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Thermal Fixation of the Photorefractive Holograms Recorded in Lithium Niobate and Related Crystals

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Thermal Fixation of the Photorefractive Holograms Recorded in Lithium Niobate and Related Crystals

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With emphasis on LiNbO₃ the basic principles, the developments over four decades, and recent applications of the thermal fixation of photorefractive holograms are reviewed. Thermal fixing is the most promising method to realize optically stable memories in photorefractive media. The microscopic origin of thermal fixing is mainly caused by screening the electronic space-charges by protons thermally activated at about 120°C. After fixing a diffraction efficiency comparable to that of untreated crystals is achieved and lifetimes of at least 2 years have been observed, whereas for special arrangements scientific sound estimates point to long terms as high as 100 years. A theoretical description is quite well established and will guide further improvements. Thermally fixed holograms have been tested in nonvolatile optical storage systems based on hologram multiplexing and are the basis in narrow-band devices with very high angular selectivity.

Keywords  thermal fixation, hologram storage, photorefraction, lithium niobate

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I. PRELIMINARIES

Recording of phase gratings based on photorefraction (a photoinduced change of the refractive indices) is underlying a variety of practical applications. First, it may be applied for a nonvolatile data storage. The memory system using the photorefractive media are characterized by a high angular selectivity of recording and reading (several μrads), which permits recording of a great number of elementary holo-
grams in the unit volume. The photorefractive storage media require relatively low laser powers for recording, that is, the recording sensitivity is high. Another type of applications of photorefractive gratings is due to their high angular selectivity strictly constrained by the Bragg conditions, which permits construction of narrow-bandwidth devices, such as, for example, optical filters, optical correlators, and so on. Both the narrow-bandwidth systems and read-only nonvolatile memories require a high stability of the recorded gratings on operating (i.e., and so on under illumination) and in the dark. However, the stability is ruled out fundamentally, because microscopically the photorefraction is based on the formation of a space charge field, which unavoidably decays due to the conductivity, either photo- or dark one. Such a volatility of photorefractive gratings is the main obstacle for their applications in nonvolatile devices. To surmount this obstacle and to realize optically non-erasable memories on the base of photorefractive media, several methods were proposed. One of them, a thermal fixing of the recorded gratings, is the subject of this review. This effect was observed in various photorefractive materials, however, as a practical method it was studied in detail in LiNbO₃ only, because the latter is the most promising photorefractive material for all aforementioned applications. Some encouraging results were obtained in its structure analogue, LiTaO₃, as well.

The number of publications on the thermal hologram fixation is swiftly increasing and a sufficient progress in the insight to this effect is achieved. The aim of this review is to characterize the present state of the problem. We concentrate mainly on lithium niobate, but the results for other photorefractive oxides are referred to as well. The data of experimental investigations will be summarized in the light of developed microscopic models of this effect. As the common approach to the mechanism of thermal fixation is based on the deciding role of the proton drift, we dwell briefly on recent studies of the protonic conductivity in LiNbO₃ and of protons (or hydroxyl ions) in oxides on a whole. To illustrate the possibilities of the thermal fixation of recorded gratings, some examples of practical applications of this procedure will be presented.

The structure of the review is as follows. In the introduction we briefly mention the fundamentals of the photorefractive effect as applied to LiNbO₃ and very briefly characterize LiNbO₃ as a photorefractive material. The basics may be found in numerous monographs and reviews. In section III the general experimental scenario of the thermal fixation in LiNbO₃ and other oxides is described along with a qualitative discussion of the occurring microscopic events. Section IV gives a simplified presentation of the basic equations in order to analyze possible ways to optimize the fixation conditions. In section V examples of experimental studies of the thermal fixing in LiNbO₃ crystals are presented and an attempt is made to summarize numerical data on storage times and diffraction efficiencies of thermally fixed gratings reported in the literature for this material. In section VI the origin of movable ions responsible for the thermal fixation is discussed and studies of hydrogen (hydroxyl) in oxides using IR spectroscopy are cited. Investigations of the thermal fixing in miscellaneous oxide photorefractives are demonstrated in section VII. Attempts of practical applications of thermally fixed photorefractive gratings are described in section VIII.

