Magnetic Resonance Study of Non-Equivalent Centers Created by 4f-Ions in Congruent and Stoichiometric Lithium Niobate

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ABSTRACT

Lithium Niobate doped with 4f-ions is of great interest for both fundamental science and advanced applications including high efficiency lasers with frequency conversion, elements for an all-optical telecommunication network and quantum cryptography. Our study has shown that 4f-ions create an unexpected variety of completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals. Dominant Nd\textsubscript{1} and Yb\textsubscript{1} centers have C\textsubscript{3} point symmetry (axial center), whereas all Er and most other Nd and Yb centers have the lowest C\textsubscript{1} symmetry. Distant defects create small distortions of the crystal field at the impurity site, which cause line broadening, but do not change the C\textsubscript{3} symmetry of observed EPR spectra. Defects in the near neighborhood can lower center symmetry from C\textsubscript{3} to C\textsubscript{1}. We concluded that Nd\textsubscript{1} has distant charge compensation, whereas the charge excess in low-symmetry Nd(Li) centers is compensated by near lithium or niobium vacancies. Since no axial centers were found for Er, models with cation vacancies can not describe our experimental data. The dominant axial Yb\textsubscript{1} center has no defects in its surrounding. One axial and one low-symmetry Yb centers are self compensating Yb(Li)-Yb(Nb) pairs. Six other centers are different complexes of Yb\textsuperscript{3+} and intrinsic defects. Obtained data can be used for defect engineering for tailoring properties of photonic materials.

INTRODUCTION

Lithium Niobate (LN) doped with 4f-ions is of great interest for both fundamental science and advanced applications including high efficiency lasers with frequency conversion, elements of an all-optical telecommunication network and quantum cryptography. Conventional LN crystals, grown from a congruent melt with lithium deficiency (X\textsubscript{melt} = X\textsubscript{Crystal} \approx 48.4\%), where $X = [\text{Li}]/([\text{Li}]+[\text{Nb}])$, contain some percent of intrinsic (non-stoichiometric) defects like antisites, lithium and niobium vacancies and their complexes, and, consequently, have strong structural disorder (Fig. 1). Crystals grown under special conditions from melts to which potassium has been added have significantly lower intrinsic defect concentrations. These samples, named stoichiometric or nearly stoichiometric (sLN), have physical properties which are often very different from properties of congruent samples.

According to data of the Extended X-ray Absorption Fine Structure Analysis, EXAFS \cite{1}, and Rutherford back scattering data \cite{2, 3, 4, 5, 6, 7}, most trivalent ions substitute for Li (with some displacement from Li site) and should create similar centers. However, six or more different centers were distinguished in congruent samples by optical absorption/emission \cite{8, 9}
and site-selective spectroscopy \cite{10, 11, 12}. In some cases, a substitution for Nb was supposed \cite{13, 14, 15}.

Figure 1. (Color online) Schematic representation of the crystal lattice of stoichiometric LiNbO$_3$ (left) and congruent Li$_{0.94}$Nb$_{1.12}$O$_3$ (right). The ball sizes do not correspond to ionic radii of Li$^+$ (0.68Å), Nb$^{5+}$ (0.69Å) and O$^{2-}$ (1.32Å). Shadow ellipses show crystal areas distorted by the presence of intrinsic defects.

Electron Paramagnetic Resonance, EPR and Electron Nuclear Double Resonance, ENDOR provides additional information about the characteristics of impurity centers and their structures. Earlier investigations \cite{16, 17, 18, 19} have shown that the most intense EPR lines belong to the center with highest possible symmetry in R3c lattice of lithium niobate (C$_3$ or axial symmetry). Some recent results obtained for congruent crystals \cite{20, 21, 22, 23, 24} are very different from those previously published \cite{, 25} or are contradictory to crystal symmetry.

In order to clear up questions concerning the structures of 4f-centers, we studied LN crystals of various composition doped with 4f-ions using EPR, ENDOR, and optical spectroscopy. Our study has shown that 4f-ions create an unexpected variety of completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals.

The EPR/ENDOR measurements were carried out in the temperature range between 4 and 50 K. Optimal temperature was different for different 4f-ions. The use of two microwave frequencies (9.8 GHz, X-band and 35 GHz, Q-band) and, correspondingly, different magnetic fields allowed us to separate the EPR lines of different centers and the Li and Nb ENDOR lines.
This separation facilitates deciphering and interpretation of observed spectra, and raises the reliability of determined characteristics and conclusions made.

