Magnetic Resonance Studies of $^7$Li, $^{93}$Nb, and Fe$^{3+}$ in Fe-Doped LiNbO$_3$*

S. H. Choh, E. K. Kim, S. S. Park and J. N. Kim

Institute of Basic Science, Korea University, Seoul 132, Korea

Institute of Solid State Physics, Pusan National University, Pusan 607, Korea

(Received 20, April 1985)

ESR of Fe$^{3+}$ and NMR of $^7$Li and $^{93}$Nb in LiNbO$_3$ single crystals, doped with 0.010, 0.077, and 0.385 wt.% of Fe, have been investigated by employing Varian spectrometers.

Though the signal intensities are proportional to the Fe concentration, the parameters are found to be insensitive with impurity levels. From NMR data of $^7$Li and $^{93}$Nb which were measured at 15 MHz, the quadrupole parameters are determined, and found to be also insensitive to the impurity concentration, compared to those found in the pure crystal. The central linewidth and $T_1$ of $^7$Li, however, turn out to be dependent on the impurity level and are discussed.

* Supported by the Basic Research Institute Program, Ministry of Education, 1984

I. INTRODUCTION

The ferroelectric LiNbO$_3$ crystals doped with transition elements have drawn considerable attention in application of the light modulation and harmonic generation devices and in reduction of the optical damage$^{7-10}$ ESR studies of Fe$^{3+}$ ion in the Fe-doped LiNbO$_3$ crystals$^{5-6}$ as well as NMR and NQR studies of $^7$Li and $^{93}$Nb in the pure crystal have been reported.$^{7-10}$

In this work ESR parameters of the Fe$^{3+}$ ion in LiNbO$_3$: Fe grown by the Czochralski method with the Fe concentration of 0.010, 0.077, and 0.385 wt.%, are investigated. The nuclear quadrupole coupling constants of $^7$Li and $^{93}$Nb have also been determined and compared to those of the pure crystal. The effect of Fe on the line width and relaxation time of the central line of $^7$Li NMR have also been examined.

II. EXPERIMENTAL PROCEDURE AND CRYSTAL STRUCTURE

The instruments used to obtain ESR and NMR spectra are Varian Model J 12 X-band
MAGNETIC RESONANCE STUDIES OF $^7\text{Li}$, $^{93}\text{Nb}$, AND Fe$^{**}$ IN Fe-DOPED LiNbO$_3$

(9.5 GHz) spectrometer and Varian WL-I 12 spectrometer, respectively. A home-made Pyrex glass dewar, which can hold about 1 liter of liquid nitrogen, was employed for NMR measurements at 77K. $^{10}$

The Curie temperature of the crystal is 12 10°C. The space and the point group of the ferroelectric LiNbO$_3$ single crystal are R3c and 3m, respectively $^{11}$. It is known that $a_H$ = 5.15 Å and $c_H$ = 13.86 Å are for the hexagonal unit cell which contains 6 molecules (Fig. 1 a), and $a_{pc}$ = 7.53 Å and $c_{pc}$ = 86.28° for the pseudocubic rhombohedral unit cell which contains 8 molecules (Fig. 1 b) $^{12}$. The shape of the single crystal used for this work was

![Diagram](image)

FIG. 1 The crystal structure of LiNbO$_3$ a) the hexagonal unit cell and b) the pseudocubic rhombohedral unit cell.

nearly cylindrical with diameter and height approximately 12 mm each, but it was cut to 3 x 3 x 3 mm$^3$ for ESR measurement, and 9 x 7 x 12 mm$^3$ for NMR at low temperature. The samples were oriented using the X-ray Laue camera.

III. EXPERIMENTAL DATA

a) ESR

The ESR spectra of Li[NbO$_4$]$_x$ doped with 0.010 wt.% of Fe measured at room temperature are shown in Fig. 2. In these spectra, the sharp line at $g = 2.0036$ is the D.P.P.H. signal and is used as a reference, and it is known that the 5, 7, and 11th lines for $\theta = 0°$ and the 3', 4', and 6'th signals for $\theta = 90°$ are due to the hyperfine interaction of Mn$^{2+}$ $^{4}$. The remaining signals are assumed to be those of Fe$^{3+}$.

