



Three-fold Symmetry Effect on Mn^{2+} Centers in a $LiNbO_3$ Crystal

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Abstract : Spin Hamiltonian for the paramagnetic center with a three-fold symmetry and high spin ($S \geq 2$) multiplicity should contain the fourth order zero-field splitting (ZFS) terms. Electron magnetic resonance transition lines of the center with $S = 5/2$ are expected to split in a pair when the magnetic field is applied off the principal axes of ZFS, while they are superimposed when the magnetic field is applied parallel to the principal axes of ZFS. In this study we report that the transition lines of Mn^{2+} centers at the three-fold symmetric sites in $LiNbO_3$, chemically equivalent but physically different, split in two due to the nonzero fourth order ZFS term.

Keywords : EMR, Line splitting, Three-fold symmetry, Spin multiplicity, $LiNbO_3$

INTRODUCTION

Lithium niobate ($LiNbO_3$) is famous for its useful physical and chemical properties - e. g. ferroelectric, piezoelectric, electro-optical, and non-linear optical. Since it is not naturally available, it is usually grown by the Czochralski method. And the crystal is grown usually congruent, of the same composition with the melt, has been known to contain many defects such as the Nb antisite due to Li-deficiency.^{1,2} However, the crystal can be made stoichiometric by the vapor-transport-equilibrium treatment or an addition of small amount of K_2O powder in the starting mixture.³⁻⁶

$LiNbO_3$ has an unusual high ferroelectric transition temperature of $T_c = 1483$ K and its space group is $R3c$ at room temperature. The crystal structure is characterized by the

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displacement of the cations along the c -axis, as shown in Fig. 1. The stacking order of the octahedral sites along the c -axis is Li – Nb – vacancy – Li – Nb – vacancy - ..., where vacancy means the structural vacancy in Fig. 1. Both cations have chemically equivalent but physically different environments. The upper neighboring oxygen triangles, marked with a little grey, of Li(a) and Li(b) are not equivalent, as shown in Fig. 1(C). Therefore, if paramagnetic centers occupy the cations, they have the three-fold symmetry and their environments are not physically identical.

In this study we investigate electron magnetic resonance (EMR) spectra for Mn^{2+} in a $LiNbO_3$ crystal and discuss the effect of the fourth-order zero-field splitting (ZFS) terms on EMR transitions for Mn^{2+} at the three-fold symmetric site in the crystal.

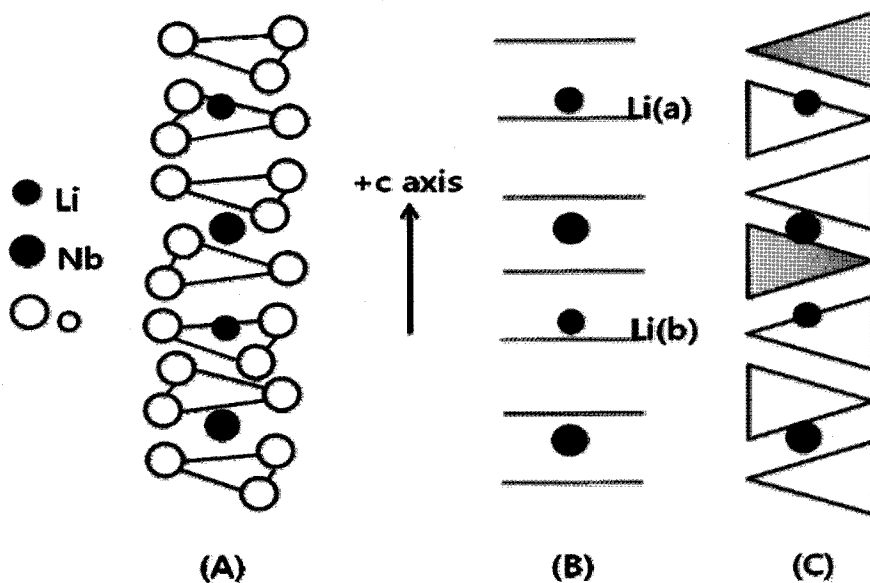


Fig. 1. (A) Crystal structure of $LiNbO_3$ at room temperature. (B) simply shows the stacking order of the cations along the c -axis, and (C) does that the upper neighboring oxygen triangles of Li(a) and Li(b) are rotated by $\pi/3$ each other.

EXPERIMENTALS

We prepared a Czochralski-grown Mn-doped $LiNbO_3$ crystal without any additional treatment such as the vapor-transport-equilibrium treatment to reduce the intrinsic defects, since an as-grown bulk crystal is processed for its applications. The single crystal was cut carefully along the crystallographic axes before experiments. Electron magnetic resonance measurements were carried out by employing a Q-band (33.9 GHz) EMR ESP300 spectrometer with a cylindrical cavity at room temperature in the crystallographic ca-plane.