**EXPERIMENT**

The line widths of observed signals for congruent and nearly stoichiometric samples (for instance, Fig. 2, left) are completely different: 10-15 mT and 1.5-2.5 mT, respectively (the line widths depend slightly on magnetic field orientation). The EPR lines in congruent samples are so broad that it is too difficult to separate lines of different centers and isotopes. This is the main reason why the hyperfine structure and satellite centers were not studied in detail earlier. The tremendous narrowing of EPR lines in nearly stoichiometric samples, when compared to those in congruent samples, allowed us to distinguish several non-equivalent centers (NEC), as well as line splitting caused by the hyperfine interaction (HFI) of 4f-electrons with the nuclear spins of low abundance magnetic isotopes, $^{143}$Nd and $^{145}$Nd (natural abundance 12% and 8% correspondingly; Fig. 2, right), $^{171}$Yb and $^{173}$Yb (14.4% and 16.2%) and $^{167}$Er (22.9%).

![Figure 2](example-image.png)

**Figure 2.** (Color online) Comparison of Nd$^{3+}$EPR spectra in congruent and stoichiometric samples (left). The assignment of lines of different nonequivalent centers and hyperfine structures of Nd$^{3+}$ (right). The $^{143}$Nd and $^{145}$Nd isotopes have nuclear spin $I$=$7/2$ and give seven satellite hyperfine EPR lines. The peak-to-peak intensity ratio for the single line of all nonmagnetic isotopes with $I$=0 (80% abundance) and one $^{143}$Nd and $^{145}$Nd line is about 80:1.5:1. X-band, $T$=19K.

Four different crystallographically non-equivalent centers were found for Nd$^{3+}$ (Fig. 2, right). The EPR lines of dominant Nd$_1$ center have no angular dependence for rotations of the magnetic field in the $xy$ crystallographic plane (Fig. 3). It means that this center has axial $C_3$ point symmetry. All sites on the $z$ (or optical $c$) axis of the crystal, including the sites of Li, Nb and the structural vacancy, $v$ - have the symmetry of the point group $C_3$. An isolated defect in any of these positions creates a $C_3$ center (in the following also labeled an “axial” center). A defect ion shift along $z$-axis does not change the center symmetry. Distant defects like lithium vacancies create small distortions of crystal field at the impurity site, which normally cause only
the EPR line broadening, but do not change the $C_3$ symmetry of observed EPR spectra. Therefore, the positive charge excess of Nd$^{3+}$ is compensated by some defect on $z$-axis or by distant defects. Three other neodymium centers have lowest $C_1$ symmetry due to the presence of lithium or niobium vacancies in the near neighborhood of Nd$^{3+}$.

![EPR Spectra Diagram](image)

**Figure 3.** (Color online) Angular dependence of the EPR spectra (road map) in nearly stoichiometric LN:Nd$^{3+}$. $T=19$ K, $\nu = 9.813$ GHz. Solid lines are calculated for axial centers using the corresponding $C_3$ symmetry spin-Hamiltonian for magnetic and non-magnetic isotopes; symbols – experimental line positions and their widths.

The spin-Hamiltonian, which describes the positions of EPR lines, can be written as

$$H_{EPR} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A}^{(i)} \cdot \mathbf{I}^{(i)}$$

(1)

Here $\mu_B$ - Bohr magneton, $\mathbf{B}$ - vector of static magnetic field, $\mathbf{g}$ - $g$-tensor, $\mathbf{S}$, $\mathbf{I}$ - electron and nuclear spins of the paramagnetic center, $\mathbf{A}$ - tensor of hyperfine interaction, $i$ - isotope number. “Visual EPR” programs [26], which are based on exact numerical diagonalization of the spin-Hamiltonian matrices, were used to simulate observed spectra and their angular dependencies.
Doping congruent lithium niobate with Mg above a threshold concentration (about 6 at.%) leads often to the appearance of additional centers. However, it is difficult to study these centers in detail due to line broadening caused by presence of Mg. In the case of crystals of stoichiometric composition, the threshold concentration and the corresponding line broadening is significantly smaller. We found that one more low-symmetry Nd$^{3+}$ center, Nd$_5$, appears in nearly stoichiometric Ln doped with 0.4 at.% of Mg (Fig. 4).