The rotation pattern measured in the crystallographic $a_H$-$c_H$ plane is displayed in Fig. 3. A considerable variation of the signal intensity was observed in measuring this rotation pattern. But, the rotation pattern in the $a_H$-$a_H$ plane, perpendicular to the $c_H$-axis, exhibited no angular dependence, and so indicates that the resonance centers have the axial symmetry about the $c_H$-axis.

On the other hand, ESR spectra of 0.077 and 0.385 wt.% Fe$^{3+}$-doped LiNbO$_3$ crystals
FIG. 2 ESR spectra of Fe$^{3+}$ in LiNbO$_3$. The magnetic field is (a) along the $c_H$-axis ($\theta=0^\circ$) and (b) perpendicular to the $c_H$-axis ($\theta=90^\circ$).

FIG. 3 Rotation pattern of Fe$^{3+}$ ESR in the $a_H$-$c_H$ plane of LiNbO$_3$.

showed no difference to those of 0.010 wt.% crystal except for the increased signal intensity which was roughly proportional to the Fe concentration. The variation of the resonance field and line shape was not distinguished within the experimental accuracy. From this fact the crystal field to the Fe$^{3+}$ ion is found to be identical and independent of the Fe concentration.
b) NMR

Both $^7\text{Li}$ ($I = 3/2$) and $^{93}\text{Nb}$ ($I = 9/2$) nuclei have the quadrupole moment and the nuclear Zeeman levels are perturbed by the quadrupole interaction. NMR measurements were made both at 15 MHz, but no appreciable difference of $^7\text{Li}$ and $^{93}\text{Nb}$ resonances from those of the pure $\text{LiNbO}_3$ was observed in the Fe-doped crystals.

The line width of the central transition of $^7\text{Li}$, however, turns out to be narrower in the doped crystals. Moreover, the r.f. saturation of the signal intensity of the central line was found to be strongly dependent on the Fe concentration as displayed in Fig. 4. In order to verify the saturation effect, the similar measurements were made with the 0.010 wt.%-Fe sample at 6 MHz, but no observable difference from the 15 MHz data was recorded.

![FIG. 4 Saturation effect of the central line of $^7\text{Li}$ NMR in $\text{LiNbO}_3$: Fe crystal, measured with 15 MHz with the magnetic field along the $c_H$-axis at 300 K.](image)

IV. ANALYSIS AND RESULTS

a) ESR result

The spin Hamiltonian of the Fe$^{3+}$ ion doped in $\text{LiNbO}_3$ can be written as follows:\textsuperscript{13}

$$H = H_z + H_{C.F.}$$

$$H_z = \beta (\mathbf{B} \cdot \mathbf{S})$$

$$H_{C.F.} = V_c + V_{aX}$$

$$= (-\frac{2}{3}) B_a (O_0^2 + 20 \sqrt{2} O_2^1) + B_1^3 O_2^1 + B_2^3 O_2^1$$

(1)

where the first term of $H_{C.F.}$ is the cubic part of the potential energy of which the $z$-axis is along the [1 1 1] direction or the $c_H$-axis of the crystal, and the second term represents the trigonal contribution. $B_1^3$, $B_2^3$, and $B_a$ are the crystal field parameters, and $O_0^2$, $O_2^1$, and $O_2^1$ are the spin operators as usual.\textsuperscript{14}
The matrix form of Eq. (1) is tabulated in Table 1, where the z-axis is along the c-axis and the direction of the external magnetic field B has the polar and azimuthal angles $\theta$ and $\phi$ with respect to the z-axis. From Table 1 energy eigenvalues for $\theta = 0^\circ$ are given by

$$E^\pm = \left(\pm \frac{1}{2} \gamma B + B_2^2 + 90B_2^2 - 60B_4 - 20B_4\right) + \left(\pm \frac{1}{2} \alpha B + B_2^2 + 90B_2^2 - 60B_4 - 20B_4\right)^2 + \frac{40(B_4)^2}{1/2}$$

But the energy eigenvalues for $\theta = 90^\circ$ cannot be evaluated analytically.

