Electron paramagnetic resonance and electron-nuclear double resonance of nonequivalent Yb\textsuperscript{3+} centers in stoichiometric lithium niobate

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1 Introduction
Lithium niobate crystals doped with ytterbium were studied using Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR). The tremendous narrowing of EPR lines in nearly stoichiometric samples, when compared to those in congruent samples, allowed us to distinguish nine non-equivalent centers, as well as line splitting caused by the hyperfine interaction of ytterbium electrons with the nuclear spins of two magnetic isotopes, \textsuperscript{171}Yb and \textsuperscript{173}Yb. Eight of the nine centers are described for the first time. It was found that three of the centers have axial C\textsubscript{3} symmetry, and all others have the lowest C\textsubscript{1} symmetry due to the presence of intrinsic defects and/or charge compensation defects in the near neighborhood of Yb\textsuperscript{3+}. Characteristics of the g-tensor for all of the centers and hyperfine tensors for axial centers were determined. The ENDOR observations of Nb nuclei in the nearest neighborhood of Yb\textsuperscript{3+} gave direct evidence that the dominated axial Yb\textsuperscript{1+} center has no charge compensator in its nearest surroundings (distant charge compensation mechanism). Both the EPR and ENDOR data for the main axial ytterbium center are explained by a supposition that Yb\textsuperscript{3+} ions substitute for Li\textsuperscript{+}. Possible models for low-symmetry centers are discussed. The obtained numerous spectroscopic parameters can be used as cornerstones for model calculations of Yb\textsuperscript{3+} centers in lithium niobate.

Axial center of Yb\textsuperscript{3+} substituted for Li\textsuperscript{+} in LiNbO\textsubscript{3} (the xy-plane projection). z-axis is parallel to C\textsubscript{3} symmetry axis and perpendicular to the drawing plane; \(\nu_{\text{oct}}\) is octahedral structural vacancy.
EPR line with a width of 5 mT or wider was registered [1]. Its position was characterized by g-factors $g_\parallel = 4.86$ and $g_\perp = 2.69$ when the external magnetic field $B$ was parallel and perpendicular to crystal axis $z$. The line was attributed to Yb$^{3+}$ substituted for Li. However, the possibility Yb$^{3+}$ substituting for Nb with a subsequent relaxation in position was not excluded. Three peaks in the optical band related to the $2F_{7/2} \rightarrow 2F_{5/2}$ transition (950–960 nm) [2], and some features in angular scans of Rutherford backscattering spectrometry (RBS) [3] were interpreted as evidence of the presence of non-equivalent centers (NEC). The NEC were associated with the non-stoichiometric defects of LN related to the usual Li deficiency of congruent samples. However, trials to interpret the nature of these centers, based on statistical perturbations produced by Nb antisites as well as Li and Nb vacancies, have failed to account for the experimentally obtained relative concentrations of these centers. Therefore, the origin of the trivalent rare earth centers was related to the local charge compensation mechanism, which would be responsible for the different RE$^{3+}$ positions.

The observed effect of crystal composition on the multicenter distribution [4] confirmed that the NEC are directly connected with this non-stoichiometry phenomenon. The splitting observed in low-temperature emission spectra [5] was considered as proof that Yb$^{3+}$ occupies more than one site in LN. Magnetic circular dichroism (MCD) [6] confirmed the crystal field quantum numbers and g-factor values obtained earlier. In the EPR study of Yb doped LN and LN codoped with Mg [7], two hyperfine satellites with a splitting of about 67 mT were observed for $B_\parallel z$. This doublet was attributed to the $^{171}$Yb isotope. Another axial spectrum with $g_\parallel = 1.9$ and $g_\perp = 2.8$ was also detected in LN:Mg. It was attributed to the Yb$^{3+}$ center at the Nb$^{5+}$ site. However, this contradicts to some extent the results of RBS experiments [8]. The characteristics of two axial Yb$^{3+}$ centers [7], along with the EPR results obtained for stoichiometric LN [9], were used for theoretical analysis of the EPR parameters [10].

The EPR spectra of Yb$^{3+}$ in congruent crystals [11–13] are very different from previously published in [1, 7]. The difference was attributed to a dominance of low symmetry centers.

In order to obtain additional information about ytterbium centers and to clear up the ytterbium position we carried out a study of LN:Yb crystals of different composition using EPR and ENDOR. Spectroscopic characteristics of eight Yb$^{3+}$ centers were determined for the first time.

