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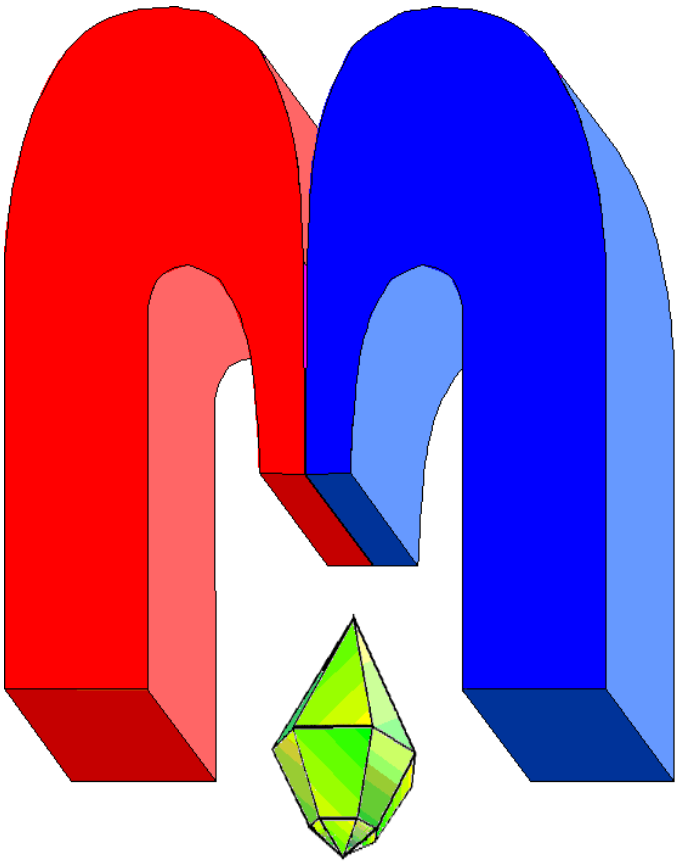

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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

High-frequency EPR of Ho^{3+} ion in the LaF_3 crystal

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In LaF_3 crystals the EPR spectra of Ho^{3+} ion replacing La^{3+} ion in a C_2 symmetry position were recorded and studied in the subterahertz frequency range. The parameters of splitting in the zero field, hyperfine structure constant and the value of g-factor are determined.

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1. Introduction

Nanocrystals activated by Ho^{3+} ions are of interest for the creation of visualizers of sub- and terahertz radiation on their basis due to the splitting of the ground state of $^5I_8$ into Stark sublevels with energy gaps falling on these ranges, as well as intense temperature-dependent luminescence observed even at high concentrations of impurity ions [1,2]. The application of an external magnetic field and the transition to cryogenic temperatures allow smooth tuning of the frequency of the resonant inter-Stark transition and provide its high absorption coefficient. Of particular interest are trifluoride crystals with the structure of yttrium fluoride (YF_3) and tysonite (LaF_3), which allow activation by Ho^{3+} ions. The crystal lattice of LaF_3 crystal (space group $P\bar{3}c1$) is two different types of layers of fluorine atoms located perpendicular to the symmetry axis, separated by a layer containing fluorine and lanthanum atoms. The local symmetry of the lanthanum position is C_2. Since lanthanum trifluoride is of interest for various applications, it has become the subject of numerous studies. Recently, the EPR spectra of various defects formed during irradiation and during the formation of nanoparticles have been studied [3, 4]. However, the EPR spectra of most rare earth ions in the LaF_3 crystal were studied more than 60 years ago [5, 6]. It was found that despite the isovalent nature of the substitution, the entry of the impurity into the lattice leads to a distortion of the position. It was assumed that the distortion is caused by the exit of lanthanum atoms from the layer [5]. While maintaining the lattice symmetry, the lanthanum positions became magnetically nonequivalent and the number of conjugate EPR spectra increased from three to six. Note that for the Gd^{3+} ion, the position symmetry did not decrease and three magnetically nonequivalent EPR spectra were observed. Previously, only Kramers rare-earth ions were studied. Due to the low symmetry of the position in the case of non-Kramers ions, the electron states turned out to be singlets and observation of the EPR spectra on standard spectrometers was impossible. With the development of subterahertz technology, it became possible to study non-Kramers ions in trifluorides. In particular, we recently recorded EPR spectra in an yttrium trifluoride crystal with a thulium impurity [7].