RESULTS and DISCUSSION

The spin Hamiltonian for the $S=3/2$ center with a three-fold symmetry is generally described as:

$$H_{3/2} = EZ + NZ + NQI + HF + 2nd\ ZFS \quad \text{e.g. [1]}$$

where EZ and NZ mean the electronic and the nuclear Zeeman term, respectively. And NQI is the nuclear quadrupole interaction, HF the hyperfine one and 2nd ZFS the second order ZFS.⁷

Mn^{2+} has the $3d^5$ ($S=5/2$, $I=5/2$) electronic configuration and its spin Hamiltonian (SH) with a three-fold symmetry should include the fourth order ZFS terms.⁷⁻⁹

$$H_{5/2} = H_{3/2} + 4th\ ZFS \quad \text{e.g. [2]}$$

The 4th ZFS with the three fold symmetry can be described as follows;

$$H_{4th\ ZFS} = (b_4^0 O_4^0 + b_4^3 O_4^3 + b_4^{-3} O_4^{-3})/60 \quad \text{e.g. [3]}$$

where b_4^0 , b_4^3 and b_4^{-3} are the parameters of O_4^0 , O_4^3 and O_4^{-3} , respectively. And O_4^n spin operators are as follows.⁷⁻¹⁰

$$O_4^3 \sim \sin^3\theta \cos\theta \cos 3\varphi \quad \text{e.g. [4]}$$

$$O_4^{-3} \sim \sin^3\theta \cos\theta \sin 3\varphi \quad \text{e.g. [5]}$$

The O_4^{-3} operator vanishes in the ZX-plane of ZFS because $O_4^{-3}|_{\varphi=0} = 0$ always in the plane. Therefore, if we obtained EMR spectra in the crystallographic ca-plane, i. e. in the principal ZX-plane of ZFS, we can eliminate the effect due to the O_4^{-3} operator (see Fig. 2).

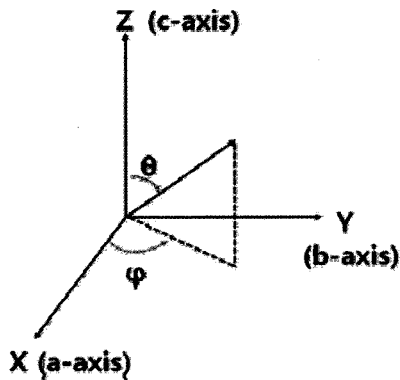


Fig. 2. Coordinate system for the principal axes and the angles.

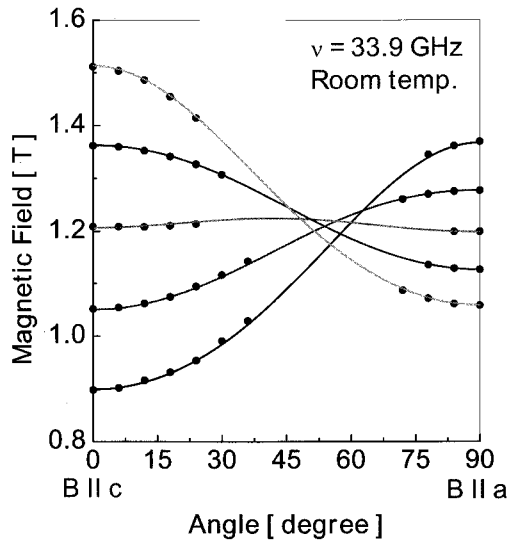


Fig. 3. Rotation pattern of Mn^{2+} fine structure in the ca-plane. The experimental data mean the centers of the hyperfine transitions.

The rotation pattern for Mn^{2+} in a $LiNbO_3$ crystal by employing a Q-band spectrometer at room temperature in the crystallographic ca -plane with an angular interval of 6° is plotted in Fig. 3. The experimental data are determined to be the centers of the hyperfine transitions, and show a typical pattern for an axially symmetric resonance center with $S=5/2$.

Fig. 4 shows the central transitions of Mn^{2+} for different alignments. In the figure $\times 2$ and $\times 4$ mean the spectra are multiplied by two and four times for the convenience, respectively. The central hyperfine transitions of Mn^{2+} are superposed when the magnetic field applies parallel to the c -axis (Fig. 4(a)) or the a -axis (Fig. 4(d)), while they split in a pair when the magnetic field does off the axes (Fig. 4(b) and (c)). The typical peak-to-peak linewidth of the first derivative curves are in the range of 1 to 2 mT, while the field differences are about 4 mT.