The number of publications on the thermal fixing of photorefractive holograms is vast. An outstanding contribution from several research groups to an insight to this problem should be emphasized. It was discovered and originally investigated in the 1970 by a group from RCA Labs., Princeton (USA). Several groups in the University of Osnabrück strongly contributed to experimental studies and an elaboration of theoretical models. Fruitful developments both of the theoretical description and of studies of the microscopic mechanism are in progress in Universidad Autonoma de Madrid (Spain). A group in CalTech contributed both to theoretical models and experimental studies. We emphasize that regularities in thermal fixing reported in the pioneering work of the RCA Labs. and a qualitative explanation of the effect proposed by them is still underlying all models proposed until recently.

II. INTRODUCTION

A. Background of the Photorefraction

We now review the fundamentals of the photorefractive effect and the holographic recording based on it. A photoinduced change of the refractive indices is due to a formation of a photoinduced space charge field \(E_{sc}\) in the illuminated part of the crystal, which in its turn leads to a variation of the refractive indices via the electrooptical effect, the linear one in non-centro-symmetric media

\[
\frac{1}{\epsilon_{ij}} = \frac{1}{\epsilon_0} + r_{ijk} E_k
\]

where \(\epsilon_{ij}\) and \(r_{ijk}\) are components of the tensors of the dielectric permittivity and the linear electrooptic effect, respectively, \(\epsilon_0\) is the initial value, \(E_k\) is a component of the space-charge field. Formation of \(E_{sc}\) consists of the following steps: a photo-excitation of charge carriers to the conduction band, their spatial transport, and a re-trapping by capture centers. In the case of photorefraction the photo-excitation occurs usually from donors (extrinsic or intrinsic defects), however the band-to-band transition of electrons via the two-photon mechanism is involved sometimes as well. The transport of photoinduced charges (a photocurrent) involves the following components

\[
j = j_{drift} + j_{pv} + j_{diff}
\]

Here we assumed the band-transport mechanism, which is the most probable for oxide insulators having a large band-gap. At...
the same time, in the case of a high impurity concentration the hopping charge transport is probable, as was shown, for example, in highly doped LiNbO$_3$:Fe.\textsuperscript{29} We now discuss in turn the parts of $E_{\text{ext}}$ caused by each component of Eq. 2. The first one in Eq. 2 is the ohmic current

$$j_{\text{diff}} = \sigma (E_{\text{ext}} + E_{\text{int}})$$

arising under external $E_{\text{ext}}$ or internal $E_{\text{int}}$ fields. An example of $E_{\text{int}}$ is given by the field of the pyroelectric current caused by a local heating of the crystal under illumination. A component of the photorefraction related to the screening of the pyroelectric field by photo-carriers was actually detected in LiNbO$_3$,\textsuperscript{40} but its contribution is negligible. The second term in Eq. 2 is the bulk photovoltaic current, which is characteristic for noncentrosymmetric (piezoelectric and pyroelectric) crystals (e.g., Refs. 36, 37), and appears under a uniform illumination. It is expressed as

$$j_{\text{pv}} = \beta_{ijk} e_j e_k I$$

where $\beta_{ijk}$ is the photovoltaic tensor, $e_j$ and $e_k$ are unit vectors of the light polarization, $I = |a^2|$ is the light intensity. With respect to symmetry considerations the photovoltaic tensor $\beta_{ijk}$ is related to the piezoelectric tensor $d_{ijk}$,\textsuperscript{37} so for LiNbO$_3$ or LiTaO$_3$ (the point symmetry group $C_{3v}$) contains the non-zero components $\beta_{31} = \beta_{32}, \beta_{33}, \beta_{23} = -\beta_{12} = \beta_{16}/2, \beta_{15} = \beta_{54}$. Most often the photovoltaic current is presented in the initial scalar form proposed by Lines and Glass\textsuperscript{36}

$$j_{\text{pv}} = k_G \alpha I$$

where $\alpha$ is the optical absorption coefficient assumed to be isotropic, and $k_G = \beta_{ijk}/\alpha$ is the so-called Glass constant characterizing the photovoltaic activity of the given impurity in a certain lattice.\textsuperscript{36} The stationary photovoltaic field achieved under the diffusion-drift equilibrium, in the scalar-presentation is expressed as

$$E_{\text{pv}} = j_{\text{pv}}/(\sigma_{ph} + \sigma_d) = k_G \alpha I/(\sigma_{ph} + \sigma_d)$$

where $\sigma_{ph}$ and $\sigma_d$ are photo- and dark conductivities, respectively. In crystals under discussion (LiNbO$_3$ and its analogues) in the range of moderate light intensities $\sigma_{ph} \gg \sigma_d$, the lux-ampere characteristics are linear, $\sigma_{ph} \approx I$, (for details see the next section), so $E_{\text{pv}}$ practically does not depend on the light intensity.