**TABLE 1.** Matrix representation of the spin Hamiltonian of Eq. (1) for $S = 5/2$ of the Fe$^{3+}$ ion, where $\alpha = g_1 \beta B \cos \theta$, $\gamma = g_2 \beta B \sin \theta e^{i\phi}$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$J = 5/2$</th>
<th>$J = 3/2$</th>
<th>$J = 1/2$</th>
<th>$J = -1/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\gamma B$</td>
<td>$\gamma B$</td>
<td>$\gamma B$</td>
<td>$\gamma B$</td>
</tr>
<tr>
<td>1</td>
<td>$2 \gamma B$</td>
<td>$2 \gamma B$</td>
<td>$2 \gamma B$</td>
<td>$2 \gamma B$</td>
</tr>
<tr>
<td>2</td>
<td>$4 \gamma B$</td>
<td>$4 \gamma B$</td>
<td>$4 \gamma B$</td>
<td>$4 \gamma B$</td>
</tr>
</tbody>
</table>

In order to obtain the ESR parameters from the measured spectra, all the transitions corresponding to the resonance lines should usually be considered. However, it was very difficult to distinguish all the transitions, since as can be seen in Fig. 2, the line intensity shows considerable irregularity and the central transitions are mixed. Therefore, all sets of the forbidden transitions were considered as well.

ESR parameters can be calculated from the spectrum for $\theta = 0^\circ$, together with the whole transitions shown in Fig. 5. The effect of the $B_4$ term may be neglected except for the region near $g = 2$ and in that region $g = 1.993$ was obtained from the $J = 1/2 \rightarrow J = -1/2$ transition. Since the natural abundance of $^{57}$Fe ($I = 1/2$) is only 2%, the hyperfine interaction was neglected, and the spectrum was analyzed using the isotropic $g$-value. Because the transitions excluding the region near $g = 2$, being 0.037 T and 0.746 T, were affected little by the $(B_2, B_4)$ term, the parameters of $B_2^0$, $B_4^0$, and $B_4$ were calculated from the corresponding transitions at 0.243 T and 0.473 T including the former two values. The results are
$B_0^2 = (0.055 \pm 0.005) \text{ cm}^{-1}$

$B_0^3 = (1.98 \pm 0.03) \times 10^{-4} \text{ cm}^{-1}$

$B_4 = (-1.18 \pm 0.05) \times 10^{-4} \text{ cm}^{-1}$

Using these parameters the transions corresponding to resonance lines for $\theta = 90^\circ$ are displayed in the energy level diagram of Fig. 6. The rotation pattern computed with these parameters is shown with lines in Fig. 3, where open circles are experimental values. The solid lines indicate stronger signals. Though the solid lines and circles are in reasonable agreement, the dotted lines are less satisfactory.
b) NMR Result

The nuclear quadrupole coupling constant, $e^2Qq/h$, of $^7$Li and $^{93}$Nb deduced from the NMR data measured with 15 MHz at room temperature and 77K is summarized in Table 2. The asymmetry parameter, $\eta$, was zero for all measurements. These results indicate that the quadrupole interaction parameters are insensitive to the Fe concentration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$e^2Qq/h$ of $^7$Li (kHz)</th>
<th>$e^2Qq/h$ of $^{93}$Nb (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>ref. 7</td>
<td>55.2 ± 0.4</td>
</tr>
<tr>
<td>crystal</td>
<td>ref. 10</td>
<td>51.9 ± 0.4</td>
</tr>
<tr>
<td>present</td>
<td>ref. 11</td>
<td>55.5 ± 0.4</td>
</tr>
<tr>
<td>work, Fe: 0.077%</td>
<td>52.4 ± 0.2</td>
<td>54.6 ± 0.1</td>
</tr>
<tr>
<td>doped</td>
<td>0.385%</td>
<td>52.0 ± 0.1</td>
</tr>
</tbody>
</table>

