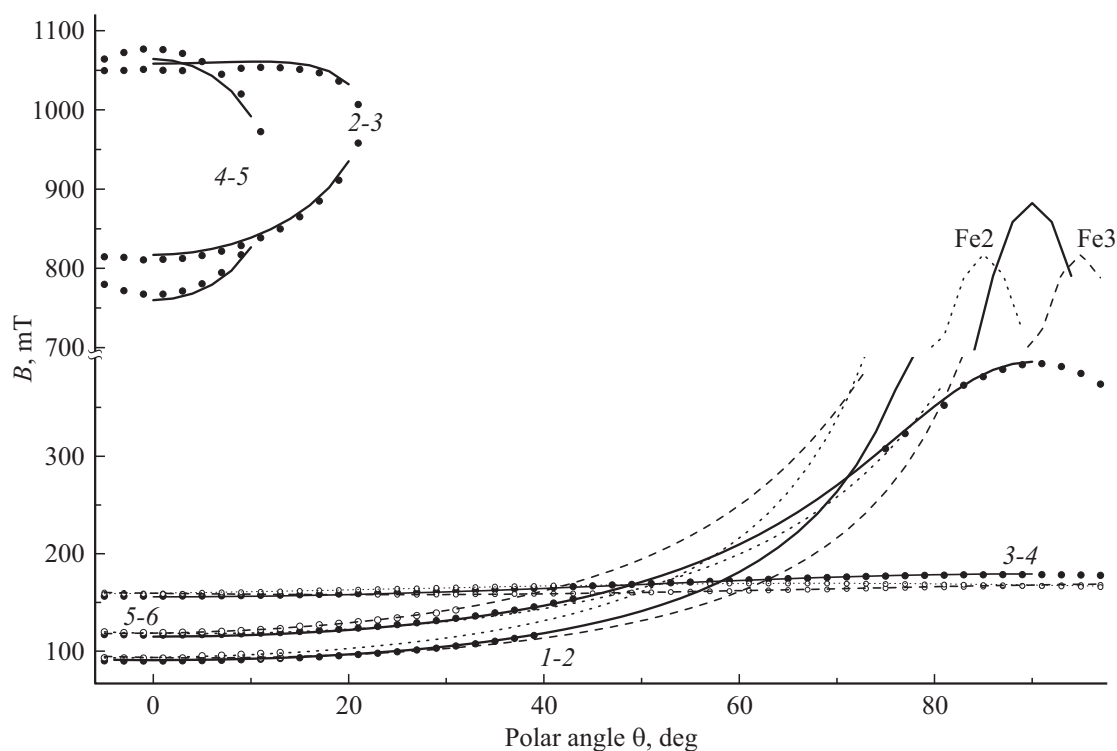


Figure 3. Polar angular dependence of transition positions $i-j$ of the monoclinic Fe1 center (solid circles) and triclinic Fe2, Fe3 centers (open circles) in the $Z(\text{Cr1})-Y \parallel \mathbf{b}$ plane at 9630 MHz. Circles — experiment, curves — calculation with parameters (2) and [19] in Table 1.

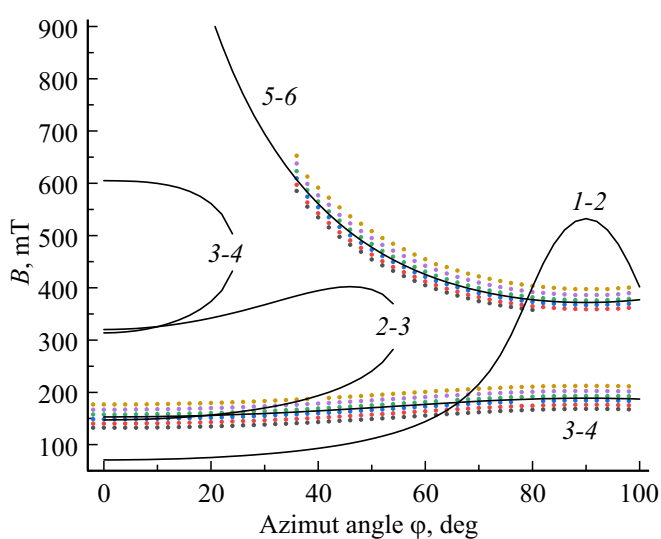


Figure 4. Azimuthal angular dependence of resonance positions $i-j$ of the Mn^{2+} centers in the Tm:ZnWO_4 crystal at 9825 MHz in the $X(\text{Fe1})-Y \parallel \mathbf{b}$ plane. Circles — our experiment, curves — calculation with parameters listed in Table 1 without considering the hyperfine interaction.