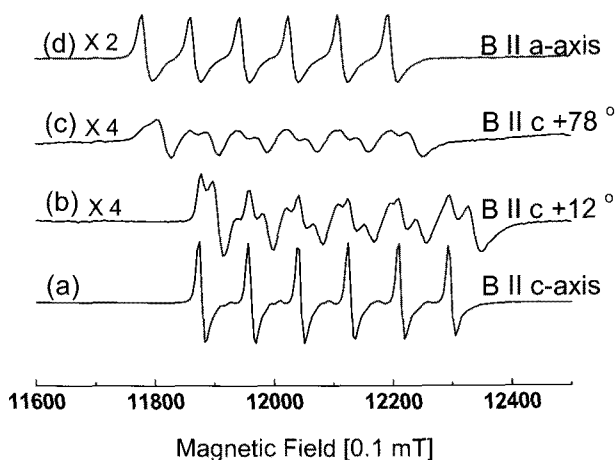


Fig. 4. The central transition of Mn^{2+} for $B||c$ -axis(a), for $B||c+12^\circ$ (b), for $B||c+78^\circ$ (c) and for $B||a$ -axis (d). $\times n$ means that three spectra are multiplied by n times.

Resonance field values for the central transitions of Mn^{2+} in a $LiNbO_3$ crystal are plotted in Fig. 5. In the figure some experimental data are missing since some signals are overlapped each other, consequently it is hard to read exact fields.

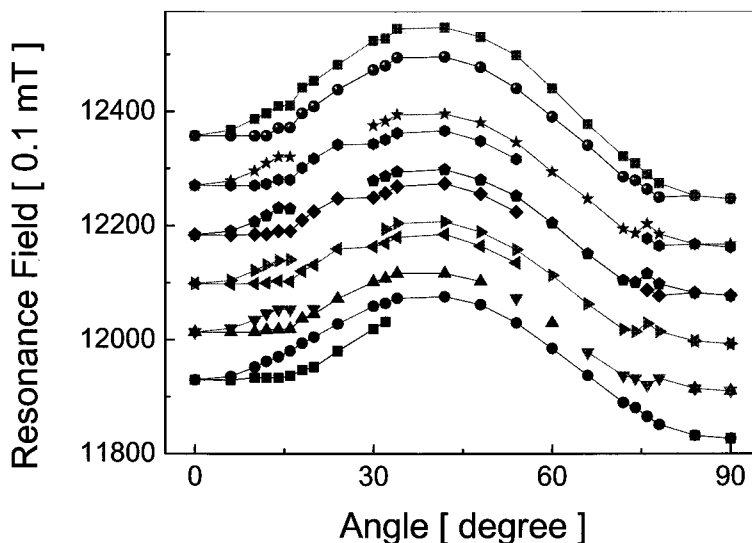


Fig. 5. Experimental data for the hyperfine transitions of the central transition of Mn^{2+} in the *ca*-plane.

If the resonance center with $S \geq 2$ substitutes for a three-fold symmetric site, its spin Hamiltonian must include the fourth order ZFS terms in Eq. (2). It has been reported that Mn^{2+} in a $LiNbO_3$ substitutes the Li site.¹⁰ If then, Mn^{2+} ions occupy chemically equivalent but physically different three-fold symmetric sites in the crystal.

The resonance signals are superimposed when the magnetic field is applied parallel to the *c*- or *a*-axis, as shown in Figs. 4 and 5. If the principal X-axis of the second ZFS is fixed as the *a*-axis for one Mn^{2+} center, that of the other Mn^{2+} one becomes a $+\pi/3$ axis. If it is the case when the applied magnetic field is parallel to the *c*- ($\theta=0$) or the *a*- ($\theta=\pi/2$) axis, the b_4^3 terms of two Mn^{2+} centers become zero because $O_4^3|_{\theta=0} = 0$ and $O_4^3|_{\theta=\pi/2} = 0$ in Eq. (4). However, when the magnetic field is applied off the *a*- and *c*-axis, the values of b_4^3 for both Mn^{2+} centers are equal in magnitude but opposite in sign because $O_4^3|_{\theta=\theta, \varphi=\varphi+\pi/3} = -O_4^3|_{\theta=\theta, \varphi=\varphi}$ in Eq. (4). Therefore, EMR signals of Mn^{2+} centers at two Li sites in the crystal can be split into a pair and the field differences of two split resonance fields are dependent on the magnitude of b_4^3 .

Similar phenomena for the resonance centers with $S=5/2$ in other crystals could be explained by the similar analogy.^{7,1}

CONCLUSION

We discussed the splitting of Mn^{2+} EMR transition lines in a $LiNbO_3$ crystal. If Mn^{2+} centers sit on the Li sites in the crystal, they have the three-fold symmetry. If so, they have chemically equivalent but physically different environments, which suggests that they have different SH parameters in the fixed principal coordinate system of ZFS each other. Therefore, the split Mn^{2+} EMR signals are explained by means of the nonzero b_4^3 term, of which magnitude determines the resonance field differences of the Mn^{2+} centers.

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