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Wideband EPR spectroscopy of $Y_3Al_5O_{12}$: Ho^{3+} crystals

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EPR spectra of Ho^{3+} impurity ions were recorded in single crystals of yttrium aluminum garnet ($Y_3Al_5O_{12}$) in the frequency range of $114-170\,GHz$, at a temperature of $4.2\,K$. The measurement results indicate the substitution of Ho^{3+} ions for Y^{3+} ions in the dodecahedral position with D_2 local symmetry. The magnitude of the g-factor, the hyperfine structure constant, and the energy interval between the main and the first excited nondegenerate sublevels of the main multiplet $^5I_8$ are determined. Weak satellite signals have also been registered, the origin of which is associated with the formation of antisite defects in the environment of Ho^{3+} paramagnetic centers.

Keywords: hyperfine interaction, rare earth ions, spin Hamiltonian, non-Kramers ion.

1. Introduction

The $Y_3Al_5O_{12}$ yttrium aluminum garnet (YAG) is a well known matrix with good mechanical, thermal and optical properties. This matrix with a number of rare earth activators has been used to create dozens of laser crystals, which are widely used in various fields of science, technology and medicine. The spectroscopic properties and laser generation of the Ho^{3+} ions in YAG have been well studied since the seventies [1]. The diagram of the Ho^{3+} ions levels allows producing the laser generation at many channels within the wave lengths from ~ 0.55 to $\sim 3\,\mu m$. The two-micron stimulated radiation at lines of the $^5I_7-^5I_8$ main laser channel of the Ho^{3+} ions produced at the YAG:Ho^{3+} crystals, too, corresponds to an absolute transparency window of the Earth atmosphere and less dangerous to human eyes. These properties provided for application of these crystals in the laser range-finders, scientific studies and material processing. The laser generation is often excited by thulium lasers radiating at $1907\,nm$, which have a smooth tunability of the wave length in order to get the maximum absorption of the pumping energy by the crystal [2]. At high powers, even low level lattice distortions or stresses present in crystals, including those introduced by „antisite" defects, may increase the thermal load on the crystal. That is why information about them is of great practical importance. Recently, the interest in the YAG:Ho^{3+} crystals has substantially grown due to their successful application in the laser surgery [3,4]. For the first time, the present study has investigated in detail the Ho^{3+} impurity centers in the YAG crystal by the wideband EPR spectroscopy method to get information about the energy interval between the main and the first excited nondegenerate sublevels of the $^5I_8$ main multiplet of the Ho^{3+} ion.

2. Experimental results

The YAG:Ho^{3+} ($0.15\,at.\%$) crystal was produced in the Institute of Physical Research of National Academy of Sciences of Republic of Armenia (Ashtarak-2, Armenia). It was grown by the vertical directional crystallization [5] using high-purity initial oxides (Y_2O_3, Al_2O_3, Ho_2O_3), molybdenum containers and seed crystals oriented along the $\langle 001 \rangle$ axis, at the growth rate of $1.5\,mm/hr$. For this orientation, facets are formed in the crystal periphery and the major part of the bulk crystal has no such defects. Following the size factors, Ho^{3+} ions in the YAG structure should replace Y^{3+} ions in dodecahedral lattice sites with 8-fold oxygen coordination, be uniformly distributed within the crystal bulk and should not introduce noticeable distortions in the lattice. The grown crystal had no light scattering inclusions and exhibited transmission of $\sim 82\%$ ($d = 0.55\,mm$) in the visible range. A sample measuring $1.5 \times 2 \times 5.5\,mm^3$ was cut from facet-free part of the crystal, which oriented using an X-ray diffractometer.

The EPR spectra were obtained in the wideband EPR-spectrometer made in Kazan Physical-Technical Institute [6]. All the measurements were made in collinear mutual polarization of the constant and microwave field ($\mathbf{B}_0 \parallel \mathbf{B}_1$). The EPR signals of the Ho^{3+} ion were observed within the frequency range of $114-170\,GHz$. The Fig. 1 shows the spectrum shape at the frequency of $170\,GHz$ in the orientation of the magnetic field $\mathbf{B} \parallel \langle 001 \rangle$. Eight lines of

the hyperfine structure (HFS) unambiguously mean that the signals belong to a holmium ion (^{165}Ho, $I = 7/2$, natural abundance 100%). Note that besides the main spectrum there are also satellite lines, whose origin is correlated to the „antisite defects". Such defects had been studied before on the YAG : Ce [7] and YAG : Tb^{3+} [8,9] crystals. In our case, the spectrum of the Ho^{3+} main ion and the Ho^{3+} spectra combining with „antisite"-defects were overlapped. That is why it was not possible to study in detail the satellites due to imposition of a big number of the lines.