In order to study the relaxation effect as a function of the Fe impurity, the resonance line shape was analyzed. The spin-spin relaxation time ($T_2$) is given by the line width depending on its shape, Gaussian or Lorentzian, in terms of the peak to peak width of the first derivative curve of the resonance signal:

$$W_G = \frac{\Delta \omega_G}{2T_2}$$

$$W_L = \frac{\Delta \omega_L}{2\sqrt{3}T_2}$$

The measured line shape is compared with Gaussian and Lorentzian form as shown in Fig. 7 and the Gaussian shape turns out to be in better agreement both in the pure and doped crystals. Consequently, $T_2$ was evaluated using Eq. (3) and the results are summarized in Table 3. The line width was also calculated theoretically in terms of the Gaussian shape:

$$f(\omega) = \frac{1}{\sqrt{2\pi}} \exp \left(-\frac{(\omega - \omega_0)^2}{2\Delta^2}\right)$$

by considering the pure dipolar interaction. The second moment is
\[ M_z = \int (\omega - \omega_0)^2 f(\omega) d\omega = \Delta^2 \]  

(6)

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>( f(\omega) )</th>
<th>( T_1 ) (sec)</th>
<th>( B_1 ) (Gauss)</th>
<th>( \Delta \omega ) (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe 0.01 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe doped 0.385 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe doped 0.385 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe doped 0.385 wt. %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The half width at the half intensity, \( \delta \), is given by

\[ \delta = 1.18 \text{ A} \]  

(7)

The relation between the full width at the half maximum \( (\Delta \omega)_{\text{FWHM}} \) and the peak to peak width of the first derivative, \( (\Delta \omega_G^{(1)}) \), is

\[ (\Delta \omega_G^{(1)})_{\text{p-p}} = 2 \Delta \]  

(8)

Therefore, the following relation is obtained with Eqs. (7) and (8)

\[ (\Delta \omega_G^{(1)})_{\text{p-p}} = 2 \Delta \]  

(9)

The dipolar interaction to the Li nucleus is Li-Li and Li-Nb pairs, hence the relation becomes

\[ \Delta \omega = \Delta \omega^2 + (\Delta \omega_G^{(1)})_{\text{HL}} + (\Delta \omega_G^{(1)})_{\text{HL}} \]  

(10)

\[ (\Delta \omega)_{\text{HL}} = \frac{1}{2} \gamma \hbar \gamma_1^2 h^2 I (1 + 1) \rightleftharpoons \Sigma_k \left( 1 - 3 \cos^2 \theta_{JK} \right) / r_{JK}^2 \]  

(11)

\[ (\Delta \omega)_{\text{HL}} = \frac{1}{3} \gamma_1^2 h^2 S (S + 1) \rightleftharpoons \Sigma_k \left( 1 - 3 \cos^2 \theta_{JK} \right) / r_{JK}^2 \]  

(12)

where \( I (S) \) is the nuclear spin of Li (Nb) and \( \gamma_1 (\gamma_2) \) is its gyromagnetic ratio. According to the Van Vleck theory on the simple cubic lattice, Eq. (11) is evaluated by including up to the 26th nearest neighbors;[6]

\[ (\Delta \omega)_{\text{HL}} = 12.3 \gamma_1^2 h^2 I (1 + 1) \rightleftharpoons \Sigma_k \left( 1 - 3 \cos^2 \theta_{JK} \right) / r_{JK}^2 - 0.187 \]  

(13)

where \( d \) is the distance between Li-Li, and \( \lambda_1, \lambda_2, \lambda_3 \) are the direction cosines of the external magnetic field. The interaction of Li-Nb can be evaluated from Eq. (12), where \( r_{JK} \) is the distance between the \( j \)th Li and \( k \)th Nb, and \( \theta_{JK} \) is the angle between \( r_{JK} \) and the applied magnetic field. The line width was calculated in terms of Eqs. (12) and (13) including up to the 32nd nearest neighbor Nb atoms. The results is \( (\Delta \omega)_{\text{HL}} = 7.6 \text{ kHz} \) along the [111] direction of the cubic cell, the \( c_h \) axis of the hexagonal unit cell. This value is slightly less than the experimental result. The \( \delta \) discrepancy may be originated from the
pseudocubic instead of the exact cubic and excluding the contribution of the second order quadrupole effect and the crystal defects.