Utilization of 1348 HFS component positions in the ZX, ZY and XY planes gave rise to values in Table 1 in the local CS of the Fe^{3+} centers (Fe1) with rms deviation between calculated and experimental frequencies of 47 MHz. In this coordinate system, tensor D of the monoclinic Mn^{2+}

center is diagonal (Table 1), but doesn't meet the standard requirement $|b_{20}| > |b_{22}|$ [33]. However, CS rotation about $Y \parallel \mathbf{b}$ at 90° leads to diagonal tensor D (Table 1) that meets this requirement. Azimuthal angular dependence of resonance positions Mn^{2+} demonstrating the spectrum description quality is shown in Figure 4. Probability of transitions 1-2, 2-3 and high-field signals 3-4 is close to zero.

Significant difference of the obtained SH parameters of the Mn^{2+} centers from the data given in [20] (Table 1) is most likely caused by the fact that study [20] uses HFS component positions only in two orientations with extremal values of resonance fields. Hyperfine interaction parameter of Mn^{2+} , according to [34], has the minus sign.

Figures 5,6 show the polar angular dependences of signal positions of the monoclinic Cr^{3+} center (Cr1) and triclinic Cr2, Cr3 centers in zinc tungstate. Optimization results for the Cr1 fine structure parameters in principal axes without taking into account the last term of Hamiltonian (1) using 268 resonance fields with an rms deviation of 32 MHz are listed in Table 2. It is seen that they agree well with the values of SH parameters from [21]. The angle between the Z-axes of the Cr1 and Fe1 centers (Figure 5) in local CSs is $+40^\circ$, and $45.2-4.2 = 41^\circ$ according to [19,21] (see the Introduction).

As in the case of Fe2 and Fe3, angular dependences of the triclinic Cr2, Cr3 positions in the $Z(\text{Fe1})-X(\text{Fe1})$ plane coincide (Figure 5). In the $Z(\text{Cr1})-Y \parallel \mathbf{b}$ plane (Figure 6), extrema of the dependences of transitions 1-2 of the Cr2, Cr3 centers are separated by approximately 42° .

