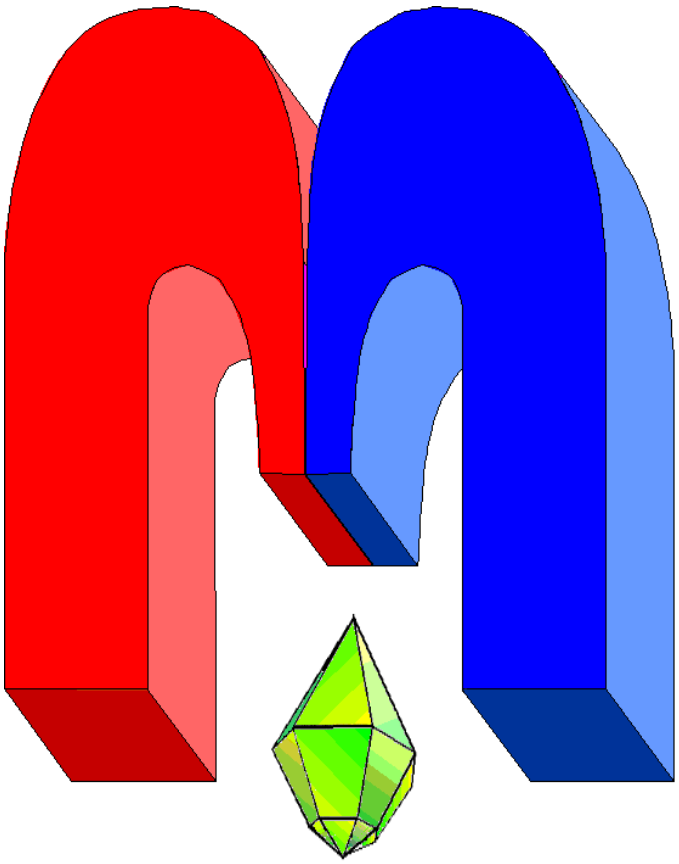
ISSN 2072-5981
doi: 10.26907/mrsej



Magnetic Resonance in Solids

Electronic Journal

Volume ***28***
Issue ***2***
Article No ***26201***
1-8 pages
2026
doi: **10.26907/mrsej-26201**

http://mrsej.ru
(http://mrsej. kpfu.ru)

Established and published by Kazan University*
Endorsed by International Society of Magnetic Resonance (ISMAR)
Registered by Russian Federation Committee on Press (#015140), August 2, 1996
First Issue appeared on July 25, 1997

"***Magnetic Resonance in Solids. Electronic Journal***" (**MRS*ej***) is a peer-reviewed, all electronic journal, publishing articles which meet the highest standards of scientific quality in the field of basic research of a magnetic resonance in solids and related phenomena.

Indexed and abstracted by
Web of Science (ESCI, Clarivate Analytics, from 2015),White List (from 2023) *Scopus* (Elsevier, from 2012), *RusIndexSC* (*eLibrary*, from 2006), *Google Scholar*, *DOAJ*, *ROAD*, *CyberLeninka* (from 2006), *SCImago Journal & Country Rank*, etc.

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

EPR Spectroscopy of Impurity Holmium Ions in Yttrium Orthosilicate Single Crystals

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(received April 22, 2026; revised May 31, 2026; accepted June 4, 2026; published June 9, 2026)

The orientation and frequency-field dependencies of continuous wave electron paramagnetic resonance (EPR) spectra were measured for the first time for impurity Ho^{3+} ions in yttrium orthosilicate single crystal in the frequency range of 140 - 200 GHz. The value of the zero field splitting of electron-nuclear levels and the magnetic characteristics of Ho^{3+} ions substituting yttrium in the Y2 crystallographic sites are determined.

PACS: 71.70.Ch, 75.10.Dg, 76.30.Kg, 71.70.Ej.
Keywords: Ho^{3+} ions, Y_2SiO_5 crystal, electron paramagnetic resonance, hyperfine interaction.