**Figure 4.** (Color online) The assignment of lines of different Nd$^{3+}$ centers in nearly stoichiometric LiNbO$_3$ doped with 0.4 at.% of Mg.

The EPR spectra of Yb$^{3+}$ ions exhibited the existence of nine paramagnetic centers (lines of some centers are indicated in Fig. 5). Due to line narrowing in stoichiometric crystals, we were able to observe hyperfine structures from the $^{171}$Yb and $^{173}$Yb isotopes, to follow angular dependencies of hyperfine components for the most intensive centers, and to determine precisely all components of the $g$-tensors and the orientations of the main axes for all Yb$^{3+}$ centers.

Angular dependencies (Fig. 6) clearly show specific features of low-symmetry Yb$^{3+}$ centers in lithium niobate:
1) the single line at $B||z$ splits into 6 lines with rotation in the $zx$ plane and into 3 lines with rotation in the $zy$ plane;
2) 6 lines show angular dependence with rotation in the $zy$ plane;
3) a “center of gravity” for the six lines of every low-symmetry center has approximately the same position for any orientation of magnetic field in $xy$ plane.

Five observed non-equivalent low-symmetry centers correspond to single Yb$^{3+}$ ions.
Three Yb$^{3+}$ centers have no angular dependence of the EPR lines for magnetic field rotation in the $xy$ crystallographic plane (axial centers). The ENDOR observations of Nb nuclei in the nearest neighborhood of the main axial Yb$_1$ center (Fig. 7) gave us direct evidence that in this center the Yb$^{3+}$ ion substitutes for Li and has no charge compensator in its nearest surroundings (distant charge compensation mechanism). Defects in the near neighborhood cause strong changes of the center characteristics and lower the center symmetry from $C_3$ to $C_1$. 

Figure 5. (Color online) The assignment of lines of different nonequivalent centers and hyperfine structures of Yb$^{3+}$.

Figure 6. (Color online) Angular dependence of the EPR spectra in sLN:Yb$^{3+}$. Symbols represent positions of observed lines. Solid lines were calculated with the help of the spin-Hamiltonian (1) for non-magnetic isotopes of six magnetically nonequivalent isolated low-symmetry centers with $S=1/2$ (green lines) and for Yb$^{3+}$-Yb$^{3+}$ pairs with $S=1$ (magenta lines). Proposed models of these centers are shown on the right.
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Figure 7. (Color online) The ENDOR spectrum for the Yb\(_1\) center in sLN:Yb\(^{3+}\) at \(B\parallel z\), \(B=158\) mT (top, left). Well distinguished lines of \(^{93}\)Nb is indicated. Angular dependence of the ENDOR spectra for the Yb\(^{3+}\) center in sLN (bottom, left) measured at \(T=6\) K and \(\nu=9.865\) GHz. Symbol positions correspond to the centers of observed ENDOR lines; symbol sizes are proportional to line intensities. Calculated solid magenta lines are plotted for \(^{93}\)Nb\(_1\) nucleus: thick lines belong to \(M_S=1/2\), thin ones – \(M_S=-1/2\). Model of the Yb\(_1\) center (right); the numbers indicate shells of surrounding nuclei.

The observed low-symmetry pair (Fig. 6) should be attributed to the Yb\(^{3+}\)-Yb\(^{3+}\) ions in the next neighbor or next-next neighbor positions (Nb #2 and Nb #3 on Fig. 7). The nearest neighbor site for Yb\(^{3+}\) substituted for Li is the Nb site located at a distance 3.01Å on the crystal axis (Nb #1 on Fig. 7). Due to small distance between nearest ions, a self-compensated pair of Yb\(_{Li}\)-Yb\(_{Nb}\) creates an axial center with rather strong exchange interaction and, correspondingly, large singlet-triplet splitting. This yields unfavorable conditions for observing EPR lines for non-magnetic isotopes. The calculated positions of satellite hyperfine lines, which belong to a pair of one non-magnetic isotope and one \(^{171}\)Yb isotope with \(I=1/2\), were very close to some observed lines.