The third photo-current component in Eq. 2 is the diffusion transport of photo-carriers that occurs under a spatially nonuniform illumination and may be expressed as

$$j_{\text{diff}}(z) = e(D_n d n/dz + D_p d p/dz)$$

$$= k_B T (\mu_n d n/dz + \mu_p d p/dz)$$

where $D_n, \mu_n, D_p, \mu_p$ are diffusion coefficients and the mobility of the electrons and holes, respectively, $k_B$ is the Boltzmann constant, and $e$ is the unit charge. For the case of two-beam hologram recording (Figure 1), a spatially varied light intensity provided by a superposition of two mutually coherent plane waves with incident intensities $I_1$ and $I_2$ is characterized by the coordinate dependence

$$I(z) = I_0 \sin(1 + m \cos Kz)$$

where $m = 2 \sqrt{I_1 I_2}/(I_1 + I_2)$ is the modulation index, $K = 4\pi \sin \theta/\lambda$ is the spatial frequency of the interference pattern, $\theta$ is the half-angle between the recording beams, and $\lambda$ is the wavelength of the recording light.

For the case of a mono-polar (electron) photocconductivity a scalar presentation of the diffusion field corresponding to the intensity distribution (Eq. 8), is

$$E_{\text{diff}}(z) = k_B T/e Kz \sin Kz/(1 + m \cos Kz)$$

Principal differences between the diffusion field (Eq. 9) and the photovoltaic one (Eq. 6) are an independence of the light polarization, $\pi/2$ with respect to the interferogram (Eq. 8).

The photoexcited carriers transferred by either of the mechanisms described earlier or by their combination are captured by traps (if any) to form a spatially modulated space charge field $E_{\text{sc}}$. If the photovoltaic mechanism is dominant, then $E(z)$ is in phase with the interferogram. This case is most often realized in doped LiNbO$_3$. Provided that the diffusion mechanism prevails, the grating is shifted by $\varphi = \pi/2$ (so-called non-local response).\textsuperscript{33, 44} This case is typical, for example, for Strontium-Barium Niobate (SBN) or BaTiO$_3$ crystals. If $E_{\text{pv}}$ and $E_{\text{diff}}$ are comparable, then the shift of the grating is less than $\pi/2$.

The electron transport and grating formation under a spatially-modulated light intensity (Eq. 8) is described by a coupled set of charge balances and rate equations, proposed in Refs.\textsuperscript{33, 44} It includes the electron continuity equation

$$\frac{\partial n_e}{\partial t} = (s_{ph} I + s_T) (N - N^+) - s_e n N^+ + \frac{1}{e} \frac{\partial}{\partial z} \frac{1}{e} \frac{\partial j_e}{\partial z}$$

\textsuperscript{10a}
the impurity ionization equation
\[ \frac{\partial N^+}{\partial t} = \left( s_{ph} I + s_T \right) (N - N^+) - s_e N^+ n_e, \]  
[10b]

the electron current density
\[ j_e = e \mu_e n_e E + e D_e \frac{\partial n_e}{\partial z} + k_G I (N - N^+) s_{ph}, \]  
[10c]

and the Poisson equation
\[ \varepsilon e_0 \frac{\partial E}{\partial z} = \rho, \]  
[10d]

where
\[ \rho = e (N^+ - N_a - n_e). \]  
[10e]

The following notations are used in Eqs. 10a–10e: \( N \) and \( N^+ \) are the donor and ionized donor densities, respectively, \( s_{ph}, s_T \) and \( s_e \) are microscopic parameters characterizing the processes of photoionization, thermal excitation and recombination, respectively; other notations were already explained. Accordingly, the Einstein relation \( D_e = \mu_e k_B T/e \) (where \( k_B \) is the Boltzmann constant). \( N_a \) describes the concentration of compensating passive acceptors in the approach of compensated semiconductor.43,44 As applied to LiNbO\(_3\):Fe, \( (N - N^+) \) and \( N^+ \) are the concentrations of Fe\(^{2+}\) and Fe\(^{3+}\), respectively.

