Mims electron-nuclear double resonance in LiYF$_4$:Ce$^{3+}$ crystal

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Abstract. We report the observation of the pulsed electron-nuclear double resonance (ENDOR) spectra from $^{19}$F and $^7$Li nuclei on impurity Ce$^{3+}$ ions in LiYF$_4$ crystal. The resolved structure from the nearby and remote nuclei in spectra is observed. The outcome shows that LiYF$_4$:Ce$^{3+}$ 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 all the nuclei of the system.

1. Introduction
As a significant class of rare earth compounds, rare earth (RE) fluorides have been 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]. The potential for using RE doped crystals as scintillators (detectors) for radioactive radiation is not disclosed [4]. 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 [5], [6], [7]. In addition, LiYF$_4$ 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 [8].

The interaction of paramagnetic ions in crystals with the magnetic moments of the ligand nuclei (super-hyperfine interaction) usually leads to broadening of the EPR lines, their overlap and even the impossibility of observing the allowed super-hyperfine structure (SHS) in the spectra [8]. Analysis of the SHS allows one to obtain important information on inter-ion interactions and distribution of electron spin density in crystals. For fluorides SHS can vary in a huge range even in the same ligand environment depending on the paramagnetic ion: from 10 MHz for RE ions up to 300 MHz for Pb$^{5+}$ [9], [10]. The nuclear Zeeman splitting for F$^-$ is also of about 10 MHz that complicates the decoding of the EPR spectra.
To the best of our knowledge, up to now SHS with only the nearest fluorine environment (first coordination sphere) has been experimentally and theoretically investigated. Here we show that exploiting pulsed electron-nuclear double resonance (ENDOR) techniques one can study the super-hyperfine interaction with the remote nuclei.

2. Experiment and Discussion
Crystals of LiYF₄ doped with ≈0.05 at % of Ce³⁺ were grown in Kazan Federal University by the Bridgman-Stockbarger technique in argon atmosphere. EPR investigations were done by using helium flow cryostats at X-band Bruker ESP 300 и Bruker Elexsys E580 spectrometers (T = 5-25 K, microwave frequency ν = 9.5 GHz). At these temperatures an intense EPR spectrum from Ce³⁺ ions was observed (Figure 1). Resonant magnetic fields, B, in the orientations B||c and B⊥c (c is the optical axis of crystal) correspond to the g-factors given in paper [11]: g|| = 2.737; g⊥ = 1.475. For Ce³⁺ ions none of the stable isotopes (¹³⁶Ce, ¹³⁸Ce, ¹⁴⁰Ce, ¹⁴²Ce) has a nuclear spin and, therefore, no intrinsic hyperfine structure (HFS) exists.

![Figure 1. EPR line with the SHS of Ce³⁺ ions in LiYF₄. B⊥c, T=20K, ν = 9.38GHz.](image)

We used two–pulse electron spin echo measurements for the primary Hahn–echo sequence (π/2–τ–π–τ–echo), where τ is the interpulse delay time of 240 ns, with initial π/2 and π pulse lengths of 18 and 36 ns, respectively.

For ENDOR experiments we used special double (for nuclei and electron) cavities and Mims pulse sequence - π/2-τ-π/2-τ-π/2 with an additional radiofrequency (RF) pulse τRF = 18 μs inserted between the second and third microwave π/2 pulses (see Figure 2). RF frequency in our setup could be swept in the range of (1-200) MHz. Magnetic field value was kept constant, corresponding to the orientation of B⊥c. Some ENDOR basics are briefly described below. Some examples of the studying petroleum asphaltenes and crude oils by ENDOR technique are presented in our recent papers [12], [13]
Figure 2. Mims pulse sequence at microwave (MW) and radiofrequencies (RF) used to obtain the ENDOR spectra as a function of stimulated electron spin echo amplitude from the frequency of RF pulse.

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

\[ \nu_{Larmor} = \gamma B_0 \equiv h^{-1} |g_I \beta_I B_0|, \]  

where \( \gamma \) is a gyromagnetic ratio of the nuclear spin \( I \), \( h \) 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). For the hyperfine coupling constant \( A \) and simple electron-nuclear coupling \((S = 1/2, I = 1/2)\), it can lead to the appearance of the characteristic features in the ENDOR spectrum at the RF frequencies

\[ \nu_{ENDOR} = \nu_{Larmor} \pm A/2 \] or

\[ \nu_{ENDOR} = A/2 \pm \nu_{Larmor}, \]

depending on the ratio between \( A \) and \( \nu_{Larmor} \).

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

\[ a_{ENDOR} \approx g \cdot g_e \cdot (1 - 3 \cos^2 \Theta)/r^3, \]

where \( g \) is a g-factor of electron spin \( S \), \( \Theta \) is an angle between directions of the parallel component of \( g \) and \( B_0 \). As it follows from (4), \( a_{ENDOR} \) depends on the distance between the electron and nuclear spins and their mutual orientation. Additionally, for \( I = 1 \) 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 \( \text{LiYF}_4 \) compound have sensible magnetic moment capable to create a perceptible additional magnetic field at the location of the rare earth impurity. In Table 1 some data for them which are important for the interpretation of ENDOR spectra are presented.

ENDOR spectra for B.Lc presented in Figure 3 are clearly due to the electron-nuclear interactions with \(^7\text{Li} \) and \(^19\text{F} \) isotopes. The ability to observe narrow ENDOR lines at various RF
frequencies from the Larmor ones testifies that Ce\(^{3+}\) is an appropriate probe to sense remote nuclei (see Eq. 4).

Interpretation of \(^7\)Li ENDOR causes troubles due to the possible influence of quadrupole interaction (see Table 1). From ENDOR pattern for \(^{19}\)F one can estimate the electron-nuclear distance to the most remote nuclei from Eq. (4) 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 \(\left(\nu_{\text{ENDOR}} \approx 4.2\right.\) MHz), the distance to the four second neighbours is of about 0.229-0.232 nm \[8\], one can see that the electron spin density of Ce\(^{3+}\) ions distributes well out of even the second coordination sphere. Technical limitations did not allow us to register low frequency (of about 1 MHz) ENDOR features.

**Table 1.** Nuclear spin, natural abundance, relative gyromagnetic ratio and calculated Larmor frequency in \(B = 4720\) G for the LiYF\(_4\) nuclei

| Nuclei | Isotope | I | Natural Abundance, % | Relative to \(^1\)H gyromagnetic ratio | Larmor frequency for \(B = 4720\) G, MHz |
|--------|---------|---|----------------------|----------------------------------|---------------------------------|
| Li     | 6       | 1 | 7.6                  | 0.1471                           | 2.96                            |
|        | 7       | 3/2 | 92.4                | 0.3887                           | 7.81                            |
| F      | 19      | 1/2 | 100                  | 0.9412                           | 18.91                           |
| Y      | 89      | 1/2 | 100                  | 0.0492                           | 0.99                            |

**Figure 3.** ENDOR spectra caused by interactions with \(^7\)Li (left panel) and \(^{19}\)F (right panel) isotopes in LiYF\(_4\): Ce\(^{3+}\) monocrysls in B\(\perp\)c orientation. B= 4721 G, T=10 K, \(\nu = 9.75\) GHz. Corresponding Larmor frequencies are marked by arrows. Dashed lines mark the minimal observed ENDOR splitting for \(^{19}\)F.

The observed features show that LiYF\(_4\):Ce\(^{3+}\) system potentially can be used as an element of quantum computing. 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, consisting of EPR and NMR (nuclear magnetic resonance) 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 QCs/QIPs [14].

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