The spin-lattice relaxation time ($T_1$) was evaluated using the formula $(\gamma_B B_t)^2 T_1 T_2 = 1$ by the gradual saturation method, together with the $T_2$ value obtained earlier. $B_t$ is the r.f. magnetic field at which the saturation occurs. The values of $T_1$ are also summarized in Table 3.

V. DISCUSSION

a) ESR

The obtained ESR parameters of Fe$^{3+}$ in LiNbO$_3$ are in good agreement with the previous reports in pure crystals as summarized in Table 4. Since these parameters are found to be not enough to account for whole spectra recorded with the X-band spectrometer, the following possibilities are considered:

1) The unaccounted signals are due to other impurities.
2) Fe$^{3+}$ ions may occupy the Li and Nb sites.
3) Fe$^{3+}$ ions reside in some structural vacancies.

<table>
<thead>
<tr>
<th>TABLE 4. The comparison of ESR parameters of Fe$^{3+}$ in LiNbO$_3$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$-value : $B_2^e$ (cm$^{-1}$) : $B_4$ (cm$^{-1}$) : $B_6$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>present: work : 1.993 : 0.055 : 1.98x10$^{-6}$ : -1.18x10$^{-6}$</td>
</tr>
<tr>
<td>ref. 4: 1.99 : 0.0553 : -1.17x10$^{-6}$ : -4.9 x 10$^{-6}$</td>
</tr>
<tr>
<td>ref. 5: 2.0024 : 0.0553 : -6.21x10$^{-4}$ : 1.36x10$^{-4}$</td>
</tr>
<tr>
<td>ref. 6: 1.995 : 0.051 : 1.19x10$^{-3}$ :</td>
</tr>
</tbody>
</table>

* Values are converted to notations in Eq. (1).

As the observed signals retain axial symmetry with respect to the $c$-axis, the second possibility seems to be the most reasonable. However, it is still unclear whether the Fe$^{3+}$ ion substitutes only either Li or Nb, or both. From the fact that only the intensity increases with the increasing Fe concentration without seeing any change of the line shape and resonance fields, Fe$^{3+}$ ions are supposed to be in the same crystal field. Therefore, the third possibility is remote. The possibility of unknown impurities still remains unsolved.

b) NMR

The nuclear quadrupole coupling constants of $^7$Li and $^{93}$Nb obtained with a pure LiNbO$_3$ crystal at room temperature and 77 K are in agreement with those of the previous reports. $^{10}$) The central line width of $^7$Li at room temperature, 10.5 ±0.4 kHz, is also in good agreement with others. $^7$-$9$) The pure dipolar effect on the resonance line was calculated theoretically and accounted for 7.6 kHz,
Though the quadrupole parameters of $^7$Li and $^{93}$Nb in Fe-doped crystals are found to be hardly different from those of the pure LiNbO$_3$, the relaxation time $T_1$ of $^7$Li turns out to be strongly dependent on the impurity level. It is $6.4 \times 10^2$ sec in the pure crystal, whereas 9.9 sec in the 0.077 wt.% Fe sample. This is due to the contribution of the spin-lattice relaxation of the paramagnetic center.\textsuperscript{18} These results are comparable with the Li NMR in LiF crystal, $T_1 = 300$ sec for the pure crystal and $T_1 = 30$ sec after X-ray irradiation.\textsuperscript{9} In conclusion this drastic change of the spin-lattice relaxation time in the Fe-doped LiNbO$_3$ seems to be a favorable factor in reducing the optical damage in LiNbO$_3$ through a faster relaxation.

ACKNOWLEDGEMENTS

Authors are grateful to Professor D. Choi of Myung Ji University for the access to the ESR spectrometer. The grant from the Ministry of Education (1984-85) is also gratefully acknowledged.

REFERENCES

14. A. Abragam and B. Bleaney, ibid, Appendix B.
15. A. Abragam, The Principle of Nuclear Magnetism\textsuperscript{1} Chap. 4 (Oxford Univ. Press. London. 196 1).