The solution to Eqs. 10a–10e gives the following general expression for the steady-state amplitude of the space-charge field43,45:
\[ E_K = -i m_e \frac{E_D - i E_{pv}}{1 + E_D/E_q - i (N^+ / N)(E_{pv} / E_q)} \]  
[11]

where
\[ m_e = m - s_{ph} I \]  
[12]

In Eq. 11 \( E_D \) is the amplitude of the diffusion field (Eq. 9), \( E_{pv} \) is the photovoltaic field (Eq. 6). The saturation or the limiting field
\[ E_q = e N t / K \varepsilon e_0 \]  
[13]

(where \( N_t = N_a N_D / N \) is the effective trap concentration) is the maximum amplitude of the space-charge field provided by the electron transport for a given spatial frequency of the grating.

The kinetics of the formation of the space-charge field (the recording) looks as follows
\[ E(x, t) = E_K [1 - \exp(-\Gamma e t)] \exp(i kx) \]  
[14]

and the erasure by a uniform illumination is given by
\[ E(x, t) = E_K \exp(-\Gamma e t) \exp(i kx) \]  
[15]

The characteristic rate \( \Gamma e \) is the same for recording and erasure. It may be presented in the following way43,45,46:
\[ \Gamma e = \Gamma_{di} \frac{1 + K^2 / K_{Deb}^2 - i K / k_{pp}}{1 + K^2 / q_D^2} \]  
[16]

where \( \Gamma_{di} = \sigma / \varepsilon e_0 \) is the dielectric relaxation rate, \( K \) is the spatial frequency of the grating, \( K_{Deb} = (e^2 N_t / \varepsilon e_0 k_B T)^{1/2} \) is the inverse Debye screening length, \( q_D \) is the inverse diffusion length, and \( k_{pp} \) is a characteristic number. With reasonable parameters for a first approximation, one may assume \( \Gamma e \approx \Gamma_{di} \). This means that the rates of the recording and optical erasure are linearly proportional to the photovoltaic conductivity \( \sigma_{ph} \), and the decay rate in the dark is proportional to the dark conductivity \( \sigma_d \).

We now shortly mention the characteristic parameters of the recording used in the experiments. The phase grating \( \Delta n(z) \) formed under the space-charge field is characterized by the diffraction efficiency \( \eta \) and the sensitivity \( S \). For recording in the transparent regime (Figure 1):
\[ \eta = I_S^{diff} / I_S, \]  
[17]

where \( I_S \) and \( I_S^{diff} \) are the intensities of the transmitted and diffracted beams, respectively. For equal intensities of two recording beams \( \eta \) is predicted by the coupled-wave theory47
\[ \eta = \exp[-\alpha L / \cos \theta] 2 (\pi \Delta n L / \lambda \cos \theta), \]  
[18]

where \( L \) is the hologram thickness, \( \Delta n = r_{eff} E_{xx} \), the exponential term takes into account the optical absorption of the crystal. The sensitivity of recording is expressed by different ways. A sensitivity per incident radiation intensity is4 A48:
\[ S_1 = 1 / (I d \Delta n / dt) = 1 / (I d \Delta \eta / dt) \]  
[19]

or
\[ S_1' = 1 / (I L d \Delta n / dt) = 1 / (I L d \Delta \eta / dt). \]  
[20]

A sensitivity per absorbed radiation energy, which is more illustrative for crystals with a high optical absorption, is
\[ S_2 = 1 / (I \alpha L d \Delta n / dt) = 1 / (I \alpha L d \Delta \eta / dt) \]  
[21]

Additionally, a customary characteristic of the sensitivity is the incident radiation energy required for recording 1% diffraction efficiency (\( W_{\eta=1\%} \)).

Comparing Equations 19–21 for the sensitivities to that for the recording kinetics (Eq. 14) one may see that \( S \), by definition, corresponds to the linear part of \( E(t) \), that is, for \( t \ll \tau_{di} = \varepsilon e_0 / \sigma \).