1. Introduction

Recently, much attention is being paid to the development of quantum technologies and their application for information processing and transmission. Among the most important problems to be solved there is the use of quantum computers for modeling of physical processes and quantum cryptography for secure data transmission. The practical implementation of quantum information systems requires physical objects whose properties obey the laws of quantum mechanics. Among them there are electron and nuclear spins of impurity paramagnetic ions in dielectric crystals [1–5]. Yttrium orthosilicate Y_2SiO_5 (YSO) single crystals doped with rare earth ions are considered as the most promising materials for a solid state quantum memory. Paramagnetic centers of Pr:YSO [6], Nd:YSO [7], Eu:YSO [8], Tm:YSO [9], Yb:YSO [10], Er:YSO [11] and Gd:YSO [12], are being investigated. Besides that, YSO crystals are also considered as promising laser hosts [13], while holmium ions is one of the most important types of active centers in solid-state lasers [14–18]. For both these applications of YSO:Ho^{3+} crystal, it is necessary to know the Stark and hyper fine structures of electron-nuclear levels of the Ho^{3+} ions in this crystal as accurately as it is possible. Holmium ions in YSO are also of interest for quantum computer science and they have been previously studied by laser site-selective and Fourier transform infrared spectroscopy [19, 20].

Ho^{3+} is a non-Kramers ion with integer total angular momentum. The low-symmetry (triclinic) electric crystal field of YSO splits the $^5I_8$ ground Ho^{3+} multiplet to 17 singlet Stark states [19, 20]. The energy of the first excited singlet Stark electron level of Ho^{3+} in YSO was estimated to be $5\,cm^{-1}$ [20]. Electron paramagnetic resonance (EPR) spectroscopy is one of the most precise and about of informative methods for studying the characteristics of electron spins in crystals. The main purpose of this work is to refine the value of energy gap between the ground and the first excited singlet electron Stark level of Ho^{3+} in YSO crystal using the EPR spectroscopy. It should be noted that the energy gap of $5\,cm^{-1}$ between the two lowest electron Stark levels is too large to be detected by conventional EPR spectrometers. We used the unique broadband frequency tunable EPR spectrometer [21]. Earlier the broadband EPR-

spectroscopy have been successfully used for the EPR spectroscopy of Ho^{3+} in KY_3F_{10} [22, 23], $CsCdBr_3$ [24], Mg_2SiO_4 [25–27], $LiYF_4$ [28, 29], $LiLuF_4$ [29], SrY_2O_4 [30], $Y_3Al_5O_{12}$ [31, 32], $YAlO_3$ [33], LaF_3 [34].

2. Experimental

YSO single crystal have monoclinic symmetry I2/a (C^6_{2h}). In this setup, the unit cell parameters are $a = 1.04$ nm, $b = 0.67$ nm, $c = 1.25$ nm, the angle between the a and c axes is 102.65 degrees, the b-axis is perpendicular to the (ac)-plane [35]. The crystal lattice has a second-order axis of symmetry parallel to the crystallographic b-axis and a sliding reflection plane perpendicular to this axis. Yttrium ions are located in two structurally non-equivalent positions with a point symmetry group C_1, designated Y1 (smaller, with a coordination number of 6 by oxygen) and Y2 (more spacious position with a coordination number of 7) [36]. Impurity rare earth ions, including Ho^{3+}, can isomorphly replace yttrium ions in YSO. It was shown in [10–12] that ytterbium, erbium, and gadolinium, respectively, substitute yttrium in both crystallographic positions in YSO crystal grown by the Czochralski method. The presence of a mirror plane in the unit cell of the crystal lattice leads to the formation of two magnetically non-equivalent centers for a paramagnetic ion in each of the Y1 and Y2 sites. The magnetic characteristics of these magnetically non-equivalent centers should be mirror symmetric with respect to the (ac)-plane.

We observed EPR spectra in the frequency range of 140-200 GHz using a homemade quasi-optical frequency-tunable spectrometer [21] at the temperature of 4.2 K in the Vogt geometry with the wave vector of the microwave radiation perpendicular to the direction of the external magnetic field $\mathbf{B}$ produced by a resistive electromagnet. Value of B can be varied in the region from -0.03 to 0.9 T so that direct measurements at the zero magnetic field were possible. The microwave magnetic field $\mathbf{B}_1$ was parallel to $\mathbf{B}$. The microwave radiation was generated by backward wave oscillators, the frequency of which was controlled by the cathode voltage value [37]. The accuracy of the frequency control in our spectrometer is about 0.5 GHz (0.017 cm^{-1}), which is substantially higher than the frequency resolution (about 0.075 cm^{-1}) of the Fourier transform infrared spectrometer used in [19, 20].

