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NMR study of intrinsic defects in congruent $LiNbO_3$. 2. "Overlapping" defects

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Abstract

Results of the computer simulations of NMR spectra of ^{93}Nb nuclei for different models of intrinsic "overlapping" defects in single crystal of congruent lithium niobate have been presented. It has been shown that the model of "overlapping" defects does not change our previous conclusion [1–3], that the most probable intrinsic defects in $LiNbO_3$ are complex $[Nb_{Li} + (2–3)V_{Li}]$ and isolated $(2–1)V_{Li}$. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

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 lithium niobate (LN) crystals have recently been reported in Refs. [1–3]. It was shown that the shapes of the resonance lines of ^{7}Li nuclei are not sensitive to the type of the intrinsic defects and observed experimentally additional NMR lines of ^{7}Li in LN are related to the mobility of Li ions [1,2]. The simulated NMR spectra of ^{93}Nb for different models of "unoverlapping" intrinsic defects suggest that most probable defects in LN are complexes $(Nb_{Li} + 3V_{Li})$ and isolated V_{Li}. There is large discrepancy yet between the shapes of simulated NMR spectra of ^{93}Nb for this intrinsic defects model and experimental ^{93}Nb NMR spectra. This discrepancy may be caused: (a) by nonjust values of the so-called effective charges of lattice ions, (b) by the influence of "overlapping" defects in the simulations which was not taken into account in Refs. [1,3], (c) by the local distortions of the lattice introduced by the defects.

There are different effective charges for Li, Nb and O ions in the literature [1,3]. However, our previous computer simulations of ^{93}Nb spectra for different effective charges of lattice ions lead to the small deviations in the simulated NMR spectra [1,3] and it should be emphasized, that the discrepancy between simulated and experimental spectra of ^{93}Nb in LN are not caused by nonreal values of effective charges of lattice ions.

In this paper, we have analyzed the NMR spectra of ^{93}Nb in LN using the computer simulations of

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the NMR spectra with models of nonisolated ("overlapping") defects. The simulations have been performed assuming that the distortions of lattice which may be introduced by the defects are negligible. The effects of the lattice distortions and computer simulations of the local electric fields in LN structure will be published in this journal [4].

2. Results and discussion

The experimental details and results were described in the first part of the paper [1]. The simulations have been performed for the models of the intrinsic defects ((a)–(f)), which were presented in Table 1 of Ref. [1]. The additional model of the intrinsic defects in LN has been considered also. This additional model (g) assumes that the defects (V_{Li}–Nb_{Li}–V_{Li}) can be formed along Li-chains [5].

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

(a) Taking into account the concentration of the given type of intrinsic defects, the defects have been localized by a random manner in the sphere with radius of 3 nm. In our calculations 200 different random defects configurations for each type of intrinsic defects have been used.

(b) For each obtained random defects configuration EFG tensors components have been calculated for all ^{93}Nb nuclei in the second sphere with 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 have been obtained in this second sphere.

(c) The simulated NMR spectra of ^{93}Nb nuclei have been obtained using the algorithm described in Ref. [1].

As in the part I [1], 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 $\boldsymbol{B}_0$ and the line width $\delta\nu$ of this line. The results of simulations and experiments [1] are shown in Fig. 1. From Fig. 1 we see that there is considerable influence of the "overlapping" defects on the simulated NMR spectra. In comparison with the simulated spectra obtained for the models of "unoverlapping" defects [1], the models of nonisolated

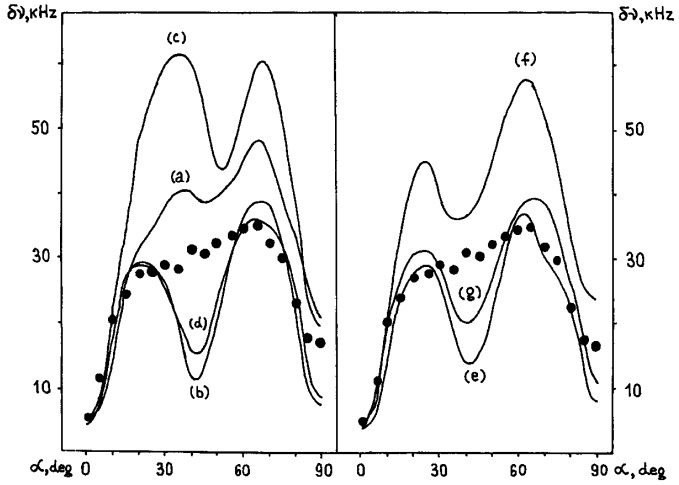

Fig. 1. Experimental (●) and calculated from the simulated spectra angular dependencies of the line width $\delta\nu$ of the NMR ^{93}Nb central transition line. α is the angle between $\boldsymbol{B}_0$ and crystal axis of symmetry c.