The angular dependence of the EPR spectra measured at the frequency of 129 GHz, when the crystal was rotated in the {001} plane, is shown in the Fig. 2. For clarity, the plot shows the dependence of only the low-field HFS component. When the rare earth (RE) ion enters the YAG crystal lattice and localizes in the Y^{3+} positions, there are six appearing magnetically-nonequivalent centers with
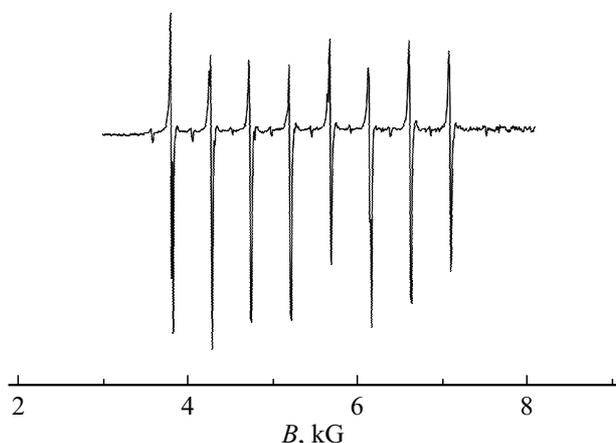

Figure 1. EPR spectrum of the Ho^{3+} ion in the Y$_3$Al$_5$O$_{12}$ crystal. The frequency is 170 GHz, orientation of the magnetic field — **B** $\parallel \langle 001 \rangle$.

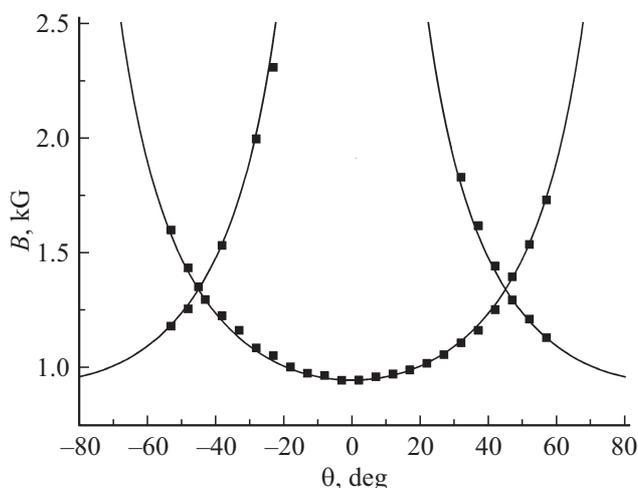**Figure 2.** Angular dependence of the EPR spectra of the Ho^{3+} ion in the Y$_3$Al$_5$O$_{12}$ crystal. Rotation of the crystal in the {001} plane, the frequency is 129 GHz. The dots — the experiment, the lines — the calculation.
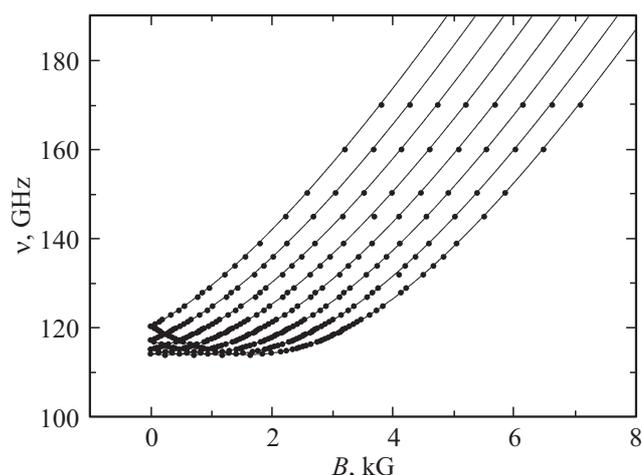

