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Defect structures and the MgO-doping-level-threshold effect on the optical absorption of reduced MgO-doped lithium niobate

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Congruent $LiNbO_3$ crystals have been doped with Mg impurity to levels of 1.0, 2.7, 5.0, and 6.0 mol %. With doping levels between 0.5 and 6.0 mol %, there was an abrupt change in the features of the optical absorption. This observation is consistent with our theoretical calculation, which independently predicted that the critical magnesium concentration, [Mg], for the threshold effect should occur at $[Mg]_c = 5.3$ mol %. The spectra exhibit anisotropy. Defect-structure models are proposed. We demonstrate that, under thermochemical reduction, the density of the crystal increases and oxygen vacancies are also formed. We propose that when congruent crystals are thermochemically reduced, the observed optical absorptions are due to defects comprising both oxygen vacancies and different types of dipolarons.

I. INTRODUCTION

The importance of Mg as an impurity in $LiNbO_3$ derives from the discovery of Zhong, Jin, and Zhongkang[1] that the optical damage due to laser-induced refractive-index inhomogeneities is strongly diminished in samples grown from a congruent melt containing 4.6 mol % MgO as compared to those with a low concentration. The optical absorptions of thermochemically reduced (TCR) crystals[2-4] and several other properties exhibit abrupt changes[5,6] when the Mg concentration is raised above a critical Mg concentration, $[Mg]_c$. This phenomenon is called the Mg-doping level threshold effect.

In recent years the questions as to the origin of the optical absorptions in the TCR crystals, the value of the critical Mg concentration, and the physical nature of the Mg-doping level threshold effect have been a matter of controversy. The optical-absorption spectra of TCR undoped and lightly Mg-doped ($[Mg] < [Mg]_c$) congruent $LiNbO_3$ crystals are characterized by a strong, thermally stable, and broad absorption band near 2.5 eV. Two interpretations were provided: F centers[7,8] and dipolarons.[5] After illumination with light of wavelength $\lambda \leq 600$ nm at $T < 80$ K, a strong absorption band emerged at 1.6 eV. It was attributed to F^+ centers[7,9] and single polarons.[8,10] For heavily Mg-doped TCR crystals the optical absorption exhibited an abrupt change. Another band appeared at 1200 nm instead of the visible band at 2.5 eV.[4,6] Its origin was ascribed to Mg^+ (Ref. 4) and the appearance of Mg^{2+} in the Nb^{5+} site,[6] respectively.

In this paper we confine ourselves exclusively to congruent $LiNbO_3$ which has a formula $Li_{0.972}Nb_{1.028}O_3$. Optical-absorption spectra of TCR $LiNbO_3$:Mg crystals doped with different [Mg] were measured to determine the critical Mg-doping level of the [Mg] threshold effect. Optical absorptions of a TCR crystal correspond to electronic transitions of defects. The abrupt change in the optical absorption spectra indicates change of the lattice defects when [Mg] is raised above $[Mg]_c$. On the basis of defect chemistry, we propose different lattice defect structures for different [Mg] doped $LiNbO_3$. It is demonstrated that as a result of TCR the density of the crystal increases and oxygen vacancies are also formed. Under TCR there would be $[Nb_{Li}\text{-}F\text{-}Nb_{Nb}]$ defect, where Nb_{Li} denotes Nb^{5+} at a Li^+ state (Vink notation), etc., which was comprised of an F center (oxygen vacancy with two electrons) and a $Nb_{Li}\text{-}Nb_{Nb}$ dipolaron, formed in undoped crystals; both $[Mg_{Li}\text{-}F\text{-}Nb_{Nb}]$ defect, which was comprised of an F center and a $Mg_{Li}\text{-}Nb_{Nb}$ dipolaron, and $[Nb_{Li}\text{-}F\text{-}Nb_{Nb}]$ defect formed in lightly Mg-doped crystal; and $[(Mg_{Li}\text{-}Mg_{Nb})\text{-}F\text{-}(Mg_{Li}\text{-}Nb_{Nb})]$ defect, which was comprised of an F center and a pair of $Mg_{Li}\text{-}Mg_{Nb}$ and $Mg_{Li}\text{-}Nb_{Nb}$ dipolarons, formed in heavily Mg-doped crystal. The appearance of Mg_{Nb} and the related defects, when the [Mg] is raised above $[Mg]_c$, should be the origin of the Mg-doping level threshold effect and our theoretical calculation predicts that the critical [Mg] for the threshold effect should occur at $[Mg]_c = 5.3$ mol %, which is consistent with our experimental observation.