The holmium-doped YSO single crystal was grown in a slightly oxidizing atmosphere by the Czochralski method at a "Kristall-2" growth station (former USSR) in an iridium crucible from the melt containing 0.001 at. % of Ho^{3+} in respect to the Y^{3+} content. After growing, the crystal was annealed in air at a temperature of 900° C for three weeks. Due to the proximity of the ionic radii and the chemical nature of Ho^{3+} and Y^{3+} ions, it can be assumed that holmium distribution coefficient between Ho:YSO crystal and the melt is close to unity, so the actual dopant concentration in the crystal is nearly equal to the Ho concentration in the melt. The orientations of the crystallographic axes of the sample were determined by X-ray diffraction. Then the optical indicatrix axes D_1 and D_2 were found by means of observation of the sample along the crystallographic b-axis (which coincides with the third optical indicatrix axis) between crossed polarizers at polarizing optical microscope Levenhuk 500T POL. The plate-like shaped samples with a thickness of about 2 mm and transverse dimensions of about 10x10 mm were used for the measurements.

3. Results and discussion

Ho^{3+} ion with the electron configuration $4f^{10}$ has the ground multiplet $^5I_8$ with the total angular momentum $J = 8$. The only stable ^{165}Ho isotope has a nuclear spin $I = 7/2$. Thus, there

are eight electron-nuclear sublevels for each Stark electron level. Therefore, the EPR spectra of holmium ions should contain eight lines corresponding to the allowed transitions between electron-nuclear sublevels with the same value of the I_z component of the nuclear spin. The value of splitting between these lines at the EPR spectra is determined by the energy of the hyperfine interaction between the electron and nuclear spins. As it was already noted, according to [20], the Stark (zero magnetic field) splitting between two lower singlet electron levels of the ground $^5I_8$ multiplet of Ho^{3+} ion, substituting yttrium at the Y2 site, is about of $5\,cm^{-1}$. The energy of the next electron level, according to the same work, is about of $39\,cm^{-1}$. In this case, the two lowest electron levels can be considered with good accuracy as an isolated quasi-doublet characterized by one-dimensional magnetism with the only nonzero principal value of the g-tensor $g_z \neq 0$ and $g_x = g_y = 0$ [38]. To describe the dependence of the energy levels on the magnetic field for such a quasi-doublet, representing two singlet levels of a non-Kramers ion with integer spin, a simple spin Hamiltonian for a fictitious spin $S = 1/2$ may be used

$$H = \Delta S_x + g_z \mu_B B_z S_z + A_z I_z S_z, \tag{1}$$

here, Δ is zero field splitting between electron levels, g_z is the z-component of the g-tensor, μ_B is the Bohr magneton, B_z is the projection of the external magnetic field $\mathbf{B}$ onto the z-axis of the paramagnetic center, A_z is the hyperfine interaction constant, and I_z is the value of the z-component of the nuclear spin. In this case, the frequencies of the eight allowed resonant transitions between electron-nuclear sublevels with the same I_z [25]

$$\nu = \sqrt{(g_z \mu_B B_z + A_z I_z)^2 + \Delta^2}. \tag{2}$$

Theoretical dependencies of the EPR spectra on the direction of the magnetic field can be easily obtained by converting expression (2)

$$B_0 = \frac{\sqrt{\nu^2 - \Delta^2} - A_z I_z}{g_z \mu_B \cos\,\phi} = \frac{B_{0z}}{\cos\,\phi}, \tag{3}$$

where B_{0z} is the value of the resonance field at $\mathbf{B} \parallel z$-axis, and ϕ is the angle between $\mathbf{B}$ and z-axis. We have studied the resonance transitions between the electron-nuclear sublevels of the lowest electron quasi-doublet of the ground multiplet of the Ho^{3+} ion in YSO. An example of the spectrum recorded at a frequency of 166 GHz with the orientation of the magnetic field $\mathbf{B} \parallel z$-axis is shown in Figure 1.