2. Experimental details and results

In this work, LaF_3:Ho^{3+} crystals were studied. The holmium concentration was 1 at.%, 0.3 at.%, and 0.1 at.% in the melt. The crystals were grown from the melt by the Bridgman method in a multichannel graphite crucible. The batch of LaF_3 and HoF_3 of 99.99 % purity was used. The growth furnace chamber was pre-evacuated to a vacuum of 10^{-4}–10^{-5} mbar and the batch was dried in a vacuum at 150°C for 6 hours. The growth took place in an atmosphere of special

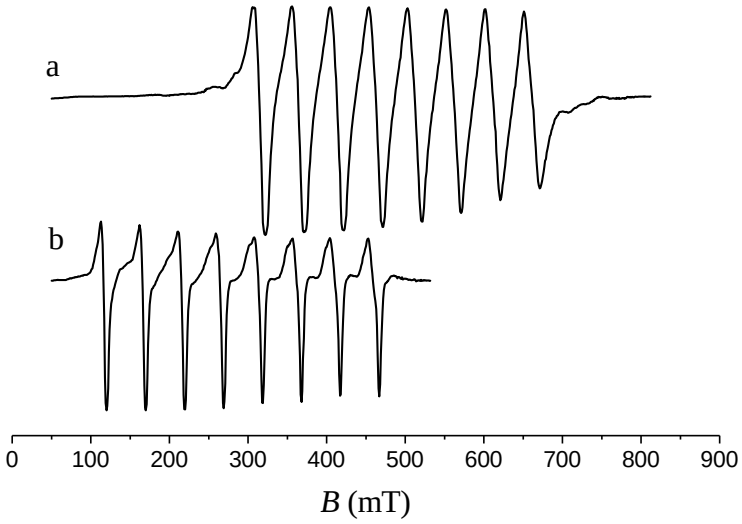

Figure 1. EPR spectra of the Ho^{3+} ion in LaF_3 crystal. a) $\nu = 170$ GHz, holmium concentration 1 %; b) $\nu = 144$ GHz, holmium concentration 0.3 %. $\mathbf{B_0} \parallel \mathbf{c}$.

purity argon (99.998 %) with additional fluorination by burning Teflon. The crystal was pulled out at a rate of 1 mm/hour.

The measurements were performed on a tunable (37-850 GHz) EPR spectrometer at a liquid helium temperature in magnetic fields up to 0.9 T [8]. The EPR spectra of the Ho^{3+} ion were recorded in the frequency range of 130-210 GHz. Figure 1 shows the spectra for the $\mathbf{B_0} \parallel \mathbf{c}$ orientation obtained at frequencies of 170 GHz (Ho, 1 %) and 144 GHz (Ho, 0.3 %). Identification of the Ho^{3+} ion ($I = 7/2$, 100 %) is based on the characteristic hyperfine structure (HFS) consisting of 8 lines. The electron configuration of the Ho^{3+} ion is $4f^{10}$, the ground state of the free ion is $^5I_8$ ($L = 6$, $S = 2$, $J = 8$). According to optical data, the ground state and first