### 2 Crystals, equipment, and computer programs

Conventional congruent lithium niobate samples are usually grown from Li-deficient melts with ratio $x_m = [Li]/([Li] + [Nb]) \approx 48.5\%$. These samples contain significant concentrations of intrinsic defects (Fig. 1, right), like antisites (Nb$_{Li}$), lithium and niobium vacancies and their complexes [14]. The intrinsic defects can efficiently compensate for the charge excess of non-isovalent impurities up to 1–2 at%. Therefore, congruent samples are tolerant to both intentional dopants and non-controlled impurities. Samples grown from stoichiometric quantities of Li$_2$CO$_3$ and Nb$_2$O$_5$ (similar to used in [1]) have usually the crystal composition $x_c$ close to 48.6%.

Three basic procedures are used for obtaining stoichiometric LN crystals with $x_c \approx 50\%$: post-growth vapor transport equilibrium (VTE) treatment of congruent samples in Li-rich powder [15, 16], double crucible growth [17, 18], and growth from melts with the addition of potassium [19–23]. Undoped stoichiometric samples have regularly ordered ideal lattices with R3c group symmetry at temperatures below ferroelectric phase transition at 1500 K (Fig. 1, left).

![Figure 1](online colour at: www.pss-b.com) 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$^+$ (0.68 Å), Nb$^{5+}$ (0.69 Å) and O$^{2-}$ (1.32 Å). Shadow ellipses show crystal areas distorted by the presence of intrinsic defects.
Two sets of crystals, grown by the Czochralski method and doped with 0.02 wt.% Yb$_3$O$_5$ in the melt, were used. One set of samples was grown from a congruent melt (cLN samples); another set was grown under special conditions from a melt with the addition of potassium. The actual composition of the latter samples, $x_\text{c} \approx 49.6 \pm 0.2\%$, was determined by analyzing the EPR line widths [24] and the blue shift of the absorption edge [25–28]. These samples have significantly reduced concentration of intrinsic defects. Due to a small deviation of crystal composition from stoichiometric, we call them “nearly stoichiometric” samples or sLN.

All samples were cut from well oriented boules. The crystal axes orientations were verified with the help of X-ray measurements and by the EPR study of trace Fe$^{3+}$ impurities at room temperature.

The EPR measurements were carried out in the temperature range of 4.2–20 K by a Bruker ELEXYS 560 with DICE ENDOR accessory (X- and Q-bands). Angular dependencies of the EPR and ENDOR spectra were measured at 6 K and microwave frequency $\nu \approx 9.865$ GHz with two-degree steps. Such steps were necessary in order to follow the variations in line positions. Treatment of the EPR spectra and their angular dependencies was done using “Visual EPR” programs [29], which are based on exact numerical diagonalization of the corresponding spin-Hamiltonian matrices.

3 Optical absorption Two features are clearly seen in optical absorption spectra (Fig. 2): a strong blue shift of the absorption edge of samples grown from melts with potassium, and a multiband structure of optical absorption related to ytterbium.

In stoichiometric crystals, the edge wavelength $\lambda_{20}$ for an absorption coefficient of 20 cm$^{-1}$ is approximately equal to 303 nm [27]. In congruent samples, $\lambda_{20}$ is usually close to 320 nm. The $\lambda_{20}$ for LN:Yb samples grown with the addition of potassium in the melt is about 305–307 nm. This means that our samples have significantly reduced concentrations of intrinsic defects (nearly stoichiometric composition). The LN:Yb samples obtained with the help of VTE treatment [30] have $\lambda_{20} \approx 310–311$ nm, and a slightly higher deviation from stoichiometric composition.

Often, doping with non-isovalent impurities may introduce defects compensating for the impurity charge and size misfit (this was observed, for instance, for Fe$^{3+}$ [31]). In our case, the ytterbium concentration used, 0.02 wt% in the melt is smaller than the estimated concentration of intrinsic defects, 0.4%. Therefore, charge compensation by intrinsic defects is expected.

The electronic configuration of a free Yb$^{3+}$ (4f$^{13}$) ion has a $^4\text{F}_{\text{g}}$ ground state and a $^4\text{F}_{\text{g}}$ excited state. The trigonal crystal field completely splits the $^4\text{F}_{\text{g}}$ and $^2\text{F}_{\text{g}}$ into four and three Kramers doublets. In the earlier investigation of LN:Yb, four strong absorption bands at 918 nm, 946 nm, 980 nm and 1010 nm were registered at room temperature in congruent LN [1]. Lowering crystal field symmetry to $\text{C}^3_1$ symmetry (due to lattice vibrations or some defects in Yb$^{3+}$ surrounding) leads to the appearance of additional side bands, which are resolved at liquid helium temperatures.