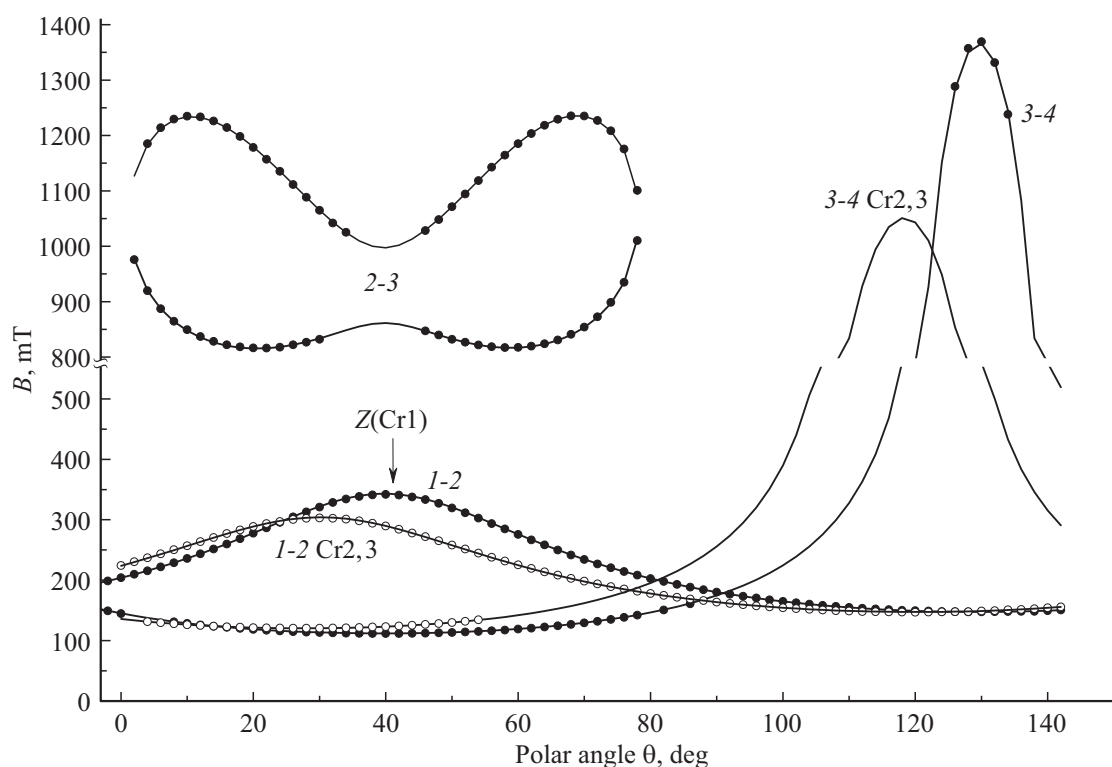


Figure 5. Orientation behavior of transition positions $i-j$ of the monoclinic Cr^{3+} center (Cr1) and triclinic Cr2, Cr3 centers in the $Z(\text{Fe1})-X(\text{Fe1})$ plane at 9126 MHz. Circles — experiment, curves — calculation with parameters of this work (Table 2).

Table 3. SH parameters of monoclinic Gd^{3+} (Gd1) centers in ZnWO_4 at room temperature (values of b_{nm} are given in MHz). It is assumed that parameters in [27] were obtained for SH with notations of [32]

Parameters	In Fe1 center CS, this work	Z c, this work	In the principal axes of tensor D, this work	In the principal axes of tensor D [27]
g	1.991	1.991	1.991	≈ 1.97
$b_{20}=\text{D}$	1398	1701	1872	1778
b_{21}	-3513	2292	0	0
$b_{22}=3\text{E}$	1877	1574	1409	1335
b_{40}	17	-57	-1.7	-38
b_{41}	-282	320	377	36
b_{42}	-263	-35	-223	76
b_{43}	264	-28	-156	374
b_{44}	-324	-330	-310	225

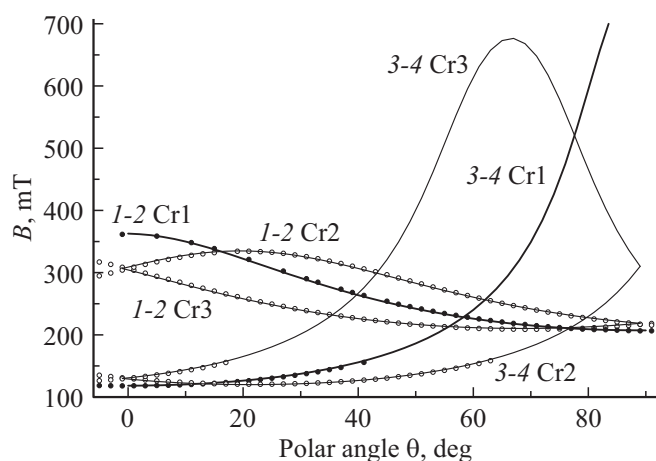


Figure 6. Angular dependence of transition positions $i-j$ of the monoclinic Cr1 center and triclinic Cr2, Cr3 centers in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane at 9630 MHz. Circles — experiment, curves — calculation with parameters of this work (Table 2).

At X-band frequencies, interdoublet transitions signals of the Cr2, Cr3 centers were not observed neither in this work nor in [23]. Information only about the behavior of intradoublet transitions 1-2 and 3-4 (Figure 5,6) cannot be used to determine the magnitude of zero-field splitting. In order to do it, the authors of [23] use the temperature behavior data of the spin-lattice relaxation time and conclude that ZFS of the Cr2 and Cr3 centers is approximately 87.4 GHz.