Measuring the orientation dependence of the spectra upon rotation of the $\mathbf{B}$ direction relative to the crystallographic axes made it possible to determine the orientations of the principal magnetic axes of the two magnetically non-equivalent centers relative to the crystallographic axes. It was found that the projections of the principal magnetic z-axes onto the crystallographic (ac)-plane are deviated from the D_2 direction by the angle of $\varphi = 16 \pm 2^\circ$, as it is shown in Figure 2 by red arrow. The relative positions of D_1 and D_2 axes in respect to the a and c crystallographic axes of YSO crystal according to [40] are shown in Fig. 2. To determine the angle θ of deviation of the z-axes directions from the crystallographic b-axis, the orientation dependence of the spectra upon rotation of the magnetic field in the (bz)-plane was measured. The results are shown in Figure 3. The minimum values of B_0 correspond to the $\mathbf{B} \parallel z$ orientations. The angle between two z-axes corresponding to the two magnetically non-equivalent centers is $70 \pm 0.5^\circ$. Accordingly, $\theta = 35.0 \pm 0.5^\circ$.

To determine the value of the magnetic moment μ associated with the electron states of the lowest electron quasi-doublet of the Ho^{3+} ion in YSO, the frequency-field dependencies of the

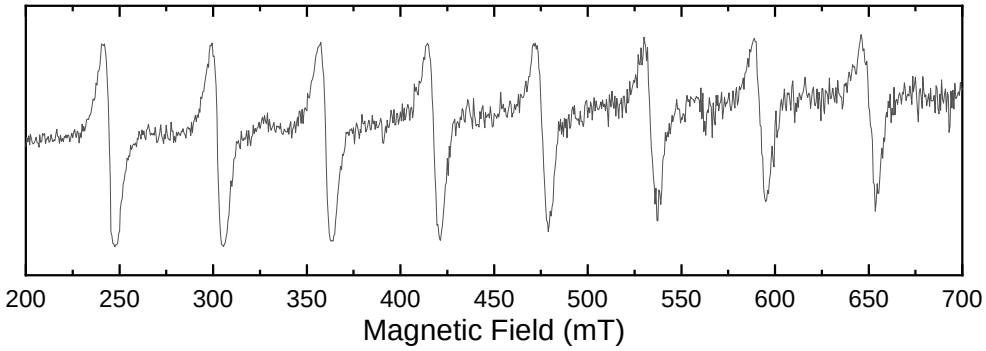

Figure 1. The EPR spectrum of the impurity Ho^{3+} ion in YSO, recorded at frequency of 166 GHz with orientation of $\mathbf{B} \parallel z$-axis.

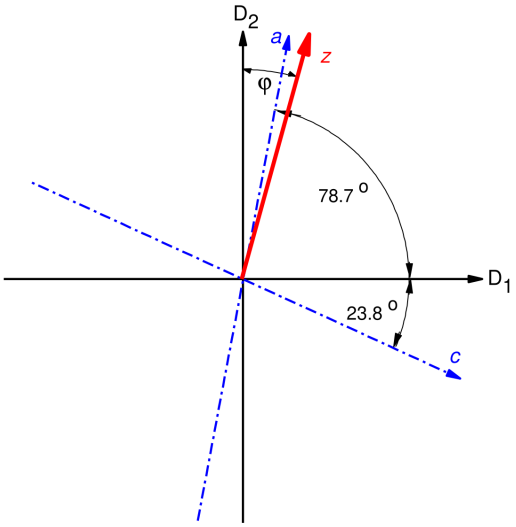

Figure 2. Orientation of the projections of the principal magnetic z-axes of Ho^{3+} ions in YSO (red bold arrow) onto the crystallographic (ac)-plane.

EPR spectra with the orientation of the magnetic field $\mathbf{B} \parallel z$ were measured. The results are shown in Figure 4.