The multiband structure of optical absorption was analyzed in detail in Refs. [1, 2, 30]. Since the structures in our samples were similar to those observed in the cited papers, we will not discuss them here. We point out that no definite conclusion about the NEC can be made from the room temperature optical spectra. Energy level positions for Yb$^{3+}$ in congruent and stoichiometric crystals are similar. However, the random distribution of intrinsic defects in congruent crystals leads to random shifts of the levels.

4 The EPR spectra and their angular dependencies The ideal LN lattice (Fig. 1, left) has two LN$\text{O}_3$ molecules in its rhombohedral elementary unit cell [32–34]. All sites on the z (or optical c) axis of the crystal, including the sites of Li, Nb and the structural vacancy, have point group symmetry $\text{C}_3$. All other positions have the lowest possible symmetry, $\text{C}_1$. Due to the three-fold axis in the lattice, each $\text{C}_3$ center has two additional magnetically non-equivalent partners, which can be transformed into each other by a rotation around the z-axis by 120° and 240°. The glide mirror plane creates the “Left” (L) and the “Right” (R) partners, which are crystallographically identical, since they have the same crystal field splitting and are not distinguishable by optical methods. However, the L and R centers are magnetically non-equivalent and can be resolved by magnetic resonance techniques. Possible models of isolated and complex centers for Me$^{2+}$, Me$^{3+}$,…, Me$^{6+}$ impurities and their relations to intrinsic defects were considered in a review [35].

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

$$H_{\text{EPR}} = \mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A}^{(0)} \cdot \mathbf{I}^{(0)}.$$  

(1)
Here $\mu_B$ – Bohr magneton, $B$ – vector of static magnetic field, $g$ – $g$-tensor, $S$, $I$ – electron and nuclear spins of the paramagnetic center, $A$ – tensor of hyperfine interaction (HFI), $i$ – isotope number.

Ytterbium has five isotopes with $I = 0$: $^{169}$Yb (natural abundance 0.13%), $^{170}$Yb (3.04%), $^{172}$Yb (21.83%), $^{173}$Yb (31.83%), and $^{174}$Yb (12.76%). It has also two stable isotopes with non-zero magnetic moments: $^{171}$Yb ($I = 1/2$, natural abundance 14.28%) and $^{172}$Yb ($I = 5/2$, 16.13%). Therefore, each magnetically non-equivalent center of $\text{Yb}^{3+}$ (electron spin $S = 1/2$) creates 9 EPR lines: one intense line caused by all non-magnetic isotopes (total natural abundance 69.59%), one hyperfine doublet and one sextet. Expected relative intensities for lines of all non-magnetic isotopes, $^{171}$Yb, and $^{173}$Yb are 1 : 0.1 : 0.04.

Crystallographically non-equivalent centers have different location for $\text{Yb}^{3+}$ in the lattice and/or a different surrounding. They have different crystal field splitting, and as a consequence, different $g$-tensors. At an arbitrary orientation of external magnetic field, every crystallographically non-equivalent $\text{Yb}^{3+}$ center can produce 9 (axial $C_3$-center) or 54 (low-symmetry $C_1$ center) EPR lines. The lines of the $C_1$ centers merge partly at specific magnetic field orientations, like $B \parallel z$ or $B$ in $z\gamma$ glide mirror plane.

This information facilitates deciphering and interpreting the EPR spectra.

5 Non-equivalent centers The linewidths of observed $\text{Yb}^{3+}$ signals for congruent and nearly stoichiometric samples (Fig. 3) are completely different: 10–15 mT and 1.5–2.5 mT, respectively (the linewidths 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 was not studied in detail earlier. The tremendous narrowing of the EPR lines in Li-rich or nearly stoichiometric samples significantly enhances the spectral resolution [36]. This allowed us to distinguish several NEC and to study the hyperfine interaction between $\text{Yb}^{3+}$ electrons and its nuclear magnetic moment.

At least nine crystallographically non-equivalent centers were definitely observed. Some of them are indicated in Fig. 3.

Since for $B \parallel z$ the evaluated transition probabilities were practically equal for all centers (despite of the strong anisotropy of $g$-tensors), the relative concentration $N_i$ of the centers can be estimated with the help of the simple expression

$$N_i \sim I_i \times A_i^2,$$

where $I_i$ is the peak-to-peak intensity of a line, and $A_i$ is the line width.