II. EXPERIMENTAL PROCEDURE

Congruent $LiNbO_3$:Mg crystals doped with 0, 1.0, 2.7, 5.0, and 6.0 mol % crystalline samples used in this paper were grown from a congruent melt with an initial Li_2O 48.6 at. % by Shanghai Institute of Ceramics, Academia Sinica. Two plates with the C axis parallel to their surface and two plates with the C axis perpendicular to their surface were polished for each $LiNbO_3$:Mg crystalline sample. One set was used as a control and the other was thermochemically reduced. Thermochemical reduction was performed by annealing the samples in vacuum (10^{-5} mm Hg) under high temperature (1000 °C) for 0.5 h.

The optical absorption due to TCR was obtained by taking the differential spectra between the TCR and the control sample. The measurements were taken with a Beckmann 5270 Spectrophotometer at room temperature. To obtain information on the symmetry of the defect centers, polarized absorption spectra were measured.

III. RESULTS AND DISCUSSION

A. Optical-absorption spectra

The differential spectra for different doping Mg levels, ($[\mathrm{Mg}] < [\mathrm{Mg}]_c$), are shown in Fig. 1. It can be seen from the figure that the absorption spectra of the samples with the *C* axis parallel to their surface are similar, exhibiting a main strong broad absorption band posited near 515 nm with two weak bands on a longer wavelength shoulder near 540 and 600 nm [Fig. 1(a)]; when the *C* axis is perpendicular to the surface two strong broad absorption bands are observed at 325 and 515 nm [Fig. 1(b)]. Therefore, it is clear that the TCR LiNbO$_3$:Mg crystals exhibit anisotropy at low concentrations. The TCR undoped crystal also exhibits anisotropy. The curves with polarization parallel and perpendicular to the *C* axis are shown by curves labeled $E \parallel c$ and $E \perp c$, respectively, in Fig. 2. The optical-absorption spectra of a TCR heavily doped ($[\mathrm{Mg}] = 6.0$ mol %) crystal are different. Strong absorption bands are observed in the infrared region instead of the visible region, as in the case of lightly doped crystals. The spectra in the two polarized orientations are shown in Fig. 3. The optical absorption data are listed in Table