For a non-local response one more characteristic of the recording is the two-beam coupling gain \( \gamma \), which describes an interaction, that is an energy transfer between the recording beams.43,44 This parameter is given by the expression
\[ I_s / I_{s0} = (I_{R0} / I_R) \exp(\gamma - \alpha) \]  
[22]

where \( I_{S0}, I_S, I_{R0}, I_R \) are initial and transmitted intensities of the signal and reference beams, respectively. The signal is a weak beam amplified by an energy transfer from the intensive reference beam. For \( I_{S0} \ll I_{R0}, I_{R0} \approx I_R \) (without a depletion of the pumping reference beam) for an optically transparent crystal,
that is for \( \alpha \ll \gamma \),

\[
\gamma = L^{-1} \ln \frac{I_s}{I_{s0}} \quad \text{(23)}
\]

For a photorefractive grating recorded by the diffusion mechanism the expression for the stationary two-beam coupling gain is

\[
\gamma = \frac{2\pi}{\lambda} (n^2 \text{reff} E_{sc}) / m \cos \theta \quad \text{(24)}
\]

The often-used geometry of recording is the grating vector parallel to the polar axis \( K \parallel z \), which means with the grating grooves normal to it (Figure 1). In this case in LiNbO\(_3\) and its analogues the expression for the effective electrooptic coefficient, \( \text{reff} \), used in (Eq. 24) is for the extraordinary polarization of the recording beams\(^{49}\):

\[
\text{reff} = r_{33} \cos^2 \theta - r_{13} \sin^2 \theta + [n_e - n_\alpha] r_{33} + r_{13} \sin^2 2\theta \quad \text{(25)}
\]

and for ordinary beams

\[
\text{reff} = r_{13}. \quad \text{(26)}
\]

**B. Basics of the Photoinduced Charge Transport and Photorefractive Properties of LiNbO\(_3\)**

The dispersion of the refractive indices is given by the expression

\[
\begin{align*}
\epsilon_0^2 &= 4.9048 + 0.11768/(\lambda^2 - 0.0475) - 0.027169 \lambda^2, \\
\epsilon_\alpha^2 &= 4.582 + 0.099169/(\lambda^2 - 0.04443) - 0.02195 \lambda^2,
\end{align*}
\]

where \( \lambda \) is the wavelength in \( \mu \text{m} \) (taken from Beijing Gospel OptoTech Co., http://www.bblaser.com/toriatukai/got/got_in.htm).

A photorefractive material, appropriate for efficient nonvolatile volume holographic data storage should combine a strong photorefraction, high sensitivity, and long memory times. One of the most prominent materials satisfying more or less these conditions is LiNbO\(_3\). We shall touch briefly on those properties of this material, which are appropriate for holographic recording and storage. The parameters of this material relevant for the photorefractive recording are presented in Table 1. Optical applications require in LiNbO\(_3\) a gradient of refractive indices along the axes not exceeding \( 10^{-5} \) per cm (see e.g., Refs. 5, 50, 51). The value of the extraordinary refractive index \( n_e \) is strongly controlled by the ratio [Li\(_2\)O]/[Nb\(_2\)O\(_5\)] (see, e.g., Refs. 5, 52) so a necessary condition of obtaining optically uniform crystals is their compositional uniformity. This so far may be achieved in congruently melting crystals (with [Li\(_2\)O] between 48.5 and 48.6 mol.\%\(^{5,52}\) grown by the Czochralski technique, whereas other compositions, particularly almost stoichiometric ones, whose growth was developed comparatively recently\(^{53–56}\) are still not so uniform. Therefore, up to day the most often commercially used composition is congruently melting LiNbO\(_3\). For general features a similar situation is characteristic for LiTaO\(_3\) as well.

