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NMR Study of Intrinsic Defects in Congruent Lithium Niobate

The simulations of NMR spectra of ^{93}Nb nuclei for different models of intrinsic defects in single crystal of congruent lithium niobate have been performed. It has been shown that the most probable defects in $LiNbO_3$ are complex ($Nb_{Li} + 3\ V_{Li}$) and isolated V_{Li}.

Keywords: crystal structure, defects, Nuclear Magnetic Resonance (NMR); $LiNbO_3$

1. Introduction

Intrinsic defects in lithium niobate (LN) crystals resulting from Li/Nb non-stoichiometry considerably change the optical, acoustical and other properties of LN. At the present time it is believed that the excess of Nb^{5+} ions in congruent LN occupy only the regular Li sites. The required local charge neutrality of LN can be guaranteed by oxygen vacancies, by Li vacancies at Li sites or by Nb vacancies at Nb sites. The oxygen vacancy model cannot explain the dependence of the density of LN on the Li/Nb ratio (KOVÁCS et al.) and thus is excluded. The Li-site vacancy model is supported by X-ray and neutron diffraction studies (IYI et al.; ZOTOV et al. 1994) and by computer simulations of defects energies (DONNERBERG et al. 1989, 1991). The Nb-site vacancy model is supported on the basis of an analysis of single crystal X-ray data (ABRAHAMS et al.) and on the basis of NMR study (PETERSON et al.). Thus, it seems that until now a definite consensus on the intrinsic defect model in LN has not been achieved.

NMR method allows to obtain direct local information about the real structure of defects in crystals. LN contains four different quadrupolar nuclei - ^{17}O (natural abundance 0.037 % ; spin I = 5/2), ^{6}Li (natural abundance 7.42 % ; spin I = 1), ^{7}Li (natural abundance 92.58 % ; spin I = 3/2) and ^{93}Nb (natural abundance 100 % ; spin I = 9/2). The quadrupolar nuclei ^{17}O have very low natural abundance and NMR ^{17}O may be observed only on the enriched samples.

The NMR of ^{7}Li in LN have been studied by several investigators (HALSTEAD; BAIQIN et al.; YATSENKO et al. 1985, 1997; BLÜMEL et al.). NMR spectra of ^{7}Li contain three basic lines and two weak additional „quadrupolar" lines (YATSENKO et al. 1985, 1997). The shapes of ^{7}Li spectra are not sensitive to the type of intrinsic defects and observed additional weak „quadrupolar" lines are related to the peculiarities of potential surface and to mobility of Li ions in distorted LiO_6 octahedron (YATSENKO et al. 1997).

The NMR spectra of ^{6}Li support this model of multiminima potential of Li ion in LN (YATSENKO 1998). The NMR studies of ^{93}Nb in LN have been reported by several investigators (PETERSON et al.; YATSENKO et al. 1997; BLÜMEL et al.). The influence of intrinsic defects in LN on the lineshape of NMR ^{93}Nb is observed as the asymmetry of the

lineshape of the central transition (+ 1/2 ↔ – 1/2). The results of the computer simulations of NMR spectra of ^{7}Li and ^{93}Nb nuclei for different models of insulated („unoverlapping") intrinsic defects in LN crystals have recently been reported (YATSENKO et al. 1997).

In present paper we analyze the NMR spectra of ^{93}Nb in LN using the computer simulations of the NMR spectra with models of nonisolated („overlapping") defects. The simulations were performed assuming that the distortions of lattice introduced by the defects are negligible.

2. Results and discussion

The experimental details and results were described elsewhere (YATSENKO et al. 1997). The simulations were performed for the models (a) ÷ (f) of the intrinsic defects presented in Table 1.

The simulations of NMR spectra of ^{93}Nb nuclei were fulfilled according the following algorithm:

(a) Taking into account the concentration of the given type of intrinsic defects, the defects were localized by a random manner in the sphere with radius of 3 nm. In our calculations we used 200 different random defect configurations for each type of intrinsic defects.
(b) For each obtained random defect configuration EFG tensors components were calculated for all ^{93}Nb nuclei in the second sphere with a radius of 2 nm (the center of this sphere coincides with the center of the first sphere). For one random defects configuration nearly 105 EFG tensors of ^{93}Nb nuclei were obtained in this second sphere.
(c) The simulated NMR spectra of ^{93}Nb nuclei were obtained using the algorithm described elsewhere (YATSENKO et al. 1997).

The main parameters of ^{93}Nb NMR spectra which have been used at the comparison of the experimental and theoretical (simulated) data are: the shape of the central NMR transition line (transition $+1/2 \leftrightarrow -1/2$) at different crystal orientations into external magnetic field $\mathbf{B}_0$ and linewidth $\delta\nu$ of this line. The results of simulations and experiments are shown in Fig. 1.