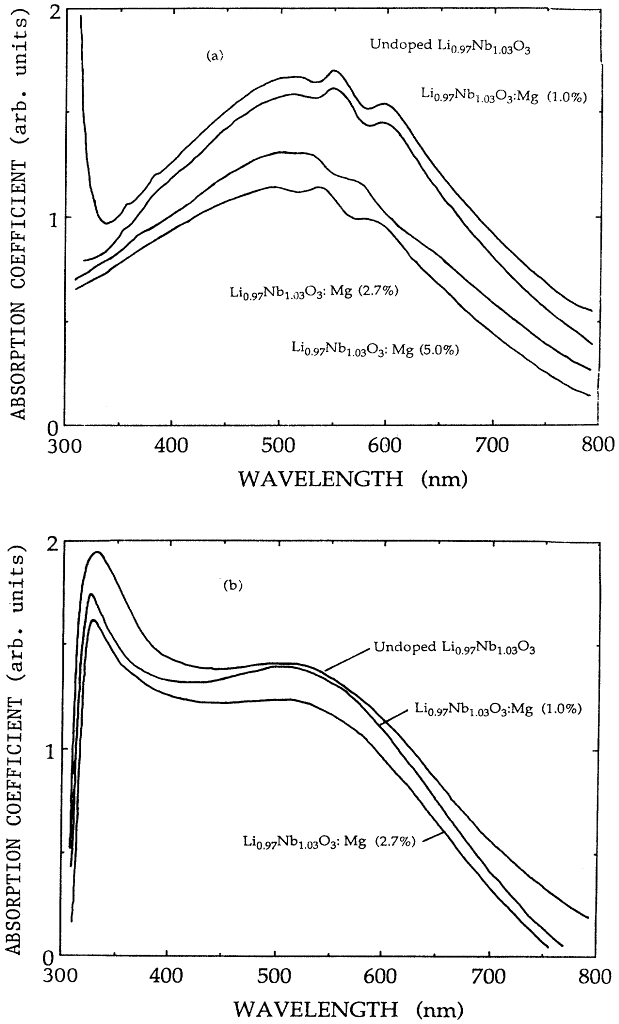

FIG. 1. Differential absorption spectra of thermochemically reduced congruent LiNbO$_3$:Mg ($[\mathrm{Mg}] \le 5.0$ mol %) crystals; (a) surfaces of the samples are parallel to the *C* axis and (b) surfaces of the samples are perpendicular to the *C* axis.

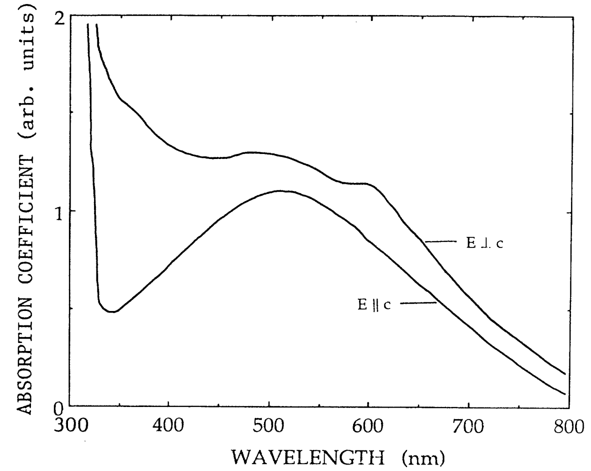

FIG. 2. Polarization absorption spectra of the thermochemically reduced undoped congruent LiNbO$_3$ with the surface of the sample parallel to the *C* axis for two different polarizations.

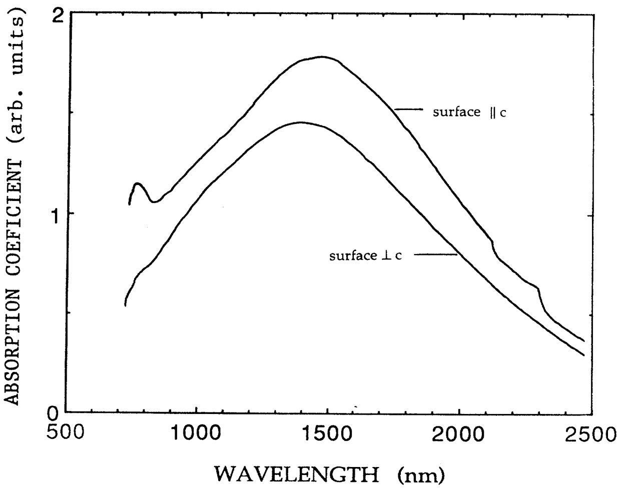

FIG. 3. Differential absorption spectra of the color centers in thermochemically reduced congruent LiNbO$_3$:Mg ($[\mathrm{Mg}] = 6.0$ mol %) crystal. Curves show the surface of the sample is parallel and perpendicular to the *C* axis.

TABLE I. Absorption data of TCR $LiNbO_3$:Mg.

[Mg] (mol %)	Surface parallel to the C axis (nm)	Surface perpendicular to the C axis (nm)
0	514	325
	540	515
	600	
1.0	514	325
	540	515
	595	
2.7	514	325
	530	515
	575	
5.0	514	325
	530	515
	590	
6.0	780	1400
	1470	

I. It can be seen from the table that the critical concentration $[\mathrm{Mg}]_c$ occurs in the region 5.0–6.0 mol %.

B. Defect structures in $LiNbO_3$:Mg

The Czochralski-grown $LiNbO_3$ with different stoichiometry can be described by $(\mathrm{Li_2O})_{50-x}(\mathrm{Nb_2O_5})_{50+x}$. The chemical equilibrium can be written as

$$(50-x)\mathrm{Li_2O}+(50+x)\mathrm{Nb_2O_5} =2(50-x)\mathrm{LiNbO_3}+2x\mathrm{Nb_2O_5}\ . \quad (1)$$