We found that $N_1$ : $N_2$ : $N_3$ : $N_4$ : $N_5$ : $N_6$ : $N_7$ : $N_{171}$ : $N_{173}$ ≈ 0.72 ± 0.02 : 0.05 ± 0.02 : 0.05 ± 0.02 : 0.05 ± 0.02 : 0.02 ± 0.01 : 0.02 ± 0.01 : 0.01 ± 0.001. Due to the presence of many small overlapping lines in the EPR spectra we cannot exclude that $\text{Yb}^{3+}$ ions create more than these nine centers in LN crystals. However, the concentration of the rest of the centers in nearly stoichiometric samples should be less than 0.02 (or at least 40 times less than that for axial $\text{Yb}_1$ centers).

No splitting of the most intense lines (center $\text{Yb}_1$) as well as $\text{Yb}_2$ and $\text{Yb}_3$ was found at arbitrary orientations of the external magnetic field relative to the crystal axes. These centers have axial $C_3$ symmetry. The lines of all other centers split when the magnetic field direction deviates from the $z$-axis. Therefore, they belong to low-symmetry $C_1$ centers.

6 The EPR of axial centers Angular dependencies of all non-magnetic and magnetic isotopes of the axial $\text{Yb}_1$ center (Fig. 4) were successfully described by the spin-Hamiltonian (1) with a mean-square deviation of about 0.05 mT using $g_z = g_{ax} = g_{yy}$, $g_y = g_{ax}$, $A_z = A_{ax} = A_{yy}$, and $A_i = A_{ax}$ listed in Table 1.

Several additional low-intensity lines without angular dependence in the $xy$-plane were attributed to axial $\text{Yb}_6$ and $\text{Yb}_7$ centers.

Table 1 $g$-tensors and hyperfine constants (in $10^{-4}$ cm$^{-1}$) for axial $C_3$ centers in LiNbO$_3$: $\text{Yb}^{3+}$, $T = 6$ K.

<table>
<thead>
<tr>
<th>Center</th>
<th>$\text{Yb}_1$</th>
<th>$\text{Yb}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_z$</td>
<td>2.706 ± 0.005</td>
<td>2.68 ± 0.02</td>
</tr>
<tr>
<td>$g_y$</td>
<td>4.46 ± 0.01</td>
<td>4.44 ± 0.02</td>
</tr>
<tr>
<td>$^{171}A_z$</td>
<td>715 ± 3</td>
<td>750 ± 20</td>
</tr>
<tr>
<td>$^{171}A_y$</td>
<td>1190 ± 3</td>
<td>1500 ± 40</td>
</tr>
<tr>
<td>$^{173}A_z$</td>
<td>207 ± 1</td>
<td>327 ± 1</td>
</tr>
</tbody>
</table>
The ENDOR spectra of axial Yb, center

The ENDOR spectra were studied for the most intense EPR line, which belongs to all non-magnetic isotopes of the Yb center. According to the perturbation theory for strong magnetic fields [38, 39], every nucleus produces $2S \cdot I = 18$ lines in the ENDOR spectrum. For Yb$^{3+}$ center with $S = 1/2$, every niobium nucleus ($I = 9/2$, natural abundance 100%), nuclear $g$-factor $g_n = 1.3712$, quadrupole moment $q = -0.28 |e| \times 10^{-24} \text{cm}^2$ gives two characteristic multiplets of nine lines: for the projections of electron spin onto the direction of the external magnetic field $M = 1/2$ and $M = -1/2$. The intensity ratios of the multiplet components are 9:16:24:25:24:21:16:9. However, often the lines, which belong to one of these $M$ values, dominate. If the hyperfine interaction is comparable with the nuclear Larmor frequency the intensity ratios may not coincide with the ratios indicated above.

For calculating the ENDOR frequencies and transition probabilities for $k$-th nucleus with desired precision, a numerical diagonalization of effective nuclear spin-Hamiltonians $H^M_k$ was used.

$$H^M_k = \langle M | H_1 | M \rangle + \sum_{M' \neq M} \langle M | H_1 | M' \rangle \langle M' | H_1 | M \rangle \frac{E_M - E_{M'}}{E_M - E_{M'}}$$

where

$$H_1 = -\mu_s g_n^{(i)} B \cdot I^{(i)} + S \cdot A^{(i)} \cdot I^{(i)} + I^{(i)} \cdot Q^{(i)} \cdot I^{(i)}$$

$\mu_s$ – nuclear magneton, $g_n^{(i)}$ – nuclear $g$-factor, $A^{(i)}$, $Q^{(i)}$ – hyperfine and quadrupole interactions tensors, $\langle M |$ and $E_M$ are wave functions and energy levels of $H_{1pr}$.