In the case of Er\(^{3+}\) only two different centers were found. Their lines practically coincide at \(B\parallel z\) (Fig. 8); however, these lines were easily distinguished for other orientations of magnetic field (Fig. 10) and in experiments at 34 GHz (Q-band). Angular dependencies of their EPR lines were successfully described using strongly anisotropic \(g\)-tensors. Both observed centers have the lowest \(C_1\) symmetry. Several possible models should be considered for low-symmetry Er\(^{3+}\) centers: Er\(^{3+}\) substituted for Li\(^{+}\) or incorporated into tetrahedral structural vacancy compensated by interstitial O\(^2-\) in both cases, and Er\(^{3+}\) substituted for Nb\(^{5+}\) compensated by an oxygen vacancy in the nearest neighborhood (local charge compensation mechanism, Fig. 9).
DISCUSSION

The observation of lines without angular dependence in the xy planes is strong evidence that our samples have the same crystal lattice symmetry as at room temperature and that a concentration of Nd and Yb dopants of about 0.02-0.2 wt. % does not cause a phase transition of the LN lattice.
Since in studied samples the observed EPR lines are ten times narrower than for congruent samples, the concentration of distant intrinsic defects (i.e. defects in the bulk) is significantly reduced. However, even in the best samples it still exceeded the concentrations of 4f-impurities used, about 0.02-0.2 wt.%.

Distant defects create small crystal field distortions at the impurity site, which normally cause EPR line broadening, but do not change the symmetry of observed EPR spectra. Defects in the near neighborhood cause strong changes of \( g \) and \( A \) tensors and lower the center symmetry.

The ENDOR data for Nd\(^{3+}\) [27] and Yb\(^{3+}\) (Fig. 7) clearly indicate that these 4f-ions substitute for Li in the case of the dominant Nd\(_1\) and Yb\(_1\) centers. There is no ENDOR data for Er\(^{3+}\).

The EPR lines of Yb\(^{3+}\) in congruent LN are very broad. Therefore, the axial center Yb\(_1\) was the only resolved center in LN:Yb [17, 18].

Our EPR data has shown that three centers have axial C\(_3\) symmetry, whereas all others have C\(_1\) symmetry. Characteristics of Yb\(_1\) centers are very close to those published [17, 18]; however, in our study [28] they were determined with a little higher precision due to line narrowing and better resolution in sLN crystals.

The angular dependence (Fig. 6), the principal values of \( g \)-tensors for Yb\(^{3+}\) centers as well as the orientations of their principal axes are completely different from those published [20, 21, 22] for congruent crystals doped with 1wt% of Yb\(^{3+}\). This dopant concentration is 50 times higher than in our crystals and is comparable with the concentration of intrinsic defects in congruent crystals; this may lead to the appearance of impurity pairs.

Several features of the published EPR spectra [20, 21, 22] are very different from those previously published [17, 18] and our spectra. Due to a lack of line assignments (similar to what is presented in our Fig. 5) and comparison of calculated line positions with experiments (similar to our Fig. 6), it is difficult to verify the correctness of EPR spectra treatment and interpretation in [20, 21, 22]. We suspect that samples used in these experiments were improperly oriented.

The observation of the Nb nuclei in the nearest neighborhood of Yb\(_1\)\(^{3+}\) is direct evidence that the main axial Yb\(_1\) center has no charge compensator in the nearest surrounding (distant charge compensation mechanism). Since the obtained characteristics for the axial Yb\(_1\) center and low symmetry centers are very similar, we can suppose that in all these centers the Yb\(^{3+}\) ion substitutes for Li\(^+\); however, the low-symmetry centers have intrinsic defects and/or charge compensation defects located in the near neighborhood of Yb\(^{3+}\) (but not in bulk, since the observed EPR lines are ten times narrower than for congruent samples). The observed variety of axial and low-symmetry centers can be related to different locations of the intrinsic defects (first, second, third and other neighbors of Li site), different configurations of two intrinsic defects like lithium vacancies around impurity ions, as well as different position of Yb\(^{3+}\) in lithium niobate lattice.

It was rather unexpected to observe Yb\(^{3+}\)-Yb\(^{3+}\) pair centers in samples grown with 0.02 wt.% Yb\(_2\)O\(_3\) in the melt. A possible explanation is the following. Nearly stoichiometric lithium niobate crystals have significantly smaller concentrations of intrinsic defects, which serve as charge compensators for Yb\(^{3+}\) substituted for Li. This deficit leads to the appearance of self compensated Yb\(_{Li}\)-Yb\(_{Nb}\) pairs.