We now touch briefly on the strength of the photorefraction and of the sensitivity in the congruent LiNbO\(_3\). The highest values of these parameters are provided by doping with transition metal (TM) impurities like Fe,\(^{36,57–62}\) Cu\(^{58–67}\) Mn,\(^{68,69}\) In stoichiometric LiNbO\(_3\) crystals the dependence of the photorefractive sensitivity on the TM-doping is not clear so far, because these ions seem to incorporate into the lattice in a way differing from that in Li-deficient (congruent) compositions.\(^{70}\)

The dominant mechanism of the free-charge transport in LiNbO\(_3\) and related crystals (LiTaO\(_3\), KNbO\(_3\), Ba\(_2\)NaNb\(_5\)O\(_{15}\)) doped with TM is the bulk photovoltaic current \( j_{pv} \) (see, e.g., Refs. 36, 37, 62). Additionally, these impurities provide deep electron traps required for long storage times. From Eqs. 5 and 14 one derives the simplified expression for the photorefractive sensitivity when recording by the photovoltaic mechanism in the

\[
\begin{array}{cccc}
\text{Table 1} \\
\text{Photorefractive and related properties of LiNbO}_3 \text{ crystals} \\
\hline
\text{Electrooptic effect} & \text{Refractive indices} & \text{Transparent range, \( \mu \text{m} \)} & \text{\( \epsilon \)} & \text{Ph. v. coefficients \( G_{ij} \), \( 10^{-9} \text{cm/V} \)} & \text{Ph. r. Sensitivity, cm/J} & \text{N. I-O. coefficients \( d_{ij} \), \( 10^{-12} \text{cm/V} \)} \\
\hline
\text{\( r_{ij} \)}, 10^{-12} \text{ cm/V} & V_{\lambda/2}, V & \text{\( n_\alpha \)} & \text{\( \lambda = 0.63 \mu \text{m} \)} & \text{\( \lambda \approx 0.4 \mu \text{m} \)} & \text{\( \lambda \approx 1.06 \mu \text{m} \)} \\
\hline
r_{33} = 32.2 & 2800 & n_0 = 2.286 & 0.35–5 & \epsilon_c = 28 & \text{LiNbO}_3: \text{Fe} & 0.02–0.1 & d_{33} = 3.44 \\
r_{13} = 10 & (k \perp c) & n_e = 2.203 & \epsilon_a = 80 & & & d_{31} = 5.95 \\
r_{22} = 6.7 & 4200 & & & \text{LiNbO}_3: \text{Cu} & G_{33} \approx 3 & d_{22} = 2.4 \\
r_{51} = 32.6 & (k||c) & & & & G_{31} \approx 2 - 3 & d_{eff} = 5.7 \\
\hline
\end{array}
\]

Abbreviations: Ph.v.—photovoltaic, Ph.r.—photorefractive, N.I-O.—nonlinear—optical. The photovoltaic coefficients \( G_{ij} = \beta_{ij}/\alpha \), (where \( \beta_{ij} \) are components of the photovoltaic tensor, \( \alpha \) is the optical absorption coefficient assumed to be isotropic) taken from Ref. 37. Other coefficients are taken from several recent reviews, particularly from Ref. 51 and from data presented by companies producing commercial LiNbO\(_3\).
range of moderate intensities

$$S_{1}^{ph} = r e g k G \alpha / \varepsilon \varepsilon_{0}$$  \[27\]

By contrast to the recording by the diffusion mechanism (Eq. 9), the sensitivity (Eq. 27) does not depend on the photoconductivity, that is, the fundamentals of the photovoltaic effect impose constraints on the value of $S$. Relatively high sensitivities in TM-doped LiNbO$_3$ are provided by large Glass constants and EO coefficients. Note that $S$ in LiNbO$_3$:TM crystals is anyhow by a factor of 4 or 5 smaller than in BaTiO$_3$, where recording occurs via the diffusion mechanism. The microscopic mechanism of the charge transport in TM-doped LiNbO$_3$ was developed on the base of studies in LiNbO$_3$:Fe and LiNbO$_3$:Cu,\textsuperscript{71,72} in which the photoinduced charge carriers were proved to be electrons. This mechanism may be summarized in the following way. As a rule TM-impurities are present in the LiNbO$_3$ lattice in two charge states (e.g., Fe$^{2+}$ and Fe$^{3+}$, Cu$^+$ and Cu$^{2+}$),\textsuperscript{36,62,73} which govern the transport of free photoexcited electrons $e^-$ according to the one-center scheme

$$Fe^{2+} + h\nu \rightleftharpoons Fe^{3+} + e^-$$  \[28\]