Excess Nb_2O_5 is denoted by x. The condition for congruent $LiNbO_3$ is $x=1.4$. Therefore the crystal has a formula $\mathrm{Li_{0.972}Nb_{1.028}O_3}$. We confine ourselves exclusively to congruent $LiNbO_3$ in this paper. The excess Nb_2O_5 will give rise to Li-deficient lattice defects. This imbalance between the two cations means that Nb^{5+} should occupy Li^+ sites[11,12] surrounded by cation vacancies. The chemical equilibrium can be written as

$$3\mathrm{Nb_2O_5}=5[\mathrm{Nb_{Li}}(\mathrm{Nb_{Nb}})_{1/5}(V_{\mathrm{Nb}})_{4/5}\mathrm{O_3}]\ , \quad (2)$$

where V_{Nb} denotes a Nb vacancy. Let the intrinsic defect $[\mathrm{Nb_{Li}}(\mathrm{Nb_{Nb}})_{1/5}(V_{\mathrm{Nb}})_{4/5}\mathrm{O_3}]$ be denoted as defect type 1.

Doped into the crystal, MgO may be incorporated with the excess Nb_2O_5 to form impurity-associated defects. A set of possible lattice defects was deduced from crystal density measurements on crystals with different [Mg].[13] The $LiNbO_3$:Mg crystals with [Mg] between 0 and 2.7 mol % contain defect type 1 and type 2 immersed in perfect $LiNbO_3$, where type 2 denotes $[(\mathrm{Mg_{Li}})_{1/2}(\mathrm{Nb_{Li}}V_{\mathrm{Nb}})_{1/2}(\mathrm{Nb_{Nb}})_{1/2}\mathrm{O_3}]$. As [Mg] increases from 0 to 2.7 mol %, type 1 decreases and type 2 increases. When [Mg] reaches 2.7 mol %, the crystal contains no defect type 1 but type 2 in the perfect lattice. Crystals with [Mg] between 2.7 and 5.3 mol % contain defect type 2 and type 3 immersed in perfect $LiNbO_3$ where type 3 denotes $[\mathrm{Mg_{Li}Nb_{Nb}O_3}+e]$. As [Mg] increases from 2.7 to 5.3 mol %, type 2 decreases and type 3 increases. When [Mg] reaches 5.3 mol %, the crystal contains no defect type 2 but type 3 in perfect $LiNbO_3$. Crystals with [Mg] between 5.3 and 10.1 mol % contain defect type 3 and type 4 immersed in perfect $LiNbO_3$ where type 4 denotes $[\mathrm{Mg_{Li}}(\mathrm{Mg_{Nb}})_{1/3}(\mathrm{Nb_{Nb}})_{2/3}\mathrm{O_3}]$. As [Mg] increases from 5.3 to 10.1 mol %, type 3 decreases and type 4 increases. Three defects of type 4 form one electrically neutral defect cluster having the formula $\mathrm{Mg_4Nb_2O_3}$, where Mg^{2+} in an Nb^{5+} site is produced.

The types and structures of defect lattice which exist in $LiNbO_3$:Mg depend on the [Li]/[Nb] ratio and the [Mg]. An as-grown congruent crystal has [Li]/[Nb]$=0.946$. The types of defects are listed in Table II.

Schirmer, Thiemann, and Wohlecke[5] and Smyth[14] argued against the existence of oxygen vacancy in the TCR congruent $LiNbO_3$ because the density of the crystal increased under TCR.[14] Under TCR some oxygen may escape from the crystal. One possible process can be described by oxygen atoms escaping from their lattice sites leaving behind F centers, where each F center denotes an oxygen vacancy with two electrons. If this is the process, the density of the TCR crystal should decrease. However, we believe there are other ways in which oxygen can escape from the crystal, followed by a contracting of the lattice. Therefore the density of the crystal can increase. In fact, the density of the crystal depends on the way oxygen escapes from the crystal under TCR. Therefore we believe that oxygen vacancies can be formed and yet be attended by an increase of density under TCR.

C. Origin of the optical absorption in TCR $LiNbO_3$:Mg and the [Mg] threshold effect

Under TCR some oxygen atoms escape, leaving behind F centers. We now propose a model to explain the observed optical absorption due to TCR and the Mg-doping level threshold effect.

