95 GHz electron paramagnetic resonance of LiYF₄: Nd³⁺ crystal in parallel orientation

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Abstract. We report the observation of the conventional and pulsed electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) spectra from ¹⁹F and ⁷Li nuclei on impurity Nd³⁺ ions in LiYF₄ crystal doped with Nd³⁺ ions in parallel orientation at microwave frequency of ν = 95 GHz (W-band). The resolved structure from the nearby and remote nuclei in spectra is observed. The outcome shows that LiYF₄:Nd³⁺ system can be exploited as a convenient matrix for performing spin manipulations and adjusting quantum computation protocols while ENDOR technique is usable for the investigation of electron-nuclear interaction with the nuclei of the system.

1. Introduction

Rare earth (RE) fluorides have become anew a research focus in the material field due to their unique applications in optical communications, three-dimensional displays, solid-state laser, catalysis, solar cells, biochemical probes and medical diagnostics [1], [2]. It is proposed that RE doped fluoride glasses as parts of laser systems could be fruitfully used for determining identity and/or quantity of a component of a fluid at a remote location such as downhole in a wellbore or inside a pipeline, particularly at elevated temperatures up to 175°C, such as an oil based mud or crude oil, and may detect components such as methane, ethane, carbon dioxide, hydrogen sulfide, etc. [3]. RE fluorides are used as tribological additives in lubricating oils [4]. The potential for using RE doped crystals as scintillators (detectors) for radioactive radiation is not disclosed [5]. To make good use of the excellent properties of metal fluorides, their morphology and microstructure should be carefully controlled. One of the powerful method of the RE doped crystals inspection is an electron paramagnetic/spin resonance (EPR/ESR).

Apart from being the cornerstone of modern laser technology, crystals and glasses doped with RE metals are known to have excellent properties for classical and quantum information storage and for performing quantum computation protocols [6], [7], [8]. In addition, LiYF₄ crystals, having a relatively simple crystalline structure and growing almost without defects, are unique model systems for studying the crystal field, electron-phonon, interionic, hyperfine interactions, and also isotopic effects [9]. The lithium ions (Li⁺) are in the centre of tetrahedra composed of four fluoride ions (F⁻). The yttrium ions (Y³⁺) are in the center of polyhedra composed of eight F⁻. Y³⁺ can be substituted by rare earth metals presenting an oxidation state of +3.

In this work we present the high-frequency (high-field) study of LiYF₄: 0.01 % Nd³⁺. crystal. It is known that such small amount of Nd³⁺ does not influence much the lattice parameters of LiYF₄ scheelite structure: a ≈ 0.517 nm; c ≈ 1.074 nm [10], [11]. (At ambient pressure, the crystal cell of LiYF₄ is tetragonal with space group I₄₁/a or C₄₁₆. This phase is commonly named the scheelite structure, in
reference to the CaWO$_4$ crystal). The obtained results are compared with those obtained in low magnetic fields (conventional for EPR X-band microwave frequency $\nu \approx 9$ GHz) and on CaWO$_4$ crystals. In our recent papers [12], [13] we have studied LiYF$_4$: Ce$^{3+}$ systems and performed pulsed electron-nuclear double resonance (ENDOR) and double electron-electron resonance (DEER) manipulations of electronic and nuclear spin states of trivalent gadolinium impurity ions in CaWO$_4$ host crystal at X-band frequencies (in the magnetic fields $B_0$ up to 1000 mT) [14].

2. Experiment and Discussion

EPR investigations were done by using helium flow cryostats at W-band Bruker Elexsys E580 spectrometer ($T = 10$-300 K, microwave frequency $\nu \approx 95$ GHz). Crystals of LiYF$_4$ doped with rare-earth ions were grown at Kazan Federal University by the Bridgman-Stockbarger technique in argon atmosphere. A piece of crystal with the linear sizes of $0.4 \times 0.2 \times 0.3$ mm was cut and placed into the EPR cavity. The impurities of neodymium were added in the forms of $\approx 0.01$ at % of neodymium oxide.