The SH parameters listed in Table 2 correspond exactly to such splitting [23]. The determined SH parameters of the Cr2, Cr3 centers (Table 2) correspond to the minimum rms deviation (9.7 MHz) in the optimization procedure with variation of the initial b_{20} within 18–43 GHz. The optimization was performed in the Cr1 coordinate system using 270 resonance fields in the $Z(\text{Cr1})-\text{X}(\text{Cr1})$ and $Z(\text{Cr1})-\text{Y}$ planes. The following parameters were obtained: $b_{20} = 22.0$, $b_{21} = -32.9$, $b_{22} = -12.1$, $c_{21} = \mp 51.9$, and $c_{22} = \pm 8.9$ (GHz). Double signs correspond to the Cr2 and Cr3 centers. Euler angles relating the principal CS of

the Cr2, Cr3 centers to the Cr1 coordinate system are as follows: $\alpha = \pm 242^\circ$, $\beta = 25^\circ$, $\gamma = \pm 199^\circ$. It is seen that β is close to the angle (24.8°) between $Z(\text{Cr2}, \text{Cr3})$ and the $\mathbf{a}$ crystallographic axis shown in [23].

As already said in the beginning of this section, small EPR signals of the Gd^{3+} centers (Gd1) are observed in the studied crystal. Polar angular dependence of transition positions of the monoclinic Gd^{3+} center in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane is shown in Figure 7. Optimized SH parameters in the Fe1 CS with an rms deviation of 18 MHz taking into account 632 resonance fields (Figure 7) are shown in Table 3.

The transformation from Fe1 CS to the local coordinate system of the tensor D of the Gd1 centers (Figure 8, Table 3) occurs via a rotation of -28.3° around the crystallographic $\mathbf{b}$ axis. It should be noted that, a transition axes non-coincidence effect is observed in the Gd1 spectrum due to its low symmetry and high spin (Figure 8) [35,36]. The principal axes of the fourth-rank fine structure tensor were not determined due to large uncertainties in the obtained parameters.

To compare the observed spectrum of Gd1 with the data of [27], orientation behavior of the Gd1 transitions in the $\mathbf{ac}$ and $\mathbf{bc}$ planes (Table 3) was calculated at a frequency close to that used in [27]. The obtained angular dependences of the transition positions in the $\mathbf{bc}$ plane (Figure 9) appeared to be close to the curves shown in Figure 3 in [27] that are assigned to the $\mathbf{ac}$ plane. Thus, regardless of the above discrepancy, it is suggested that the matter concerns the same gadolinium center.

Like for the paramagnetic Fe and Cr centers, in the neighborhood of most of the Gd1 transitions, at the angular dependence ($Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$) weak satellites are seen (Figure 7) that split when moving away from $B \parallel \mathbf{b}$ and shall be assigned to the Gd2, Gd3 transitions with local excess charge compensation that have a triclinic symmetry. Due to the low intensity, behavior of these signals can be traced only in the range of 35° .

Optimization of SH parameters (1) of the triclinic Gd2, Gd3 centers with an additional parameter of the zero