According to the stacking fault model of congruent $LiNbO_3$, there would be $\mathrm{Nb_{Li}}$ adjacent to a $\mathrm{Nb_{Nb}}$ forming a $\mathrm{Nb_{Li}}$-$\mathrm{Nb_{Nb}}$ dipolaron, as shown in Fig. 4(b). The oxygen atoms adjacent to the $\mathrm{Nb_{Li}}$-$\mathrm{Nb_{Nb}}$ dipolarons are more thermally unstable. They can be, prior to escape from the crystal and form F centers, under TCR. Since the bonding of an Nb^{5+} ion to its neighboring O^{2-} ions has a rather covalent behavior, it tends to trap additional electrons. Therefore, the two electrons from the F center should be shared with two adjacent Nb^{5+} forming a

TABLE II. Defects contained in $LiNbO_3$:Mg with different [Mg].

MgO-doping level	Types of defect
$[\mathrm{MgO}]=0$	1
$0<[\mathrm{MgO}]\le 2.7$ mol %	1 and 2
$2.7<[\mathrm{MgO}]\le 5.3$ mol %	2 and 3
$5.3<[\mathrm{MgO}]\le 10.1$ mol %	3 and 4
$[\mathrm{MgO}]>10.1$ mol %	4

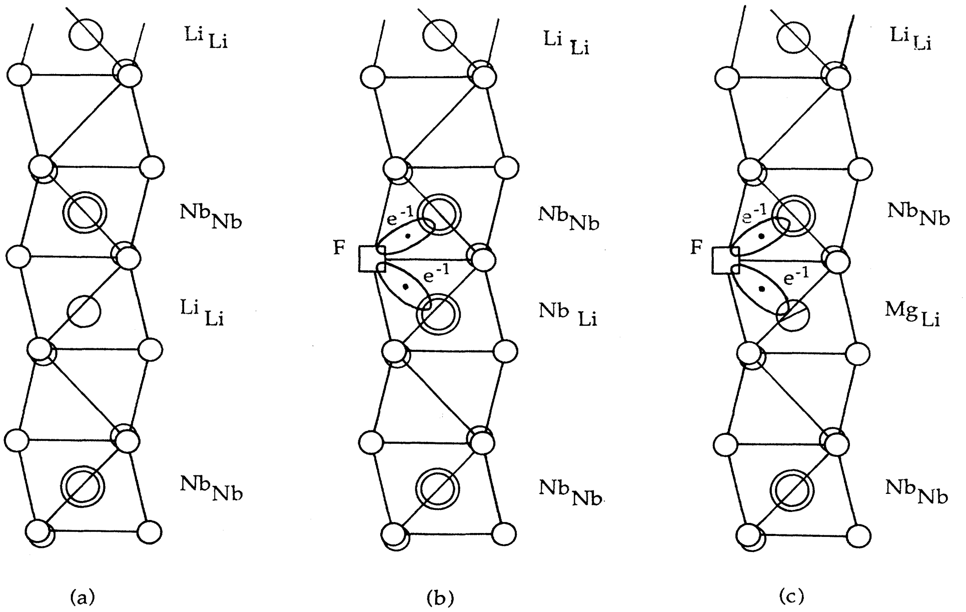

FIG. 4. Structures of perfect lattice (a), [Nb_{Li}-F-Nb_{Nb}] defect (b), and [Mg_{Li}-F-Nb_{Nb}] defect (c).

[Nb_{Li}-F-Nb_{Nb}] defect. This [Nb_{Li}-F-Nb_{Nb}] defect has as its main features the F center proposed by Sweeney *et al.*[4] and a Nb_{Li}-Nb_{Nb} dipolaron proposed by Schirmer, Thiemann, and Wohlecke,[5] as shown in Fig. 4(b). The Nb^{5+} ions adjacent to the F center can trap additional electrons. Under these conditions electrons are mostly found near the Nb neighbors of oxygen vacancy,[15] and exhibit partly Nb^{4+} behavior.[16] To what extent the Nb exhibits Nb^{4+} behavior depends on the position of the electron it shared with the oxygen vacancy. This center is associated with the Nb antisite, so its concentration decreases with increasing [Li]/[Nb] ratio in the TCR undoped crystal. We propose that the optical absorptions of the TCR undoped crystal are mainly caused by the [Nb_{Li}-F-Nb_{Nb}] defect. This is consistent with the observation that the optical absorption strongly decreases with increasing [Li]/[Nb] ratio.[17]