where Fe$^{2+}$ and Fe$^{3+}$ (or Cu$^+$ and Cu$^{2+}$) are electron donors and traps, respectively. The photoconductivity for such a one-center scheme in a simplified form may be presented as

$$\sigma_{ph} = n e \mu = g \tau e \mu = (g e \mu / h\nu)(s_{ph}/s_{c})(N_{D}/N_{C})I$$  \[29\]

where $g = g \alpha / I / h\nu$ is the photo excitation rate, $\tau = 1/s_{C}$, $N_{C}$ is the life-time of the photo carriers in the conduction band, $\mu$ is the mobility, $g$ is the quantum efficiency, $\alpha = s_{ph}N_{D}$ is the optical absorption coefficient, $s_{c}$ is the recombination coefficient, $s_{ph}$ is the probability of the donor photo-excitation, $N_{C}$ and $N_{D}$ are concentrations of the donors and traps, respectively. So, the photoconductivity for such a scheme is a linear function of the light intensity and of the concentration ratio of donors and traps.

These relations were experimentally proved for LiNbO$_3$:Fe and LiNbO$_3$:Cu,\textsuperscript{62,71,72}:

$$\sigma_{ph}/I = ([Fe^{2+}]/[Fe^{3+}])10^{-12} \text{ cm Ohm}^{-1} \text{ V}^{-1},$$

$$\sigma_{ph}/I = ([Cu^{+}]/[Cu^{2+}])10^{-12} \text{ cm Ohm}^{-1} \text{ V}^{-1}$$  \[30\]

The photovoltaic current in LiNbO$_3$:Fe and LiNbO$_3$:Cu was shown in Ref. 62 to depend on the donor concentration

$$j_{pv} = \beta I = k G S_{ph}[Fe^{2+}]I.$$  \[31\]

The relations (Eqs. 28–31) are valid in a wide range of light intensities, so at relatively low $I$ (when $\sigma_{ph} > \sigma_d$) the photorefraction comes to saturation, which occurs in LiNbO$_3$:Fe even at $I \approx 1W/cm^2$. From Eqs. 6, 30 and 31, we obtain the following relations\textsuperscript{62,71}:

$$E_{pv} \sim [Fe^{3+}], E_{pv} \sim [Cu^{2+}].$$  \[32\]

for LiNbO$_3$:Fe and LiNbO$_3$:Cu, respectively.

However, these relations sometimes are no more valid at high light intensities, which may provoke a non-equilibrium population of shallow traps. This leads to a dependence of $\alpha$ on $I$ and non-linearities in the lux-ampere characteristics $\sigma_{ph} \approx I' \cdot x \neq 1$. As a consequence, $E_{pv}$ and $S$ strongly depend on $I$ in the high-intensity range. An involvement of shallow traps in the charge transport process violates the one-center scheme (Ref. 28). This is especially detectable in the crystals with low Fe concentrations,\textsuperscript{74,75} or nominally undoped ones, where nonlinearities and intensity dependencies of $E_{pv}$ and of the sensitivity $S$ were observed in the range of $10^5$ W/cm$^2$.\textsuperscript{75–77}

According to the currently accepted model\textsuperscript{78,79} the most probable shallow electron traps in LiNbO$_3$ are Nb-ions on Li sites (so-called Nb-antisites), whose existence in congruent (Li-deficient) LiNbO$_3$ was proved by structure methods.\textsuperscript{80} In a two-center charge transport scheme with an additional electron trap Nb$_{1}$, the Fe$^{3+}$-like ions serve as the deep electron traps as before. We emphasize again that for LiNbO$_3$ both the one-center charge transport scheme (Eq. 28) and a refined two-center scheme involving a shallow (secondary) trap are based on the assumption of $n$-type photoconductivity. Strictly speaking, this consideration cannot be extended, for example, to the stoichiometric crystals in which the photoconductivity type has not yet been determined. The photovoltaic constants in Fe- and Cu-doped LiNbO$_3$ together with $\sigma_{ph}$ (Eq. 30) provide in LiNbO$_3$:Fe and LiNbO$_3$:Cu values of $E_{pv}$ of the order of $10^5$–$10^6$ V/cm, which with an account to electrooptical coefficients lead to saturation values of a photorefractive of $\Delta n \approx 10^{-3}$–$10^{-4}$. The diffusion field (Eq. 9), unlike $E_{pv}$ does not depend on the material parameters and is governed by the grating period $\Lambda$ (the spatial frequency $K$) only. Its amplitude value is $E_{diff} = (k_{B}T/\varepsilon)K$, so for $\Lambda = 1/\mu m$ $E_{diff} = 1.12 10^3$ V/cm, which gives in saturation $\Delta n \approx 10^{-5}$. This amount is incomparable to the contribution from the photovoltaic mechanism. In as-grown (non-treated) LiNbO$_3$:Fe and LiNbO$_3$:Cu crystals the photorefractive recording proceeds predominantly by the photovoltaic mechanism (Eq. 6). The diffusion mechanism becomes noticeable in the case of an increasing conductivity, which lowers $E_{pv}$ (Eq. 6).