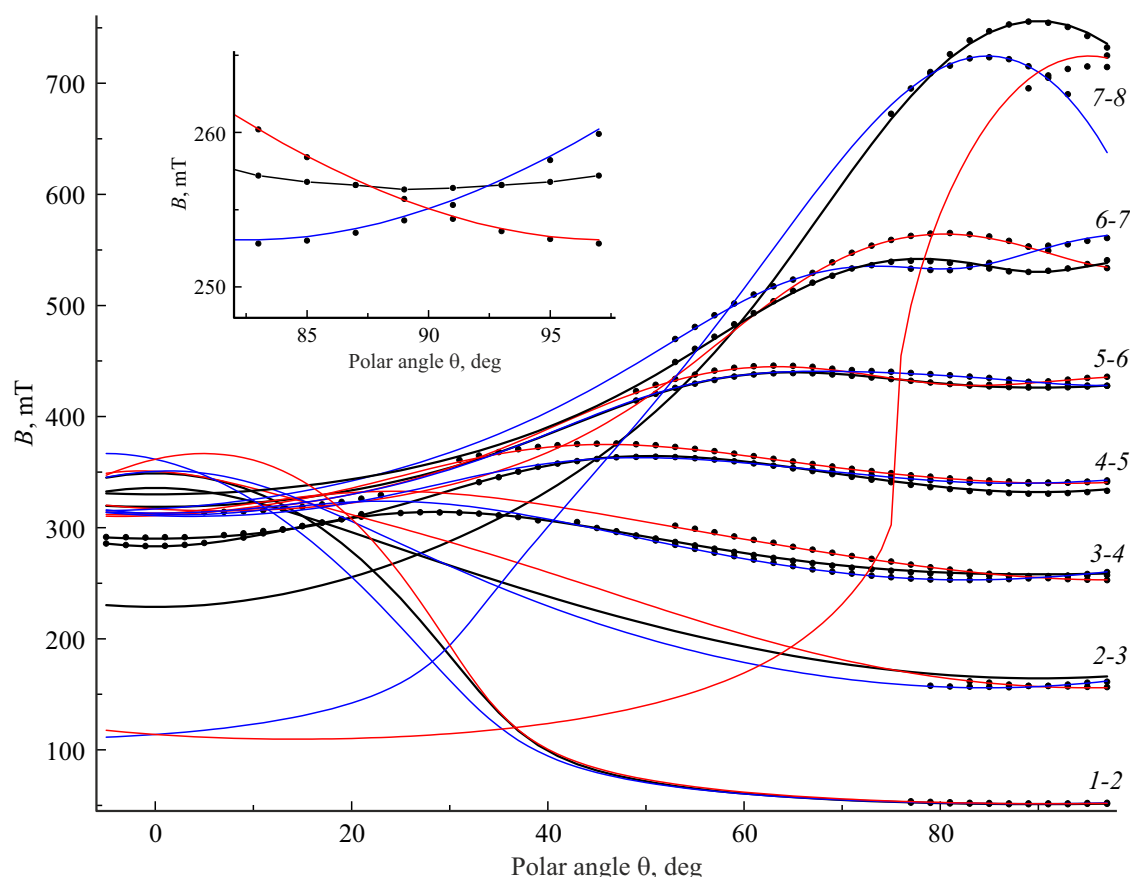


Figure 7. Polar angular dependence of transition positions $i-j$ of the monoclinic Gd1 center (black curves) and triclinic Gd2 (red curves) and Gd3 (blue curves) centers in the $Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ plane at 9630 MHz. Circles — experiment, curves — calculation with parameters determined in this work (Table 3, 4). The inset shows the experimental positions of transitions 3-4 of three Gd^{3+} centers.

field splitting of sixth-rank using 450 resonance transition positions in two $\{Z(\text{Cr1})-\text{Y} \parallel \mathbf{b}$ and $Z(\text{Fe1})-\text{X}(\text{Fe1})\}$ magnetic field planes gave rise to a set of parameters with an rms deviation of 22 MHz from the experimental data (Table 4).

Results of diagonalization of the second-rank tensor $\mathbf{D}$ are shown in the last column in Table 4. Primary axes of tensor $\mathbf{D}$ of the Gd2, Gd3 centers are linked to Cr1 CS by the Euler angles $\alpha = \pm 6.1^\circ$, $\beta = 61.3^\circ$, $\gamma = \pm 177^\circ$. The fourth-rank fine structure tensor was not reviewed due to high errors of the obtained parameters.

Unlike the Mn^{2+} ions, which enter the ZnWO_4 structure isovalently, the incorporation of the Fe^{3+} , Cr^{3+} , and Gd^{3+} ions into Zn^{2+} positions via a heterovalent mechanism requires effective positive excess charge compensation. In case when no any charge compensator (e.g. lithium or sodium ions [5,6,10,21]) are intentionally introduced into the crystal, such compensators are generated spontaneously within the crystal. In the ZnWO_4 crystal, these may be zinc vacancies V_{Zn} [23] or an interstitial oxygen ion O_i^{2-} [27].