Chemical formula (48.4 % Li_2O)	Models of defects[**] and distributions of defects in lattice	Model
$Li_{0.9371}Nb\,O_{2.9686}$ [BOLLMANN]	Random distribution of $6V_{Li}$ and $3V_O$	(a)
	Random distribution of 3 complexes V_O+2V_{Li}	(b)
	Random distribution of Nb_{Li} and $4V_{Li}$	(c)
$[Li_{0.947}Nb_{0.0106}]\,Nb\,O_3$ (LERNER et al.; ZOTOV et al. 1995]	Random distribution of complex $Nb_{Ii}+3V_{Ii}$ ($3V_{Ii}$ are sited above Nb_{Li}) and V_L	(d)
	Random distribution of complex $Nb_{Ii} + 3V_{Ii}$ ($3V_{Ii}$ are sited below Nb_{Li}) and V_{Li}	(e)
	Random distribution of complex $V_{Ii} - Nb_{Ii} - V_{Ii}$ along Li-chains	(g)
$[Li_{0.947}Nb_{0.053}]Nb_{0.9576}O_3$ (ABRAHAMS et al.)	Random distribution of 4 complexes ($Nb_{Li} + V_{Nb}$) and Nb_{Li}	(f)

[*] V_{Li}, V_O and V_{Nb} denote vacancies of Li, O and Nb ions respectively, while Nb_{Li} denotes Nb ion at Li site.
[**] per 100 formula units approximately.

Table 1: Models of intrinsic defects in congruent LN [*]

From Fig. 1 we see that, in comparison with the simulated spectra obtained for the models of „unoverlapping" defects (YATSENKO et al.1997), the models of nonisolated defects into

cation sublattice ((d), (e) and (g)) give the best agreement between the experimental and simulated data. Nevertheless there is a large discrepancy yet between the experimental and simulated $\delta\nu$ values for the crystal orientations at $\alpha \approx 40^0$ (Fig. 1). The source of this discrepancy illustrates Fig. 2, which presents the simulated integral shapes of ^{93}Nb NMR central line at $\alpha = 40^0$ for the defect model (d).

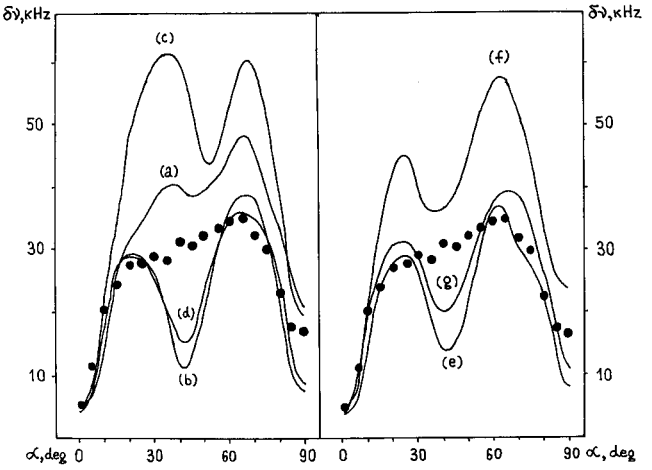

Fig. 1: Experimental (dark circles) and calculated (continuous lines) from simulated spectra angular dependencies of the linewidth $\delta\nu$ of the NMR ^{93}Nb central transition line. α is the angle between $\mathbf{B}_0$ and crystal axis of symmetry **c.** The symbols denote the corresponding models.

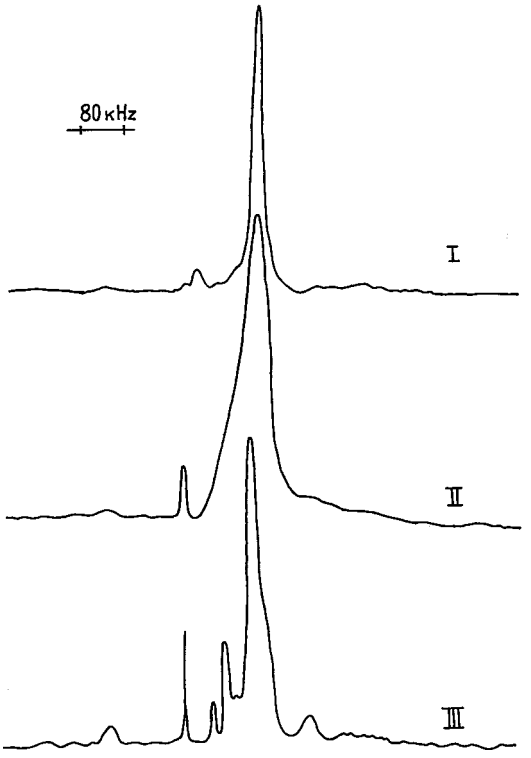

Fig. 2: Simulated integral shape of the NMR ^{93}Nb central transition line for (d) model of the intrinsic defects at $\alpha = 40^0$: (I) - model of the nonisolated („overlapping") defects, and (II, III) - model of the isolated („unoverlapping") defects. For the case II the calculated values of $V_{ZZ}^{(i)}$ and $\theta^{(i)}$ were considered as expected values of respective Gaussian distributions functions with standard deviations $\sigma(V_{ZZ}^{(i)}) = 0{,}03\ V_{ZZ}^{(i)}$ and $\sigma(\theta^{(i)}) = 2^0$. For the case III each simulated NMR line broaden by the Gaussian functions with Van-Vleck second moment .

