EPR STUDY OF IMPURITIES CENTERS IN $LiNbO_3$

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The single crystal $LiNbO_3$ with paramagnetic impurities was studied by the EPR method in the X-band at room temperature. Comparing experimental and theoretically calculated angular dependences of spectra we found from their shape and symmetry that in the crystal impurity ions Fe^{3+} and Mn^{2+} were present.

I. INTRODUCTION

The single crystal $LiNbO_3$ was provided by „Monokrystaly Turnov". Our aim was to find the types of impurities in the crystal. The impurities could be present in the melt or they could penetrate into the crystal during the growing process. They are present in trace concentrations impossible to be determined by chemical analysis. To solve this problem the electron parametric resonance method was used (EPR).

The measurements were made in the X-band (9.3 GHz) at room temperature and at the temperature of liquid nitrogen. The angular dependences of the spectra were measured for two different rotation axes. For one of these orientations also the thermal dependences of the spectra were measured in the range 300—100 °K.

II. EXPERIMENT

The $LiNbO_3$ crystal has a rhombohedric cell with a space symmetry of R3c (C^6_{3c}). The elementary cell of the crystal has the parameters $a = 5.494$ Å and $\alpha = 55°52'$. The ions Nb and Li, displaced along the axis [111] or the structural vacancy are surrounded by six oxygen ions in the form of an octahedron [1, 2].

There are three possible sites for an impurity ion in the crystal: a Li site

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a Nb site or a structural vacancy. Due to the charge compensation it seems to be very probable that the paramagnetic ion prefers the site Nb or Li [3].

For the identification of the kind of the paramagnetic ion and its position in the crystal lattice, the angular dependences of the EPR spectra were measured for two different rotation axes:

1. the rotation axix identical with the trigonal axis (angular dependence *a*)
2. the rotation axis perpendicular to the trigonal axis (angular dependence *b*)

In the angular dependence *a* the magnetic field was perpendicular to the rotation axis, which was identical with the trigonal axis of the crystal. The crystal was rotated by 5° from 0° to 360°. The experimental spectra consist of three sextets at the *g*-factor 2.16 and of the sharp resonance line at the *g*-factor 4.73. They have no angular dependence. It was found from the symmetry of the spectra, that paramagnetic ions responsible for the spectrum lines were displaced along the trigonal axis.

In the angular dependence *b* the rotation axis was perpendicular to the trigonal axis and the angle of the external d. c. magnetic field H with the trigonal axis was Θ. The spectra were measured by 5° for Θ from 0° to 360°. The spectra with a symmetry of the type C_{2V} were more complicated than at the angular dependence *a*.

From spectra of the angular dependence *a* it was found that two sorts of paramagnetic ions were present in the crystal. The first ion is responsible for the spectrum line at $g = 4.73$, the second ion for the three sextets. The intensities of lines in each sextet are the same. If hyperfine structure is caused by more nuclei, the intensities of hyperfine sextets are different. The equal intensity magnitudes of lines from one sextet are caused only by the interaction with one nucleus.

To find the impurity ions a selection was done from ions having the nuclear momentum $I = \frac{5}{2}$. After theoretical considerations Mn^{4+} was selected from 17 possible elements [4]. Several factors were taken into account: the possibility of spectrum measurement at room temperature, the value of its *g*-factor, the value of hyperfine constant A. These values [5] were compared with the experimental values. According to [6—9] manganese in $LiNbO_3$ is usually in the form of Mn^{2+}. But in this case the spectrum would consist of five sextets. From experimental spectra it follows that the intensities of lines decrease symmetrically in both directions from the middle sextet. It can be supposed that the last two sextets have such small intensities of lines that they are imperceptible. The thermal dependences of $LiNbO_3$ spectra at the angular dependence *a* were determined in the range of 300—100 °K. But even at 100 °K the last two sextets were not found. The angular dependence calculated from parameters of the spin hamiltonian by H. H. Towner, Y. M. Kim and M. S. Story [10] from the ion of Mn^{2+} is identical with the experimental angular dependence.