Two options are available.

a. Charge compensator may locate at a considerable distance from a paramagnetic center without introducing any significant perturbations into the crystal field around

Table 4. SH parameters of the triclinic Gd2, Gd3 centers in ZnWO_4 at room temperature (values of b_{nm} and c_{nm} are given in MHz). Double signs of c_{21} and c_{22} correspond to the Gd2, Gd3 centers

Parameters	In the Cr1center CS	In the principal axes of tensor $\mathbf{D}$
g	1.991	1.991
b_{20}	251	1854
b_{21}	3469	0
b_{22}	2943	1400
b_{40}	-62	—
b_{41}	9	—
b_{42}	-27	—
b_{43}	-383	—
b_{44}	-219	—
b_{60}	4	—
c_{21}	± 621	0
c_{22}	± 566	0

the latter — a so-called non-local charge compensation is implemented. In this case, monoclinic symmetry centers (Fe1, Cr1, Gd1) are formed.

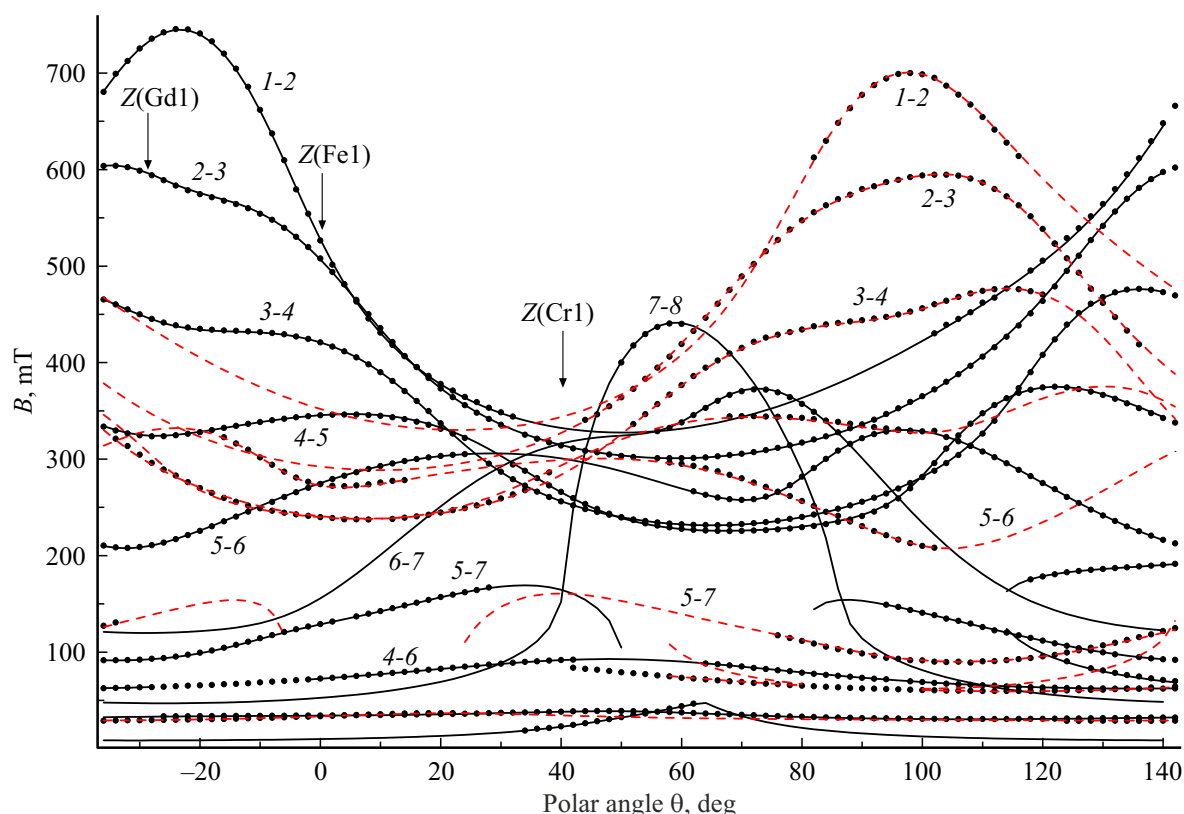


Figure 8. Orientation behavior of transition positions $i-j$ of the monoclinic Gd1 center (black solid curves) and triclinic Gd2, Gd3 centers (red dashed curves) in the $Z(\text{Fe1})$ – $X(\text{Fe1})$ plane at 9126 MHz. Circles — experiment, curves — calculation with parameters listed in Tables 3, 4.