Since the main isotope $^7$Li ($I = 3/2$, natural abundance 92.5%, $g_n = 2.17096$) has a very small quadrupole moment ($q = -0.040 |e| \times 10^{-24} \text{cm}^2$), lithium triplets usually have quadrupole splitting of about several dozen kHz. Such splitting is smaller than widths of typical ENDOR lines in lithium niobate (about 100 kHz). Several strong unresolved singlet lines of $^7$Li nuclei were observed near Larmor frequency of Li between 2 MHz and 5.5 MHz (Fig. 5).
The most intense multiplet of nearly equidistant lines, which has average splitting of about 1 MHz (Fig. 6), was assigned to $^{93}\text{Nb}$. The lines of this multiplet did not split with a deviation of magnetic field orientation from $B \parallel z$. This means that they belong to one nucleus on the center axis.

Best fitting of the observed lines (Fig. 6) was obtained with the following parameters for $^{93}\text{Nb}$:

\[
A_{xx} = A_{yy} = \pm (10.25 \pm 0.5) \text{ MHz},
\]

\[
A_{zz} = \mp (3.11 \pm 0.02) \text{ MHz},
\]

\[
Q = 3Q_{zz}/2 = (0.545 \pm 0.005) \text{ MHz}.
\]

Since this multiplet is characterized by the strongest hyperfine interaction with ytterbium electrons, it is reasonable to assign it to the nearest surrounding, namely, to the Nb nucleus in the first shell of surrounding nuclei (Fig. 7).

The following model of the Yb$_1$ center explains both the EPR and ENDOR data: Yb$^{3+}$ ion substituted for Li$^+$. The center has the Nb nucleus in its nearest neighborhood and no local charge compensator (Fig. 7).

In the case of Yb$^{3+}$ substitution for Nb, the ENDOR spectra should have non-split lines of the Li nucleus in the nearest neighborhood of Yb$^{3+}$. For Yb$^{3+}$ incorporated in the structural vacancy, the split lines of both Li and Nb nuclei should have the highest hyperfine interactions. The observed ENDOR spectra do not agree with the last two models.

**8 The EPR of low-symmetry Yb$^{3+}$ centers**

Angular dependencies (Fig. 8) clearly show specific features of low-symmetry Yb$^{3+}$ centers in lithium niobate: 1) the single line at $B \parallel z$ 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.

Since this multiplet is characterized by the strongest hyperfine interaction with ytterbium electrons, it is reasonable to assign it to the nearest surrounding, namely, to the Nb nucleus in the first shell of surrounding nuclei (Fig. 7).
The lines of non-magnetic isotopes were successfully followed for five non-equivalent centers. Their dependencies were described by the spin-Hamiltonian (1) using parameters given in Table 2.

The six component representation of the \( g \)-tensor is very convenient for calculations of angular dependencies as well as for comparing with \textit{ab-initio} calculations of \( g \)-tensor. A transformation of the six-component \( g \)-tensors to the three principal values and three Euler angles (or nine cosines), which characterize the directions of principal axes with respect to crystal axes, can be easily made, for instance, with the help of a free program \textit{CosEul.exe} [29].

In cubic crystals, the directions of \( g \)-tensor axes for non-cubic centers are related with some specific directions in the crystal, like \( \langle 100 \rangle \) or \( \langle 111 \rangle \), and this helps to establish the center models. However, in the case of non-cubic crystals like LiNbO\(_3\), the situation is more complicated, since an off-axis defect in the nearest neighborhood of an axial center causes a low-symmetry distortion of the already anisotropic \( g \)-tensor. Therefore, the directions of \( g \)-tensor axes for low-symmetry centers do not coincide with any specific direction in the crystal, and they are not very helpful for clarifying local structures of these Yb\(^{3+}\) centers.

The principal values of \( g \)-tensors \( g_{11}, g_{22}, g_{33} \) are presented in Table 2 for convenience when comparing our results with published data.