It is worth mentioning that the synthesized LiYF$_4$ sample exhibited the traces of various rare-earth ions including, Gd$^{3+}$. It is known that EPR of Gd$^{3+}$ can be observed in a wide temperature range from liquid helium to room temperature, since the ground state $^8S_{7/2}$ of the Gd$^{3+}$ ion is an orbital singlet weakly interacting with the crystal lattice. Presence of Gd$^{3+}$ ion (which concentration was estimated as less than 0.005 wt % in X-band measurements) gives an opportunity to orient crystal in the external magnetic field $B_0$ by its rotating at $T = 300$ K and $T = 50$ K and observing the shifting the whole spectrum (and especially its high-field component) to the strongest magnetic field characterized by $g$-factor $g_{||}$(Gd$^{3+}$) $\approx 1.99$ [7].

Figure 1 demonstrates the EPR spectrum detected in conventional mode (cw) at $T = 50$ K and microwave power of $10 \mu$W for $B_0 \parallel c$. (Due to the saturation effect, the intensities of the main components are out of the analog-digital converter range while the lineshapes of the observed components are is closer to absorption lines rather than first derivatives). The spectrum at this temperature EPR lines is due to $S = 7/2$ for Gd$^{3+}$ ions. The cw and pulsed EPR spectra of Gd$^{3+}$ ions in various host crystals, particularly in CaWO$_4$ single crystal, had been extensively studied at lower microwave frequencies [7]. It was shown that the most intense lines are from the $M \leftrightarrow M \pm 1$ transitions ($M = -7/2, -5/2, \ldots, 7/2$). Lower intense lines are from $M \leftrightarrow M \pm 3$ and $M \leftrightarrow M \pm 5$ transitions. The smallest signals are from the “forbidden” transitions $M \leftrightarrow M \pm 2$ and $M \leftrightarrow M \pm 4$. The exact assignment of components of the experimental EPR spectrum to the calculated one for different crystal orientation is on the way.

![EPR spectrum at T = 50 K](image.png)
We used two–pulse electron spin echo measurements for the primary Hahn–echo sequence ($\pi/2$–$\tau$–$\pi$–$\tau$–echo), where $\tau$ is the interpulse delay time of 240 ns, with initial $\pi/2$ and $\pi$ pulse lengths of 12 and 24 ns, respectively, to detect the field-swept (FS) electron spin echo (ESE) EPR spectra at lower temperatures. Figure 2 shows an appearance of additional line in FS ESE with $g_{||} = 1.987$ which we assign to Nd\(^{3+}\) ($g_{||} = 1.987$; $g_{\perp} = 2.554$, see [9], [15]). The corresponding relaxation times for Nd\(^{3+}\) at $T = 10$ K are measured to be $T_{2e} = 2.0(2)$ $\mu$s and $T_{1e} = 26(1)$ $\mu$s.

![Figure 2. FS ESE EPR at T = 10 K.](image)

Applying the pulses of various length one can directly prove that the appeared Nd\(^{3+}\) line ($S = 1/2$) does not belong to one of the possible (“forbidden”) transitions for Gd\(^{3+}\) with $S = 7/2$: their ESE amplitudes and phases change differently with the length of $\pi/2$ pulse. The shape of the Nd\(^{3+}\) line is mainly defined by the unresolved superhyperfine structure which is known to be the most resolute exact for $B_{0} \parallel c$ at X-band frequency [9]. Conventionally, at W-band the lines become broader due to the various reasons and it seems to be quite problematic to extract the details of superhyperfine structure from the high-frequency EPR but in many cases it can be done from ENDOR experiments [12], [13].

For ENDOR experiments we used special double (for nuclei and electron) cavities and Mims pulse sequence - $\pi/2$–$\tau$–$\pi/2$–$T$–$\pi/2$ with an additional radiofrequency (RF) pulse $\pi_{RF} = 18$ $\mu$s inserted between the second and third microwave $\pi/2$ pulses. RF frequency in our setup could be swept in the range of (1-200) MHz. Magnetic field value was kept constant, corresponding to the position of Nd\(^{3+}\). Recent review of ENDOR applications for quantum computing is presented elsewhere [16]. Some ENDOR basics are briefly described below.