b. Charge compensator can be located in the immediate vicinity of a paramagnetic ion and form a dimer associate with the latter, and sometimes also associates with a more complex structure. This type of charge compensation is referred to as local compensation. In this case, the crystal field of the paramagnetic ion experiences significant perturbations, leading to a lowering of the centers local symmetry. As a result, the C_2 symmetry operation of the crystal replicates the resulting triclinic center into two. Such associates should be attributed to the paired triclinic centers, as was done in [23] for Cr2 and Cr3, and in our work for the paired centers Gd2, Gd3 and Fe2, Fe3.

The authors of [27], based on a comparison of the directions of the principal axes of the D tensor of the

gadolinium center with the directions from Zn^{2+} sites to oxygen ligands and interstitial positions, suggest that these centers are $\text{Gd}^{3+}-\text{O}_i^{2-}$ type dimers. In our opinion, this conclusion is unconvincing, particularly due to the lack of details regarding such analysis in the cited work. The principal Z-axes of the tensors D of the monoclinic Fe1, Cr1, Gd1 centers, that apparently occupy zinc positions, are in a plane perpendicular to the $Y \parallel \mathbf{b}$ axis, while don't coincide with each other (Figure 8). Symmetry of angular dependences with respect to the $\mathbf{a}-\mathbf{c}$ plane is demonstrated in Figure 7 and Figure 3, a in [27]. This indicates that the relationship between the principal axes and directions to the surrounding ligands is more complex. Moreover, a value of g -factor unusual for the gadolinium centers and a far from ideal agreement between the experimental and calculated angular dependences shown in Figure 3 in [27] should be noted.

As a result of calculation of the integral intensities of EPR signals (by double integration of the first derivative of the absorption signal) and taking into account the difference in electron spins of the Cr^{3+} , Fe^{3+} , Gd^{3+} centers [37], and the calculated probabilities of the observed transitions, concentration ratios of the triclinic and monoclinic Fe, Cr, and Gd centers were evaluated (Table 5). Integral intensities of the EPR signals were determined using spectra in the $B \parallel Z(\text{Cr1})$ and $B \parallel Y \parallel C_2$ orientations, where triclinic

Table 5. Ratios of integral intensities, transition probabilities and concentrations for the monoclinic and triclinic Fe^{3+} , Cr^{3+} and Gd^{3+} centers in the studied ZnWO_4 crystal

Centers	Integral intensity ratio	Transition probability ratio	Concentration ratio
Fe1/Fe2	153/5.4	4/7	≈ 50
Cr1/Cr2	656/123	5.1/9.6	≈ 10
Gd1/Gd2	50.3/38.6	13.7/27	≈ 2.5

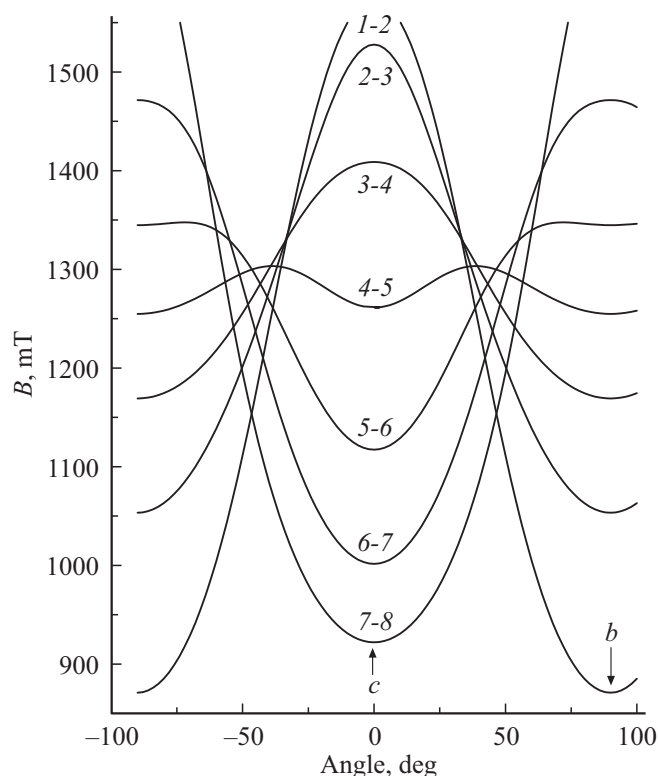


Figure 9. Calculated orientation behavior of Gd1 transition positions in the *bc* plane (SH parameters in Table 3 at $Z \parallel c$) at 35195 MHz.