Figure 3. Frequency vs. field dependence of the EPR spectra of the Ho^{3+} ion in the Y$_3$Al$_5$O$_{12}$ crystal, for the $B \parallel \langle 001 \rangle$ orientation. The dots — the experiment, the lines — the calculation.

magnetic axes directed along the crystallographic axes of the second and fourth order. In our case, the directions of the maximum g-factor of the centers coincided with the directions of the $\langle 001 \rangle$ type. This fact agrees with a dependence obtained earlier for the YAG : Tb^{3+} crystal [4].

For orientation of the crystal in the external magnetic field **B** $\parallel \langle 001 \rangle$, the frequency vs. field dependence of the EPR spectra of the Fig. 3 has been measured. It follows from the form of this dependence that the observed resonance transitions are between the sublevels of the quasi-doublet, which is divided by the initial splitting near 114 GHz. Note that the zero splittings of the center lines with the „antisite" defects were laid within the main spectrum and could not be measured due to line imposition. However, for one center, the most high-frequency line of HFS was not imposed on the main spectrum and was measured by a direct method. Its ZFS was 125 GHz. Based on the discussions in the papers [8,9], this center is caused by the „antisite" defect with substitution of the octahedrally coordinated aluminum ion by yttrium in the nearest environment of the Ho^{3+} paramagnetic center.

3. Discussion

The formation of the quasi-doublet with the evident resonance transitions therein is correlated to splitting the main multiplet of the $^5I_8$ holmium ion inside the crystal field of the D$_2$ symmetry in the dodecahedral yttrium position of the yttrium aluminum garnet. According to the optical data, the next excited level is removed from the main one already by 41 cm^{-1}. That is why the electron system can be considered to be a two-level one with good approximation. In this case, for the non-Kramers ions there is only one non-zero component of the magnetic dipole moment and it is possible to apply the analysis based on the effective spin Hamiltonian (the effective spin $S = 1/2$) [10]. In doing

so, we have neglected the nuclear Zeeman energy and the quadrupole interaction energy. Assuming that the direction of the $z \parallel \langle 001 \rangle$ local magnetic axis within the space of the electron & nucleus states corresponding to the electron quasi-doublet and the $I = 7/2$ nuclear spin, the effective spin Hamiltonian takes the following form:

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

The respective dependences of the resonance frequencies ν on the magnetic field parallel to the z axis are determined for the holmium ions by the following expression:

$$h\nu = \left[\Delta^2 + (Am + g_z \mu_B B_z)^2 \right]^{1/2}, \tag{2}$$

where m determines projections of the nuclear spin ($\pm 1/2$, $\pm 3/2$, $\pm 5/2$, $\pm 7/2$) onto a direction of the electron magnetic moment. Then, the angular dependence of the EPR spectra will be determined by the expression (see Fig. 2):

$$B(\theta) = \left\{ \left[(h\nu)^2 - \Delta^2 \right]^{1/2} - Am \right\} / g_z \mu_B \cos(\theta), \tag{3}$$

where θ — the angle between the external magnetic field **B** and the crystallographic directions.

As obtained from the modeling of the frequency vs. field dependences, the values of the Δ initial splitting of the quasi-doublet, g-factor and the A hyperfine interaction constant for the holmium ion are: $\Delta = 114.2$ GHz, $g = 16.61$, $A = 10.88$ GHz. The parameters obtained were used to build calculated orientation and frequency vs. field dependences of the EPR spectra, which are shown in the Figures 2 and 3 by solid lines.

4. Conclusion

The method of the wideband EPR spectroscopy has allowed finding and studying the Ho^{3+} non-Kramers ions in the yttrium aluminum garnet, which substitute the Y^{3+} ions in the dodecahedral position of the crystal lattice. The $Y_3Al_5O_{12}$ crystals have a value of the g-factor (16.61), the hyprfine structure constant (10.88 GHz) and the energy interval between the main and the first excited sublevels of the $^5I_8$ main multiplet of the Ho^{3+} rare earth ion determined.

Conflict of interest

The authors declare that they have no conflict of interest.

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