In $LiNbO_3$:Mg crystal with [Mg] ≤ 2.7 mol %, as [Mg] increases, the Nb_{Li}-Nb_{Nb} dipolarons would be progressively replaced by the Mg_{Li}-Nb_{Nb} dipolarons. Under TCR, the oxygen vacancies adjacent to the Mg_{Li}-Nb_{Nb} dipolarons may also be formed, resulting in [Mg_{Li}-F-Nb_{Nb}] defects. Its structure is shown in Fig. 4(c). In this defect, both Nb and Mg have partly covalent behavior and would trap additional electrons. The electron spin resonance (ESR) results reported by Sweeney *et al.*[4] and the x-ray photoemission spectroscopy (XPS) results reported by Feng, He, and She[16] showed that the lightly Mg-doped $LiNbO_3$ ([Mg] < $[Mg]_c$) exhibited Nb^{4+} rather than Mg^{+} signals. This suggests that the position of two F electrons is nearer to the Nb than to the Mg. Since the [Mg_{Li}-F-Nb_{Nb}] defect is associated with defect type 2, which is comparable in structure with the [Nb_{Li}-F-Nb_{Nb}] defect, they should possess similar optical-absorption features.

The $LiNbO_3$:Mg crystals with [Mg] between 2.7 and 5.3 mol % contains defect type 2 and type 3. In type 3, where the monovalent Li^{+} ion is replaced by the divalent Mg^{2+} ion and an additional electron is trapped, the neighboring O^{2-} ion is thermally more stable against F-center formation. Therefore, we believe that the optical absorptions of the TCR crystals are mainly caused by the [Mg_{Li}-F-Nb_{Nb}] defects.

The $LiNbO_3$:Mg crystals with [Mg] between 5.3 and 10.1 mol % contain defect type 3 and 4. The electrically neutral defect cluster formed by three defects of type 4 is stacked by two cation prisms in the C direction with an oxygen ion at the center of one prism as shown in Fig. 5. The oxygen is surrounded by one Nb_{Nb}, one Mg_{Nb}, and two Mg_{Li}. Since both Mg^{2+} and Nb^{5+} have partly covalent behavior, this oxygen ion is thermally more unstable than the oxygen ion in the other lattices. Therefore, under TCR it is easy to escape resulting in a [(Mg_{Li}-Mg_{Nb})-F-(Mg_{Li}-Nb_{Nb})] defect. This defect has as its main features the F center and both the Mg_{Li}-Mg_{Nb} and

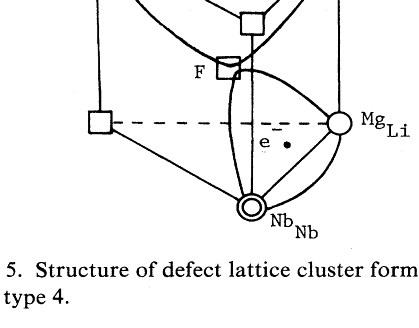

FIG. 5. Structure of defect lattice cluster formed by three defects of type 4.