**9 The EPR of Yb\(^{3+}\)–Yb\(^{3+}\) pair centers**

There are two possibilities for describing observed angular dependencies of pair centers. The first one is to suppose that singlet-triplet splitting is much larger that Zeeman splitting and to use effective spin \( S = 1 \) for the triplet state of the pair. In this case the spin-Hamiltonian for non-magnetic isotopes can be written as

\[
H^{(S=1)} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{q=2,3,1,2} b_q^S O_q^S(S)/3. \tag{4}
\]

Here \( g^S \) – common \( g \)-tensor of the pair; \( O_q^S \) – irreducible tensor operators (details and discussion of different forms of (4) can be found in [40–45] and references therein). The spin-Hamiltonian (4) has 11 fitting parameters for low-symmetry centers: 6 components of the symmetrical \( g^2 \)-tensor and 5 parameters \( b_q^S \).

The second approach uses the spin-Hamiltonian for two ions with spins \( S^A = S^B = 1/2 \) [46–48]

\[
H^{4B} = \mu_B \mathbf{B} \cdot (g^A \cdot \mathbf{S}^A + g^B \cdot \mathbf{S}^B) + S^A \cdot \mathbf{J}^{4B} \cdot S^B. \tag{5}
\]

**Table 2**

<table>
<thead>
<tr>
<th>center</th>
<th>( g_{xx} )</th>
<th>( g_{yy} )</th>
<th>( g_{zz} )</th>
<th>( g_{xz} )</th>
<th>( g_{yz} )</th>
<th>( g_{zx} )</th>
<th>( g_{zy} )</th>
<th>( g_{11} )</th>
<th>( g_{22} )</th>
<th>( g_{33} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb(_2)</td>
<td>2.84</td>
<td>2.48</td>
<td>4.56</td>
<td>0.22</td>
<td>±0.45</td>
<td>±0.02</td>
<td>2.45</td>
<td>2.73</td>
<td>4.69</td>
<td></td>
</tr>
<tr>
<td>Yb(_3)</td>
<td>2.63</td>
<td>2.67</td>
<td>4.35</td>
<td>−0.15</td>
<td>±0.10</td>
<td>±0.17</td>
<td>2.46</td>
<td>2.82</td>
<td>4.37</td>
<td></td>
</tr>
<tr>
<td>Yb(_4)</td>
<td>2.65</td>
<td>2.44</td>
<td>4.56</td>
<td>0.21</td>
<td>±0.38</td>
<td>±0.08</td>
<td>2.41</td>
<td>2.59</td>
<td>4.65</td>
<td></td>
</tr>
<tr>
<td>Yb(_5)</td>
<td>2.64</td>
<td>2.44</td>
<td>4.56</td>
<td>0.21</td>
<td>±0.39</td>
<td>±0.024</td>
<td>2.41</td>
<td>2.57</td>
<td>4.66</td>
<td></td>
</tr>
<tr>
<td>Yb(_6)</td>
<td>2.71</td>
<td>2.765</td>
<td>4.36</td>
<td>0.11</td>
<td>±0.14</td>
<td>±0.07</td>
<td>2.64</td>
<td>2.81</td>
<td>4.38</td>
<td></td>
</tr>
</tbody>
</table>

Signs ± reflect the presence of mirror conjugated centers with \( g_a(L) = -g_a(R) \), \( g_a(L) = -g_a(R) \).

Estimated errors are ±0.01 or less.
Here \( g^A, g^B \) – six-component g-tensors of the A and B ions; \( J^{AB} \) – nine component second rank tensor, which includes in general case all possible interactions of two magnetic momenta: isotropic Heisenberg exchange interaction \( J_{\text{HE}} S^A \cdot S^B \), anisotropic Dzyaloshinski-Moriya interaction \( J_{\text{DM}} S^A \times S^B \) and magnetic dipole-dipole interactions \( S^A \cdot J^{AB} \cdot S^B \).

\[
J_{gy} = \frac{\mu_B^2}{R} \sum_{n=x,y,z} R_n \sum_{m=x,y,z} g_{nm}^A g_{nm}^B \left( \sum_{n=x,y,z} R_n \sum_{m=x,y,z} g_{nm}^B R_m \right),
\]

where \( R \) is radius-vector from the ion A to the ion B.