Fig. 2 reveals that nonisolated defects increase the alteration of the components of the EFG tensors at the sites of nuclei Nb and cause a narrowing of the observed central NMR line of ^{93}Nb nuclei. The observed discrepancy between the simulated and experimental NMR spectra can be explained if we assume that the distribution of the intrinsic defects in the structure of LN is not random and there are ranges with high and small defects concentrations of the defects. However, this discrepancy may also be caused by local distortions of the lattice by defects. Using the method of local electric fields ($\mathbf{E}_{loc}$) calculations into ferroelectrics, we obtained that even one Li vacancy only leads to changes of $\mathbf{E}_{loc}$ at the sites of nearest oxygen ions by 3.8 10^{10} V/m. It is clear that these large electric fields introduced by the defects must lead to sufficient local distortions of the LN crystal structure. These distortions will increase distances between ions and must lead to a decrease in the quadrupolar interaction constants of ^{93}Nb nuclei or must lead to a decrease in the alterations of the EFG tensor components at the sites of Nb nuclei.

Finally, it should be emphasized that the interesting peculiarity of the ^{93}Nb NMR spectra was not mentioned earlier (YATSENKO et al. 1997). For all defect models (both insulated as well as nonisolated defects) containing isolated defect V_{Li} the simulated NMR spectra of ^{93}Nb nuclei contain the well-resolved additional central NMR line at some crystal orientations into external magnetic field $\mathbf{B}_0$ (Fig. 3). This additional line arises from the Nb nuclei which occupy the sites above V_{Li} and the intensity of this line is proportional to the concentration of the defects V_{Li} in LN. We observed this additional NMR line at $\alpha \approx 10^0$ for all the five investigated samples of the congruent LN (Fig. 3). The experimental relative intensity of this line is between 0.5 % and 1.2 %. The comparisons of the simulated and experimental NMR spectra at $\alpha = 10^0$ suggest that the defect models (e) and (e) + (d) are preferable.

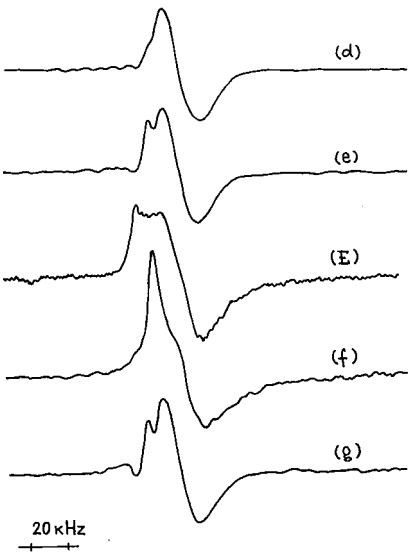

Fig. 3: Experimental (E) and simulated NMR spectra of ^{93}Nb nuclei for different models (d), (e), (f) and (g) of the intrinsic „overlapping" defects in LN at $\alpha = 10^0$.

The observed difference in the splitting between the main and additional lines for the simulated and experimental spectra can be explained in terms of the influence of the chemical shift of ^{93}Nb nuclei. As shown earlier (IVANOVA et al. 1995), the chemical shift of ^{93}Nb nuclei in LN is relatively large at $B_0 = 1.4$ T. It is clear that the chemical shift of the

^{93}Nb nuclei which occupy the sites above V_{Li} may be different from the chemical shift of the ^{93}Nb nuclei in the ranges of crystal where influences of the defects are small.

3. Conclusions

From our results on the simulations of ^{93}Nb NMR spectra for different models of intrinsic nonisolated („overlapping") defects in congruent LN it may be concluded that the most possible intrinsic defects in LN structure are the [Nb_{Li} + (2 to 3) V_{Li}] complexes and isolated (2 to 1) V_{Li}. The observed additional central line of ^{93}Nb spectra at the some crystal orientations into external magnetic field supports this model of the intrinsic defects. It is also shown that the observed discrepancy between the simulated and experimental spectra of ^{93}Nb may be related with the local deformations of crystal lattice by intrinsic defects. However, these results may be considered, as preliminary ones since the influence of lattice distortions by the defects on NMR spectra are not completely accounted.

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