The \( g \)-tensor components for all axial centers in sLN differ markedly from \( g_{||} = 1.9 \) and \( g_{\perp} = 2.8 \) for the second axial center observed in LN codoped with Mg, which was attributed to the Yb\(^{3+}\) center at the Nb\(^{5+}\) site [18]. The following possible models should be considered for
these axial centers: 1) the Yb$^{3+}$ ion substitutes for Li and has an intrinsic defect on the center axis (for instance, niobium vacancy), 2) the Yb$^{3+}$ ion substitutes for Nb and has no defect in the nearest surrounding (distant charge compensation mechanism), 3) the Yb$^{3+}$ ion incorporates into a structural vacancy, 4) the Yb$^{3+}$ ion in LN codoped with Mg substitutes for Nb$^{5+}$ and has Mg$^{2+}$ ions substituted for Li$^{+}$ in the nearest surrounding (local charge compensation mechanism). Additional investigation is required in order to verify definite models for these centers.

**Figure 10.** (Color online) Angular dependence of the EPR spectra in sLN:Er$^{3+}$. Symbols represent positions of observed lines. Solid lines were calculated for non-magnetic isotopes using characteristics for lithium vacancy models [19].

In the measured EPR spectra of Er$^{3+}$ there are obviously no lines, which have the same line positions at arbitrary orientation of magnetic field in xy plane (Fig. 10). It means that there are no axial Er$^{3+}$ centers in both congruent and stoichiometric LN. According to previously proposed center models [19], in which the Er$^{3+}$ charge excess is compensated by lithium vacancies in different positions creating axial and tilted centers, such a center should have dominant EPR lines. Since line positions calculated with characteristics from [19] (Fig. 10) do not agree with our observation, these models have no experimental confirmation. We did not observe also the Er$^{3+}$ center with “cubic” symmetry [24]. A center with cubic symmetry should be characterized by isotropic g-factor, and its EPR lines should not have angular dependence of position and intensity in any crystallographic plane. Our spectra as well as published spectra [24] have no lines with these features.
At present, we do not have sufficient data supporting one of models in Fig. 9 or other models for Er$^{3+}$ centers observed in stoichiometric lithium niobate. It should be noted that number of different Er$^{3+}$ centers in stoichiometric samples (only two) is unexpectedly smaller than the number of centers distinguished by optical absorption/emission [8, 9] and site-selective spectroscopy [10, 11, 12] in congruent samples (six or even more). Intrinsic defects probably play a more important role in congruent samples and thus create a wider variety of centers.

CONCLUSIONS

Distant defects create small distortions of crystal field at the impurity site, which cause line broadening, but do not change the C$_3$ symmetry of observed EPR spectra. Defects in the near neighbourhood of an impurity center cause strong changes of the center characteristics ($g$ and $A$ tensors in the case of 4f-ions) and lower the center symmetry from C$_3$ to C$_1$.

Four Nd$^{3+}$, nine Yb$^{3+}$, and two Er$^{3+}$ centers were found and described.

Dominant Nd$_1$ center has C$_3$ point symmetry (axial center), whereas three others have lowest C$_1$ symmetry. We concluded that Nd$_1$ has distant charge compensation, whereas the charge excess in low-symmetry Nd$_{1i}$ centers is compensated by lithium or niobium vacancies in the near neighborhood of Nd$^{3+}$ out of z-axis of the center.

The Yb$^{3+}$ ions create three C$_3$ and six C$_1$ centers. The ENDOR observations of Nb nuclei for dominant axial Yb$_1$ center gave us direct evidence that there are no defects in its surrounding (distant charge compensation). One axial center and one C$_1$ center are self compensated Yb(Li)-Yb(Nb) pairs. Six other centers are different complexes of Yb$^{3+}$ and intrinsic defects. Different location of the defects around the impurity is the reason of the existence of these NEC.

Both Er$^{3+}$ centers have C$_1$ symmetry. Since no axial centers were found, models with cation vacancies can not describe our experimental data.

A fundamental understanding of the structures and properties of impurity defects in lithium niobate is important for both basic science and applications. Stoichiometric crystals brought real breakthrough to the study of impurity centers in lithium niobate. The obtained numerous spectroscopic parameters can be used as cornerstones for model calculations of defects in crystals. They can also be used for comparison with ab initio simulations of structural properties of crystals. Discussed models can be helpful for defect engineering for tailoring properties of photonic materials.

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