For arbitrary anisotropic g-tensors, the \( J^{AB} \) also has an isotropic part. Therefore, the splitting between singlet and triplet states is determined by

\[
J_{iso} = J_{xx} + (J_{xy} + J_{yy} + J_{zz})/3.
\]

If \( J_{iso} \gg \mu_B B \) there are no transitions between the singlet and triplet states, positions of observed lines do not depend on \( J_{iso} \) and there is no way to determine \( J_{iso} \) from the EPR data, nor to determine separately \( J_{xx} \) and \( J^{AB} \). Moreover, comparing (4) and (5) shows that in the best case only 11 of the 21 parameters of (5) can be determined from experiments. This is caused by hidden symmetry in spin-Hamiltonians [43]. These conclusions were supported by our computer simulation of the EPR spectra. It was found that only the positions and intensities of the week forbidden transitions, which appear at \( J_{iso} \approx \mu_B B \), depend on \( J_{iso} \). Since they were not observed in our experiments, their intensities are one order of magnitude lower than intensities of allowed transitions. Therefore, observed EPR lines belong to centers with \( J_{iso} \) larger than \( \mu_B B \).

Taking into account above considerations, the observed angular dependencies of nonmagnetic isotopes of the Yb\(^{3+}\)–Yb\(^{3+}\) pairs (Fig. 9) were successfully described with the help of the reduced spin-Hamiltonian

\[
H^{AB} = \mu_B B \cdot g^A \cdot \left( S^A + S^B \right) + \sum_{q=-2,0,2} J_q^2 \left( S^A_q, S^B_q \right).
\]

The relations between the \( J^2 \), \( Q^2 \) and Cartesian parameters and operators are

\[
J_x^2 = (2J_x - J_y - J_z)/6, \quad J_y^2 = J_y + J_z, \quad J_z^2 = J_x + J_y , \quad J_{xy} = J_{yx} , \quad J_{xx} = J_{yy} , \quad J_{yy} = J_{zz} , \quad J_{xx} = J_{yy} = J_{zz} ,
\]

The presence of additional lines of hyperfine structure with similar angular dependence (indicated by arrows in Fig. 9) supports the assignment of the Yb\(^{3+}\) ions in next neighbor or next-next neighbor positions.

The nearest neighbor site for Yb\(^{3+}\) ion in the Nb site located at a distance 3.01 Å on the crystal axis.

**Figure 9** (online colour at: www.pss-b.com) Angular dependence of the EPR spectra for all nonmagnetic isotopes of low-symmetry Yb–Yb pair (Yb\(_5\) center) in sLN-Yb\(^{3+}\). Symbols represent positions of observed lines. Calculated solid lines correspond to the first reference center (other magnetically non-equivalent centers are not shown). Magenta and green lines correspond to L and R partners; these lines coincide in the yz-plane.
Numerous low-intensity lines (Yb₃⁺ center), which can be attributed to such a pair. It was rather difficult to follow these lines due to their overlapping with lines of other centers. Therefore, the reliability of the line identification and parameter determination for Yb₄⁺ is lower than for the Yb₂⁻ Yb₄⁺ centers. The angular dependence of the line from nonmagnetic isotopes was described with $g_{∥} = 3.00 \pm 0.02$ and $g_\perp = 4.88 \pm 0.02$. The positions of satellite hyperfine lines, which belong to a pair of one non-magnetic isotope and one $^{171}$Yb isoaline with $I = 1/2$, were calculated using these values of g-tensor, the hyperfine parameters of Yb, center and $J_m > 300 \text{ cm}^{-1}$. The calculated lines were very close to some observed lines in xz and yz-planes and lines without angular dependence in $xy$-plane. This supports the proposed interpretation of Yb₁⁺ lines.

The lines of pairs with two $^{171}$Yb isotopes or one $^{171}$Yb isotope and one $^{173}$Yb isoaline were not resolved in our spectra. However, their relative intensities are significantly smaller than observed ones.

There is an alternative description of the Yb₃⁺ lines: an axial center of a single Yb⁺⁺ ion. In this case the satellite lines of the $^{171}$Yb isoaline have $A_x = 390 \pm 20$ and $A_y = 620 \pm 40$ (in $10^{-4} \text{ cm}^{-1}$).

### 10 Discussion and conclusions

The EPR lines of Yb⁺⁺ in congruent LN are very broad. Therefore, the axial center Yb₁⁺ was the only resolved center in LN:Yb [1, 7]. Our nearly stoichiometric crystals still have concentrations of intrinsic defects that exceed the Yb⁺⁺ concentration. Distinct defects create small distortions in crystal field 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 the center characteristics ($g$- and $A$-tensors in the case of Yb⁺⁺) and lower the center symmetry.