The best description of the experimental data by the theoretical dependencies presented by the lines in Figure 4 is obtained for the following parameters of the spin Hamiltonian (1): $\Delta = 142.5 \pm 1\,\text{GHz}$ $(4.75 \pm 0.03\,\text{cm}^{-1})$, $g_z = 16.8 \pm 0.1$, $A_z = 11.2 \pm 0.1\,\text{GHz}$. The value of $\mu = J_z \cdot \mu_B = 6.72\,\mu_B$. Here $J_z = g_z/2g_L$ is the total angular momentum characterizing the electron states of the ground electron quasi–doublet, $g_L = 1.25$ is the Lande g-factor. The value of J_z is close to the maximum possible value of $J = 8$ for the ground $^5I_8$ multiplet of the Ho^{3+} ion. The value of the A_z parameter makes it possible to determine the hyperfine interaction constant for the Ho^{3+} ion in YSO $A_p = A_z/2J_z = 833 \pm 8\,\text{MHz}$. This value is close to $A_p = 812\,\text{MHz}$ for free Ho^{3+} ion [39] that was used for the calculations in [19]. The value $\Delta = 4.75\,\text{cm}^{-1}$ is also close to the value $\Delta = 4.72\,\text{cm}^{-1}$, previously measured by optical spectroscopy for the impurity Ho^{3+} ion substituting yttrium at the Y2 site of the YSO crystal lattice [19]. The very slight difference between our results and those of [19,20] indicates the high reliability of the data obtained.

The orientation of the projections of the principal magnetic z-axes on the (ac)-plane shown

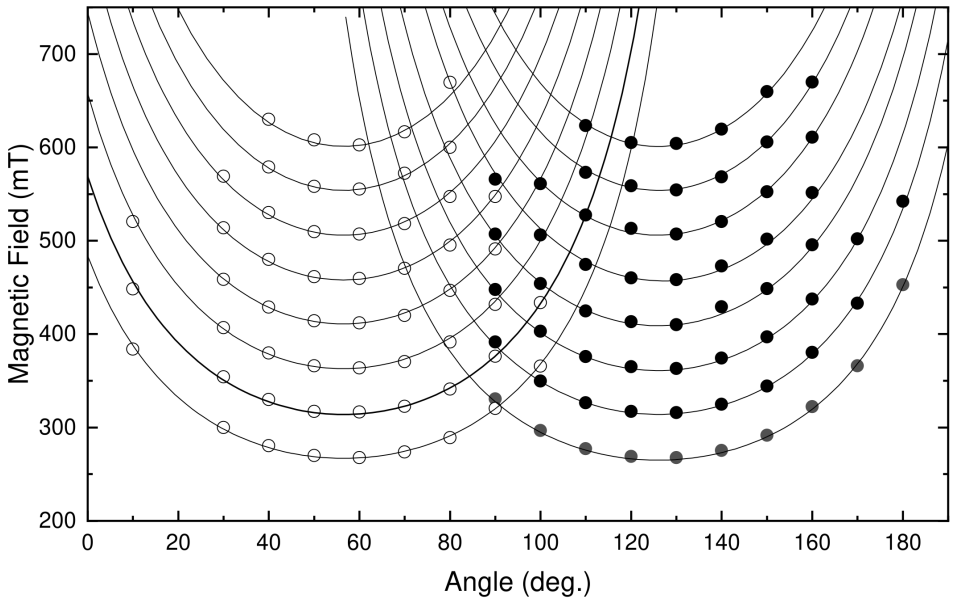

Figure 3. The dependencies of the resonant values of the magnetic field B_0 on the orientation of the magnetic field in the (bz)-plane. $\mathbf{B} \parallel b$-axis at angle 90°. Filled and open circles correspond to the experimental signals from two magnetically non-equivalent centers. Lines are calculations using expression (3). The operating frequency of the spectrometer is 176 GHz.