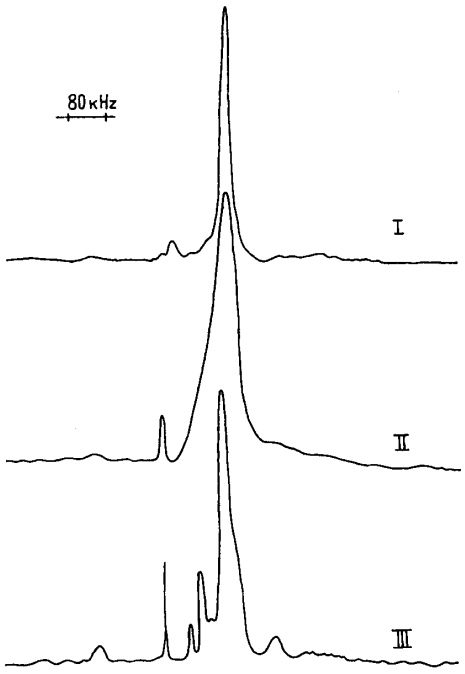

Fig. 2. Simulated integral shape of the NMR ^{93}Nb central transition line for (d) model of the intrinsic defects at $\alpha = 40°$. I – model of the nonisolated ("overlapping") defects. II, III – model of the isolated ("unoverlapping") defects. For the case II the calculated values of $V_{ZZ}^{(i)}$ and $\theta^{(i)}$ were considered as expected values of respective Gaussian distributions functions with standard deviations $\sigma(V_{ZZ}^{(i)}) = 0.03V_{ZZ}^{(i)}$ and $\sigma(\theta^{(i)}) = 2°$ [1]. For the case III each simulated NMR line was broadened by the Gaussian functions with Van-Vleck second moment [1].

defects into cation sublattice ((d), (e) and (g)) lead to the best coincidence of the experimental and simulated data (Fig. 1). Nevertheless, there is a large discrepancy yet between the experimental and simulated $\delta\nu$ values for the crystal orientations at $\alpha \approx 40°$ (Fig. 1). The source of this discrepancy illustrates Fig. 2, which presents the simulated integral shapes of ^{93}Nb NMR central line at $\alpha = 40°$ for the defects model (d). From Fig. 2 we see that the nonisolated defects increase the alteration of the components of the EFG tensors on the sites of nuclei Nb and cause the narrowing of the observed central NMR line of ^{93}Nb nuclei. If we assume that the distribution of the intrinsic defects in the structure of LN is not random but ranges with high and low concentrations of defects, then it appears in principle to present the possibility of explaining the observed discrepancy between the simulated and experimental NMR spectra. However, this discrepancy may be caused also by the local distortions of the lattice introduced by the defects. Using the method of local electric fields ($\boldsymbol{E}_{loc}$) calculations into ferroelectrics [4], we obtained that even one Li vacancy only leads to the changes of $\boldsymbol{E}_{loc}$ at the sites of the 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 the sufficient local distortions of the LN crystal structure. These distortions will increase the distances between ions and must lead to the decreasing of the quadrupolar interaction constants of ^{93}Nb nuclei or must lead to the decreasing of the alterations of the EFG tensor components on the sites of Nb nuclei.

Finally, we want to emphasize the interesting peculiarity of the ^{93}Nb NMR spectra which was not mentioned in the part I [1]. For all defects models (as insulated so 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 $\boldsymbol{B}_0$ (Fig. 3). This additional line arises from the Nb nuclei which are sited 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 $\alpha \approx 10°$ for all five investigated samples of the congruent LN (Fig. 3). The experimental relative intensity of this line is 0.5–1.2%. The comparisons of the simulated and experimental NMR spectra at $\alpha = 10°$ suggest that the defects models (e) and (e) + (d) are preferable. The observed difference in the splitting between the main and additional lines for the simulated and experimental spectra can be explained by the influence of the chemical shift of ^{93}Nb nuclei [6]. As it was shown earlier [6], the chemical shift of ^{93}Nb nuclei in LN is relatively largest at $B_0 = 1.4$ T. It is clear that the chemical shift of the ^{93}Nb nuclei which are sited above V_{Li} may be different from the chemical shift of the ^{93}Nb nuclei sited in the ranges where influences of the defects are small.

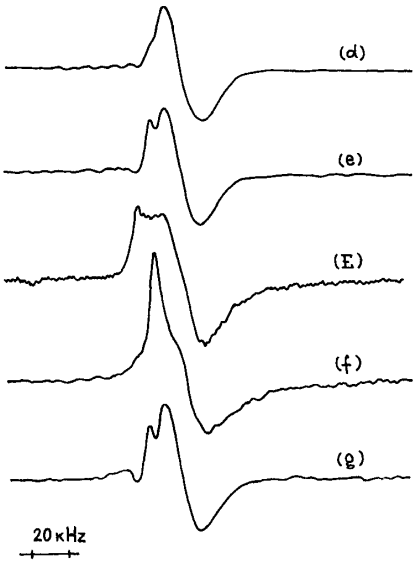

Fig. 3. Experimental (E) and simulated NMR spectra of ^{93}Nb nuclei for different models (d–g) of the intrinsic "overlapping" defects in LN at $\alpha = 10°$.

3. Conclusions

From the presented results on the simulations of ^{93}Nb NMR spectra for different models of intrinsic nonisolated ("overlapping") defects in congruent LN follows that the most possible intrinsic defects in LN structure are the $[Nb_{Li} + (2–3)V_{Li}]$ complexes and isolated $(2–1)V_{Li}$. The observed additional central line of ^{93}Nb spectra at some crystal orientations into the external magnetic field supports this model of the intrinsic defects. It was shown also that the observed discrepancy between the simulated and experimental spectra of ^{93}Nb may be related with the local deformations of crystal lattice caused by the intrinsic defects. The present results can be considered however, as preliminary ones since the influences of the lattice distortions introduced by the defects on NMR spectra are not fully accounted.

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