Comparing our spectrum at the angular dependence *b* for $\Theta = 0°$ with the spectrum from [10] it was found that the shapes and the line positions were identical. The comparisons between the two spectra were done at the same orientation and the same angle. The $LiNbO_3$ crystal in [10] was doped by 0.01 % Fe^{3+}, hence we can expect that the second impurity ion in our crystal will be Fe^{3+}. The position of lines in the spectra at the angular dependence *a* does not exclude this possibility.

The position of spectrum lines in the magnetic field had to be identified from the experimental spectrum at the angular dependence *b*. The position was measured by proton resonance. The values of the magnetic field between the two experimental points were calculated by linear interpolation. The absolute error of the magnetic field value in the position of the spectrum lines measured by the gauge of the proton resonance was 2.8 G, it was caused by the small shift of the gauge from the axis of the resonance cavity. The dependence of the spectrum line position in the magnetic field on the rotation of the crystal was studied.

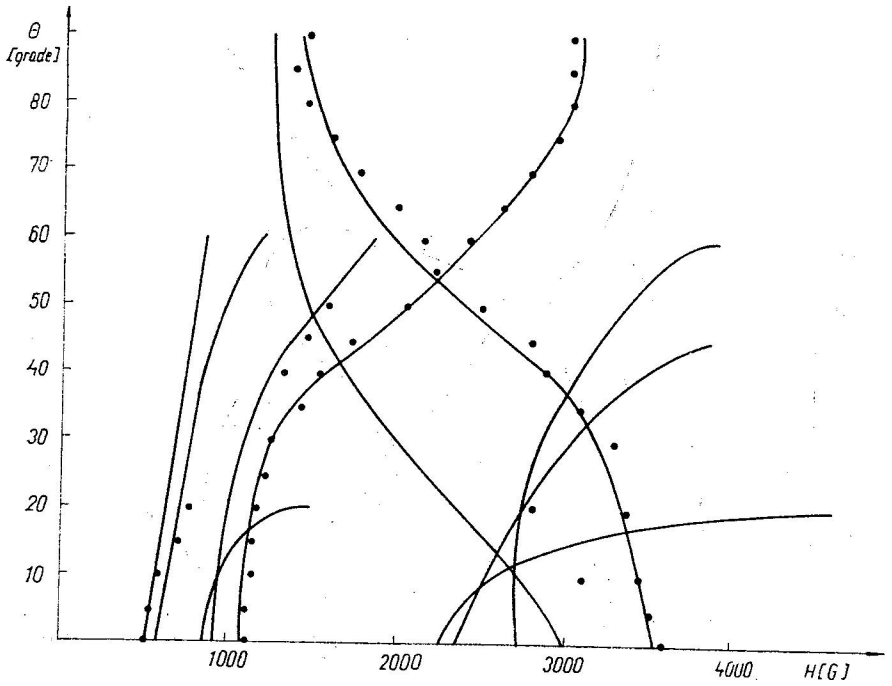

Fig. 1. The angular dependence of the ion Fe^{3+} in $LiNbO_3$.

The comparison of theoretical and experimental angular dependences b for the ions Fe^{3+} and Mn^{2+} is shown in Figures 1 and 2 (the full lines are the theoretical curves, the points are the experimental positions of the spectrum lines). The dispersion between the experimental and the theoretical values for Fe^{3+} is at most 100 G and for Mn^{2+} 120 G. The difference could be caused by several factors:

1. the spin hamiltonian $\hat{\mathscr{H}}_s$, used for the theoretical calculation of the angular dependence does not describe the crystalline field correctly, especially the rhombic distortion of the field.

2. The deviation of several 10 G from the correct values can be caused by the graphic interpolation of the magnetic field values at the transition point and by the identification of the spectrum line positions of the spectra.

The agreement of the experiment with theory is good.