In the case of a “free” nucleus, RF pulse applied at the Larmor frequency

$$\nu_{Larmor} = \frac{\gamma B_{0}}{\hbar} \approx \hbar^{-1} g_{I} \beta_{I} B_{0},$$

(1)

where $\gamma$ is a gyromagnetic ratio of the nuclear spin $I$, $\hbar$ is a Planck constant, $g_{I}$ is a nuclear g-factor and $\beta_{I}$ is a nuclear Bohr magneton, can change the state of the nuclear spin (the population of the nuclear sublevels).

The ENDOR splitting, $a_{ENDOR}$, can help not only to identify a type of nuclei coupled with the electron spins but also provide spatial relationships between them. For the pure electron-nuclei dipole-dipole interaction in the point model, the electron-nuclear distance, $r$, from the ENDOR splitting can be estimated from

$$a_{ENDOR} \approx g \cdot g_{I} \cdot (1-3\cos^{2}{\theta})/ r^{3},$$

(2)
where $g$ is a g-factor of electron spin $S$, $\Theta$ is an angle between directions of the parallel component of $g$ ($g_\parallel$) and $B_0$. As it follows from (2), $a_{ENDOR}$ depends on the distance between the electron and nuclear spins and their mutual orientation. ENDOR splitting should be maximal for ions with the maximal g-factors and orientations. Additionally, for $I$ equals or larger than one, an electric nuclear quadrupole coupling exists that can split or shift the ENDOR lines: the nuclear quadrupole interaction is sensitive to the electric field gradient at the site of the nucleus.

All nuclei in LiYF$_4$ compound have sensible magnetic moment capable to create a perceptible additional magnetic field at the location of the rare earth impurity (see [9], [12], [13]). Well-resolved ENDOR spectra for $^{19}$F nuclei in parallel orientation presented in Figure 3 which is due to the electron-nuclear interactions of Nd$^{3+}$ and with $^{19}$F. From ENDOR pattern for $^{19}$F one can estimate the electron-nuclear distance to the most remote nuclei from Eq. (2) as $r \approx 0.66$ nm. Taking into account that in the YF$_8$ octahedra of LiYF$_4$ structure, the four first F neighbours are situated at 0.224-0.226 nm ($a_{ENDOR} \approx 4.2$ MHz), the distance to the four second neighbours is of about 0.229-0.232 nm [12], one can see that the electron spin density of Nd$^{3+}$ ions distributes well out of even the second coordination sphere. Detailed interpretation of ENDOR spectra from the angle and frequency dependencies is a matter of the ongoing research.

![ENDOR spectra for $^{19}$F nuclei in LiYF$_4$: Nd$^{3+}$ monocrystal in $B_0 \parallel c$ orientation. $B_0 = 3380$ mT (Nd$^{3+}$ line), $T=10$ K, $\nu = 93.967$ GHz.](image)

**Figure 3.** ENDOR spectra caused by interactions with $^{19}$F nuclei in LiYF$_4$: Nd$^{3+}$ monocrystal in $B_0 \parallel c$ orientation. $B_0 = 3380$ mT (Nd$^{3+}$ line), $T=10$ K, $\nu = 93.967$ GHz.

3. **Conclusions**

The rich, well-resolved, intensive ENDOR spectra show that LiYF$_4$:Nd$^{3+}$ system potentially can be used as an element (or model system) of the many qubit quantum computer. Indeed, it is known that electrons are natural candidates as physical qubits to be exploited for quantum computing and information processing (QC/QIP), and therefore magnetic resonance techniques, are among the most appropriate techniques to be exploited for quantum computing. Pulsed EPR enables manipulation of electron spin and nuclear spin qubits in an equivalent manner and ENDOR can be used as the most useful spin manipulation technology in implementing QC/QIPs [16]. The corresponding experiments are on the way.

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