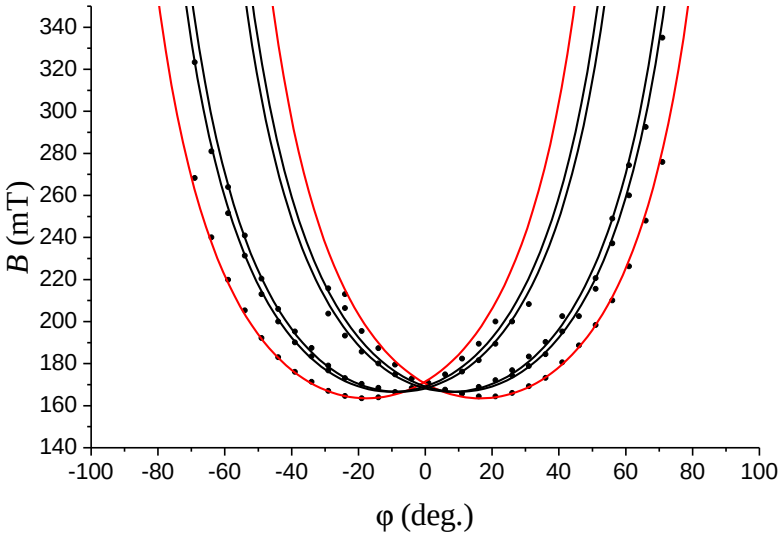

Figure 2. Angular dependence of the resonant magnetic field in $\{11\bar{2}0\}$ plane at frequency of 150 GHz of the EPR signals of Ho^{3+} ions in crystal LaF_3. Symbols-experiment, lines-approximation by function $B(\varphi) = B(\varphi_0)\cos\varphi$, where $\varphi_0 = 0$.

excited levels of holmium in LaF_3 are singlets with an interval of 4.5 cm^{-1} between them, and the next excited singlet is separated from the ground by 42 cm^{-1} [9]. The spectra we observed

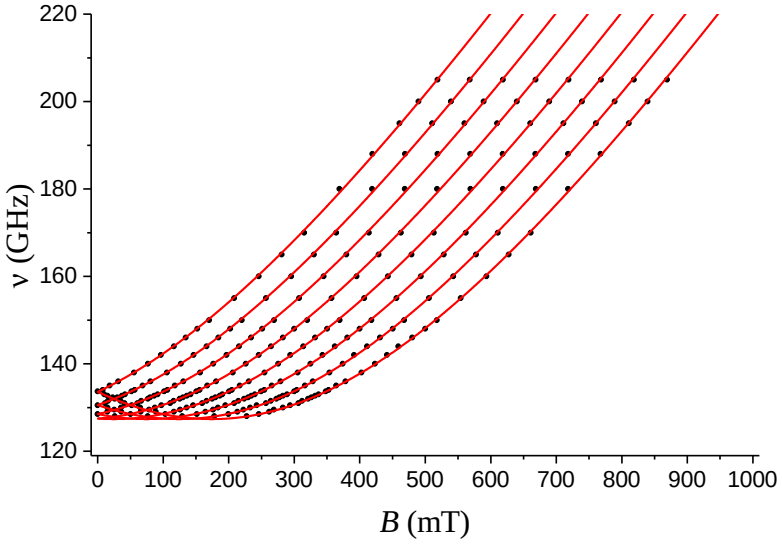

Figure 3. Frequency vs. field of resonant transitions of Ho^{3+} ions in LaF_3 crystal. $\mathbf{B}_0 \parallel \mathbf{c}$. Symbols-experiment, lines-calculation results.