Our EPR data has shown that the Yb₁⁺, Yb₂⁺ and Yb₃⁺ centers have axial $C_3$ symmetry, whereas all others have $C_1$ symmetry. Characteristics of Yb₃⁺ centers are very close to those published [1, 7]; however, in our study they were determined with a little higher precision due to line narrowing and better resolution in sLN crystals.

The observation of lines without angular dependence in $xy$-planes is strong evidence that our samples have the same crystal lattice symmetry as at room temperature and that the concentration of Yb dopant used does not cause a phase transition of the LN lattice.

The angular dependence (Figs. 4, 8, 9), the principal values of $g$-tensors for Yb₁⁺, Yb₂⁺ as well as the orientations of their principal axis are completely different from those published [11–13] for congruent crystals doped with 1wt% of Yb⁺⁺. This dopant concentration is 50 times higher than in our crystals and is comparable with the concentration of intrinsic defects in congruent crystal; this may lead to the appearance of impurity pairs.

Several features of the EPR spectra [11–13] are very different from those previously published [1, 7] and our spectra: positions of the EPR lines at $B \parallel z$ (around 200 mT instead of 155 mT), an absence of a display of crystal symmetry properties in angular dependences (mirror plane and $C_2$ axis), strong deviation in principal values of $g$-tensors for $^{173}$Yb and non-magnetic isotopes, strong deviation of $g_x/g_y$ and $g_\perp/g_\parallel$ ratios from $A_x/A_y$ and $A_\perp/A_\parallel$ ratios, successful interpretation of six EPR lines for $^{173}$Yb isoaline and a failure to observe the doublet of $^{171}$Yb isoaline, which has lines with relative intensity 2.5 times larger than lines of $^{173}$Yb. The lines of the axial center (they usually dominate in both congruent and stoichiometric crystals) were not observed. The authors [11–13] relate the last to “the details of preparation of the LN crystal”. However, improper crystal orientation is not excluded. Due to a lack of line assignments (similar to what is presented in our Fig. 3) and comparison of calculated line positions with experiments (similar to our Figs. 4, 8, 9), it is difficult to verify the correctness of EPR spectra treatment, the interpretation of the spectra, and even the number of non-equivalent centers in [11–13].

The observation of the Nb nuclei in the nearest neighborhood of Yb⁺⁺ is direct evidence that the main axial Yb⁺⁺ center has no charge compensator in the nearest surrounding (distant charge compensation mechanism). Since the obtained characteristics for the axial Yb⁺⁺ center and low symmetry Yb₂⁺, Yb₃⁺, Yb₄⁺, Yb₅⁺, Yb₆⁺, Yb centers are very similar, we can suppose that in all these centers the Yb⁺⁺ ion substitutes for Li⁺; however, the low-symmetry centers have intrinsic defects and/or charge compensation defects located in the near neighborhood of Yb⁺⁺ (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 and third neighbors of Li site), different configurations of two intrinsic defects like lithium vacancies around impurity ions, as well as different position of Yb⁺⁺ in lithium niobate lattice.

The g-tensor components for the axial Yb₁⁺ center (see Table 1) differ markedly from $g_\parallel = 1.9$ and $g_\perp = 2.8$ for the second axial center observed in LN codoped with Mg, which was attributed to the Yb⁺⁺ center at the Nb⁺⁺ site [7]. The following possible models should be considered for these axial centers: 1) the Yb⁺⁺ ion substitutes for Li and has an intrinsic defect on the center axis (for instance, niobium vacancy), 2) the Yb⁺⁺ ion substitutes for Nb and has no defect in the nearest surrounding (distant charge compensation mechanism), 3) the Yb⁺⁺ ion incorporates into a structural vacancy, 4) the Yb⁺⁺ ion in LN codoped with Mg substitutes for Nb⁺⁺ and has Mg⁺⁺ ions substituted for Li⁺ in the nearest surrounding (local charge compensation mechanism). At present, we do not have sufficient data in order to verify definite models for these centers.

It was rather unexpected to observe Yb₁⁺–Yb₁⁺ pair centers in samples grown with 0.02 wt% YbOₓ 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\(_{12}\)–Yb\(_{ab}\) pairs (Yb\(_a\) and Yb\(_b\), centers).

The fundamental understanding of structures and properties of impurity defects in lithium niobate is important for both basic science and applications. The obtained numerous spectroscopic parameters can be used as cornerstones for model calculations of defects in crystals (similar to [10]). They can also be used for comparison with \textit{ab initio} simulations of structural properties of crystals [49].

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References