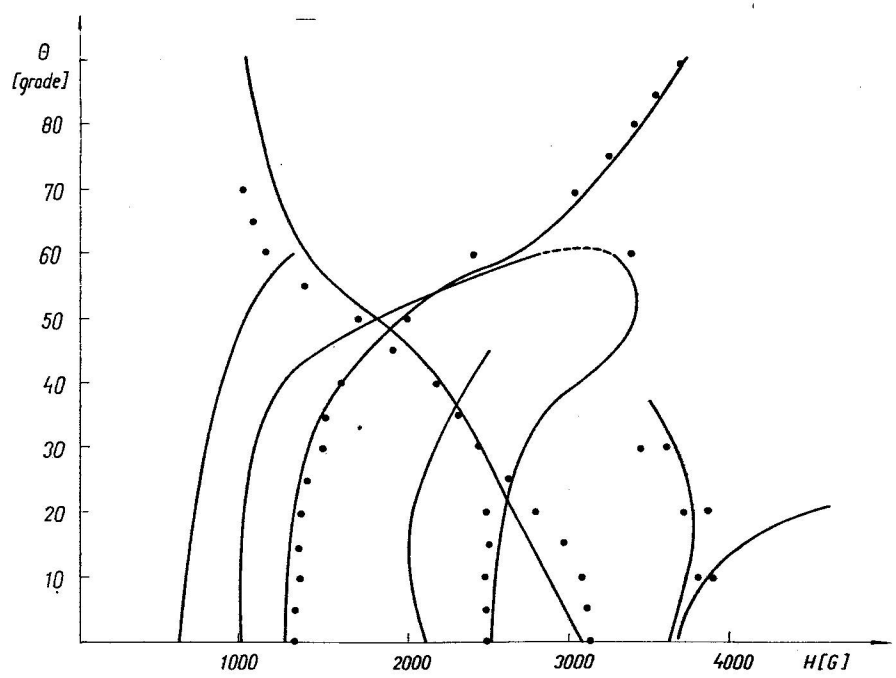

Fig. 2. The angular dependence of the ion Mn^{2+} in $LiNbO_3$.

III. CALCULATION OF THE ANGULAR DEPENDENCE FOR Mn^{2+} AND Fe^{3+}

Analyses of spectra at the angular dependence b were done by the spin hamiltonian for a crystalline field with trigonal symmetry [10]:

$$\begin{aligned}\hat{\mathscr{H}}_s = \hat{\mathscr{H}}_z &+ B_2^0\{3\hat{S}_z^2 - S(S+1)\} + B_4^0\{35\hat{S}_z^4 - 30S(S+1)\,\hat{S}_z^2 \\ &+ 25\hat{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2\} + \\ &+ B_4^3\{\tfrac{1}{4}[\hat{S}_z(\hat{S}_+^3 + \hat{S}_-^3) + (\hat{S}_+^3 + \hat{S}_-^3)\,\hat{S}_z\}.\end{aligned} \tag{1}$$

Using a spherical coordinate system, the operators $\hat{S}_+$ and $\hat{S}_-$, Zeeman's member of the spin hamiltonian can be transformed into the form:

$$H_z = g_{\parallel}\beta H \cos\Theta\hat{S}_z + \tfrac{1}{2}\,g_{\perp}\beta H \sin\Theta(e^{-i\varphi}\hat{S}_+ + e^{i\varphi}\,\hat{S}_-). \tag{2}$$

If we suppose the basic state of the system to be an orbital singlet with the effective spin $S = \frac{5}{2}$, the spin hamiltonian can be substituted by a $(2S+1) \times (2S+1)$ matrix. The energy levels into which the basic state is split in the magnetic field can be computed by a numerical diagonalisation of the matrix for different $\vec{H}$ values.

The calculations were performed on the computer GIER for 7 values of the magnetic field within the range 0—400°G for 10 different values of Θ and $\varphi = 0°$. The parameters of the crystalline field for Fe^{3+} are $B_2^0 = 600$ G $B_4^0 = -1$ G, $B_4^3 = 10$ G and for the ion Mn^{2+} we have $B_2^0 = 760$ G, $B_4^0 = -9$ G, $B_4^3 = 0$ G [10, 6].

The magnetic field values for the allowed or the forbidden resonance transitions were found by graphic interpolation. In the same way the angular dependence was found.

IV. CONCLUSION

From the agreement between the theoretically calculated angular dependences for Mn^{2+} and Fe^{3+} ions and the experimental angular dependences it can be shown that these elements from the iron group are present in the crystal $LiNbO_3$. The g-factor was practically isotropic and therefore $\varphi = 0°$ and $\Psi = 0°$ were used. From the symmetry of the spectra it can be supposed that the parametric ions have a local symmetry C_3.

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