are due to resonance transitions between the ground and first excited singlets. In such cases, the EPR spectra are recorded in parallel ($\mathbf{B}_1 \parallel \mathbf{B}_0$) microwave magnetic fields [10]. Signals from six magnetically nonequivalent holmium positions were observed in an arbitrary orientation. Figure 2 shows the angular dependence of the EPR spectra obtained by rotating the crystal in the $\{11\bar{2}0\}$ plane. Since the HFS lines overlapped each other, which did not allow the exact determination of the positions of all the HFS lines, the graph shows the behavior of only the low-field HFS component. In this case, due to a small deviation of the plane of rotation from the crystallographic plane, the lines that should have been merged turned out to be slightly bifurcated. Taking into account the remoteness of the second excited singlet, our system of levels can be of approximately considered two-level. The angular dependence is described by the inverse cosine function. The angle of deviation of the direction with the maximum g-factor from the symmetry axis was ~16 degrees. This direction will be further called the z-axis of the center. For the $\mathbf{B}_0 \parallel \mathbf{c}$ direction, i.e. when the lines from all six centers are merged, the frequency-field dependence (Figure 3) of the EPR spectra is constructed. The values of the spectral parameters were obtained using the effective spin Hamiltonian ($S = 1/2$) in the form [11]

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

where the first term is the Zeeman energy, the second is the hyperfine interaction, and the third term describes the splitting of the electron-nuclear sublevels in a zero magnetic field. Fitting the experimental points of the frequency-field dependence of the EPR spectra (Figure 3) to the analytical expression

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

where ν is the frequency, μ_B is the Bohr magneton, m is the projection of the nuclear spin, Δ is the zero-field splitting (ZFS), α is the angle of deviation of the z axis from the crystallographic axis, A is the hyperfine structure (HFS) constant, we obtained the following values: $g_z = 17.2$, $\Delta = 127.4\,\text{GHz}$, $A = 11.9\,\text{GHz}$. Using the obtained parameters, the calculated curves were plotted. For the sample with a holmium concentration of 1 %, in addition to the lines of the isolated center, satellite lines were observed (Figure 1). These lines probably belong to paired

Ho^{3+}–Ho^{3+} centers. Due to the small signal-to-noise ratio and the overlapping of the dimer spectrum with the spectrum of the isolated ion, their study was not possible. However, note that at frequencies near 195 GHz, the satellites are recorded in lower magnetic fields than the spectrum of an isolated ion. (Figure 4). Since we have a two-level system, four lower electron

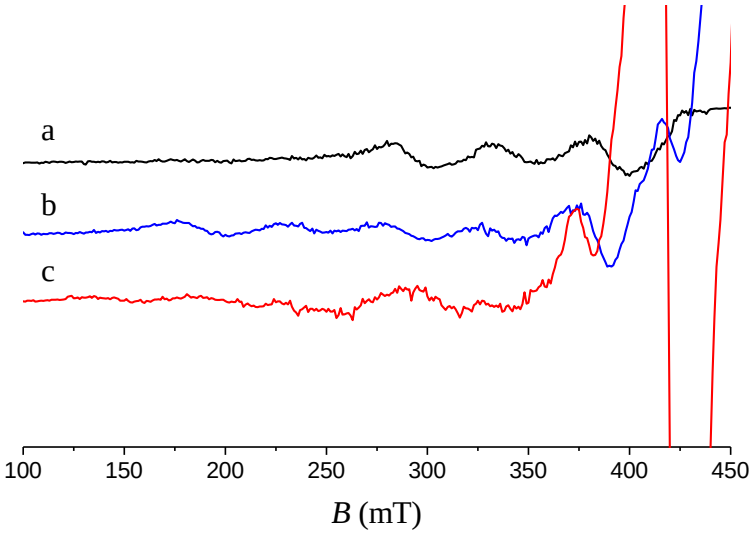

Figure 4. Satellite lines in EPR spectra of LaF_3:Ho^{3+} crystal. a) 205 GHz, b) 195 GHz, c) 188 GHz, $\mathbf{B}_0 \parallel \mathbf{c}$.

states are expected for the dimer, between which two resonant transitions are allowed by parity. It can be assumed that one of the splittings between the dimer levels practically coincides with the Stark splitting of the isolated ion, therefore the dimer lines are superimposed on the lines of the isolated ion. Whereas the second resonant transition of the dimer takes place between states separated by an interval of ~ 180 GHz.

Acknowledgments

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