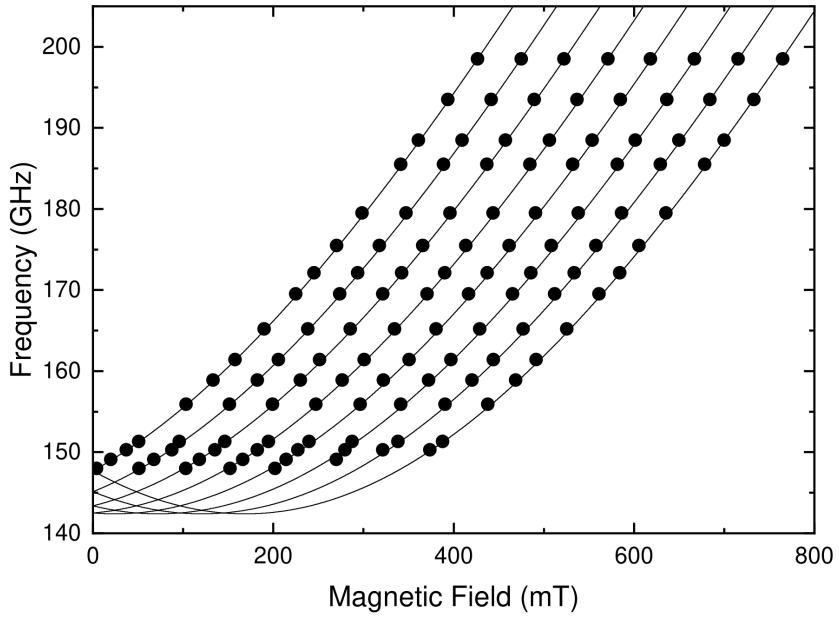

Figure 4. Frequency-field dependencies of resonance transitions between the electron-nuclear sublevels of the ground and first excited electron levels of the Ho^{3+} ion in YSO. Circles are experiment, lines are calculation using expression (2).

in Fig. 2, essentially differs from the data given in [19, 20]. Table 1 presents a comparison of our and the literature [19, 20] data for the values of J_z angular momentum projections onto the D_1 and D_2 directions and b-axis. The reason for the discrepancy may be related to the fact that transitions between the ground Ho^{3+} multiplet $^5I_8$ and excited multiplets $^5I_7$ or $^5I_6$ were measured in [19, 20]. In this case the Zeeman energies of both multiplets contribute to the dependence of the energy levels on the magnetic field. In the calculations [19, 20] it was

Table 1. Projections of angular momentum J_z onto the D_1 and D_2 directions and b-axis.

	D_1	D_2	b
Our data	1.07	3.72	5.53
[19, 20]	3.01	2.75	5.12

assumed that the orientations of the magnetic moments for all multiplets for Ho^{3+} ion in the Y2 site coincide. This may not be entirely justified. At least it was found for Kramers ions Er^{3+} and Yb^{3+} in YSO that the orientations of the principle axes of the g-tensors differ markedly for different multiplets [40, 41].

It is reported in the article [19] about the observation of optical spectra from Ho^{3+} ions substituting Y^{3+} in both Y1 and Y2 crystallographic sites. The zero field splitting between the ground and the first excited electron levels of the ground $^5I_8$ multiplet of Ho^{3+} ions in Y1 and Y2 sites differ by only $0.15\,cm^{-1}$ (4.5 GHz), according to this paper. Therefore, when measuring the orientation and frequency-field dependencies of the EPR spectra, we should have seen EPR signals from Ho^{3+} ions in the Y1 site, but we did not see them. This is probably due to the fact that the content of holmium in the Y2 site significantly exceeds the holmium content in the Y1 site in our experimental sample.

4. Summary

The magnetic characteristics of Ho^{3+} impurity ions in Czochralski grown Y_2SiO_5 single crystal doped by 0.001 at. % Ho^{3+} have been studied by submillimeter tunable EPR spectroscopy. It has been established that the EPR spectra belong to two magnetically nonequivalent holmium ions substituting yttrium in the Y2 crystallographic site. The Stark splitting between the ground and first excited singlet electron levels of holmium ion in this crystal was measured to be $\Delta = 142.5 \pm 1$ GHz ($4.75 \pm 0.03\,cm^{-1}$). It has been revealed that Ho^{3+} ion is characterized by one-dimensional magnetism with an effective g-factor $g_z = 16.6 \pm 0.2$ and the parameter of hyperfine interaction between electron and nuclear spins $A = 833 \pm 8$ MHz. The orientations of the principal z-axes of the two magnetically nonequivalent holmium ions relative to the crystallographic axes have been found.

Acknowledgments

The authors are grateful to V.A. Shustov for X-ray orientation of the sample relative to the crystallographic axes. The work of V.F. Tarasov was supported in the framework of the state assignment for the FRC Kazan Scientific Center, Russian Academy of Sciences.

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