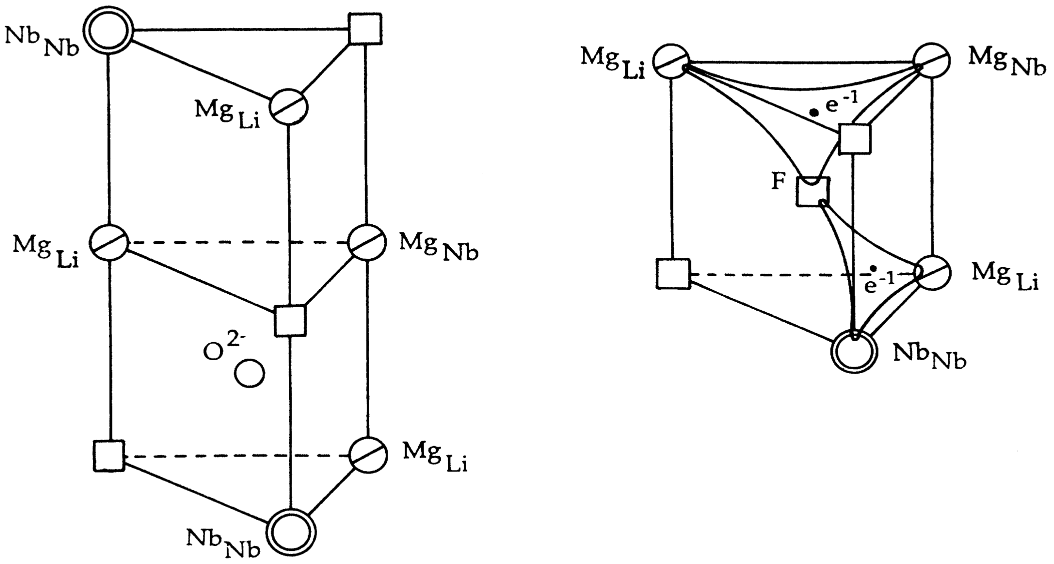

FIG. 6. Structure of $[(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Mg}_{\mathrm{Nb}})\text{-}F\text{-}(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Nb}_{\mathrm{Nb}})]$ defect.

the $\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Nb}_{\mathrm{Nb}}$ dipolarons, as shown in Fig. 6. The two F electrons in this defect are shared by the four partly covalent cations, raising the ground state of the system and making the optical absorptions of the center occurring in the longer-wavelength region. Optical absorption of the TCR heavily Mg-doped LiNbO_3 ($[\mathrm{Mg}] > 5.3$ mol %) is mainly caused by this type of defect. Therefore the TCR heavily doped crystal exhibits an abrupt change on the optical absorption features. The appearance of $\mathrm{Mg}_{\mathrm{Nb}}$ in the heavily Mg-doped crystal has been confirmed by OH^- infrared absorption measurements.[18,19] We believe that the Mg^+ ESR signal for a heavily Mg-doped crystal observed by Sweeney *et al.*[4] should be originated from this type of defect rather than from real Mg^+ ions.

IV. CONCLUSIONS AND SUMMARY

From the above discussion we conclude that the optical absorptions in the TCR LiNbO_3 crystals are caused by the $[\mathrm{Nb}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ defect for the undoped crystal; by the $[\mathrm{Nb}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ and $[\mathrm{Mg}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ defects for the crystals doped with $[\mathrm{Mg}] < 5.3$ mol %; and by the $[(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Mg}_{\mathrm{Nb}})\text{-}F\text{-}(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Nb}_{Nb})]$ defect for the crystals doped with $[\mathrm{Mg}] > 5.3$ mol %. The $[\mathrm{Mg}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ defect is similar in structure to the $[\mathrm{Nb}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ defect, so the TCR lightly doped crystals are similar in optical absorption features to the TCR undoped crystal. However, the $[(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Mg}_{\mathrm{Nb}})\text{-}F\text{-}(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Nb}_{\mathrm{Nb}})]$ defect is far different in structure from the $[\mathrm{Nb}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{\mathrm{Nb}}]$ and $[\mathrm{Mg}_{\mathrm{Li}}\text{-}F\text{-}\mathrm{Nb}_{Nb}]$ defects. Therefore the TCR heavily doped crystal exhibits an abrupt change on the optical-absorption spectra. All three types of defect are of low symmetry. Therefore the optical absorption features of the TCR LiNbO_3:Mg with different [Mg] are anisotropic. The threshold effect of the LiNbO_3:Mg crystal originates from the appearance of $\mathrm{Mg}_{\mathrm{Nb}}$ attended $[(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Mg}_{\mathrm{Nb}})\text{-}F\text{-}(\mathrm{Mg}_{\mathrm{Li}}\text{-}\mathrm{Nb}_{\mathrm{Nb}})]$ defect created under TCR. The critical [Mg] for the Mg-doping level threshold effect should be $[\mathrm{Mg}]_c = 5.30$ mol %, which falls in the region 5.0–6.0 mol % and is consistent with our experimental results.

ACKNOWLEDGMENTS

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