center transitions 2, 3 are degenerate and a sufficiently good signal resolution is observed for the centers of interest. Transition probabilities were calculated using the wave functions obtained from numerical diagonalization of the SH matrix with optimal parameters of the corresponding centers.

Table 5 clearly shows that the given set of paramagnetic centers (Fe^{3+} , Cr^{3+} , Gd^{3+}) has an obvious trend towards an increasing degree of local charge compensation. A high degree of local compensation of excess charge is also likely realized for the Tm^{3+} ions used to dope the sample.

The above-mentioned procedure was also used to evaluate the concentration ratio of Fe^{3+} , Cr^{3+} , Gd^{3+} and Mn^{2+} ions. The obtained $c(\text{Fe})/c(\text{Cr})$ appeared to be equal to ~ 4.5 and almost coincides with the Cr and Fe concentration ratio measured using ICP MS in [16] for the „reference crystal“ sample (0.7 wt. ppm and 0.15 wt. ppm, respectively).

The number of the Mn^{2+} ions in the studied crystal appeared to be approximately 15 times as low as that of the Fe^{3+} ions. This value almost coincides with the ratio between the Fe concentration measured in [16] for the „reference crystal“ sample and the Mn detection limit in this crystal (0.05 wt. ppm). Assuming that the actual Mn content in the „reference crystal“ is not too much lower than the specified detection limit, then it is fair to say that the EPR data also agree well with the ICP MS data in terms of $c(\text{Fe}^{3+})/c(\text{Mn}^{2+})$ taking into account that a considerable

part of Fe is in a divalent state in the crystal as mentioned above.

The number of the Gd^{3+} ions in the crystal is close to the Fe concentration $c(\text{Gd})/c(\text{Fe}) \approx 2$. Tm_2O_3 reagent introduced in the charge in the amount of 4 at.% during crystal growth is apparently the source of a relatively large number of the Gd^{3+} centers in the sample. Due to the proximity of the chemical properties of thulium and gadolinium, it is very difficult to get rid of trace amounts of the Gd^{3+} ions and other unintentional rare-earth ion impurities in the Tm_2O_3 reagent. At the same time, having crystallochemical properties similar to other rare-earth ions, gadolinium may serve as an adequate marker of structural localization of other REI, direct observation of which by the EPR methods is a more complex task requiring cryogenic conditions.

3. Conclusion

EPR spectra of accidental Fe^{3+} , Cr^{3+} , Gd^{3+} and Mn^{2+} impurities were detected at room temperature at the ZnWO_4 single crystal doped with thulium ions, detected at room temperature. Spectra of monoclinic centers of all above-mentioned ions are observed and are induced by inclusion of these ions into zinc positions with non-local excess charge compensation (no compensation is required for the Mn^{2+} centers).

In addition signals were detected from the triclinic Fe^{3+} , Cr^{3+} , Gd^{3+} centers that probably corresponded to the paramagnetic ion associates with a charge compensator: zinc vacancy or interstitial oxygen ion. Spin Hamiltonian parameters were determined or evaluated for all identified paramagnetic centers, principal axis orientations of the second-rank fine structure tensors were found. Integral intensities and calculated probabilities of the EPR transitions were used to evaluate the concentration ratios of the identified paramagnetic centers. Thus, the results provide data that may be useful in future studies aimed at the interpretation and analysis of the EPR spectra of ZnWO_4 crystals co-doped with rare-earth activators and charge compensators (Li^+ , V^{5+} , etc.) deliberately introduced in the crystal.

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Conflict of interest

The authors declare no conflict of interest.

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