This was found for example in congruent LiNbO$_3$ doped with Mg or Zn\textsuperscript{81–83} and stoichiometric LiNbO$_3$\textsuperscript{84} where $\sigma_{ph}$ is very strongly enhanced. In stoichiometric LiNbO$_3$ doped with Fe\textsuperscript{85} and LiNbO$_3$:Zn\textsuperscript{86} a partial contribution from the diffusion field results in $\gamma \neq 0$.

We now dwell on one of the most crucial criteria of the storage material, namely the storage time $\tau$ in the dark, which is governed by the dark conductivity $\sigma_d$. In LiNbO$_3$ crystals storage times as long as 1 month\textsuperscript{10} or even 1 year\textsuperscript{13} were reported at ambient conditions, which corresponds to $\sigma_d$ in the range from $10^{-18}$ to $10^{-19}$ Ohm$^{-1}$ cm$^{-1}$. Obviously, direct measurements of such low values are impossible, so $\sigma_d$ at room temperature is estimated either from a linear extrapolation of $\ln[\sigma_d(1/T)]$ obtained at high temperatures, or by means of measuring the decay kinetics of the recorded grating in darkness. The dark conductivity in undoped as-grown LiNbO$_3$ depends on the temperature as $\sigma_d = \sigma_d(0) \exp(-E_d/k_{B}T)$ with $E_d$ of about 1eV
(for references see Ref. 20), from which the first method gave $\sigma_d = 10^{-18}$ Ohm$^{-1}$ cm$^{-1}$. In LiNbO$_3$:Fe $\sigma_d$ was shown to increase with the Fe concentration$^{20,88,89}$ and in highly doped crystals the storage time becomes as low as seconds. In this composition in view of its practical importance the concentration dependence of $\sigma_d$ was studied in more detail$^{20,21}$. At low Fe concentrations $<2 \times 10^{-17}$ cm$^{-3}$ (i.e., $<0.05$ wt% Fe) $\sigma_d$ was shown to depend only very slightly on iron. Other dopants such as Mn or Ce at low concentrations do not affect $\sigma_d$, either.$^{90}$ It is governed mainly by the ionic conductivity, which according to the current model is the protonic one (for details see later). The latter is at room temperature in the range of $10^{-19}$ to $10^{-20}$ Ohm$^{-1}$ cm$^{-1}$ providing the aforementioned long storage times. With growing concentration, a contribution from Fe to $\sigma_d$ increases and becomes dominant at [Fe] > 0.25 wt%. At these concentrations $E_u \approx 0.28$ eV$^{96}$ and the transport mechanism is most probably electron tunnelling between iron sites$^{21}$ rather than the band one. This is especially pronounced in reduced LiNbO$_3$:Fe, where an enhanced [Fe$^{2+}$/Fe$^{3+}$] ratio results in a drastic increase of $\sigma_d$. At intermediate Fe concentrations the dark conductivity is due to a combination of the ionic transport and electron tunnelling.

C. Possible Ways to Produce a Non-Erasable Photorefractive Grating (A General Overview)

Summarizing this information, one can conclude that the problems of the holographic sensitivity and long storage times in LiNbO$_3$ may be more or less solved by an appropriate choice of the impurity type and its concentration. A more important problem remaining to be solved is the optical erasure of a stored grating under the readout. The reason of the erasure during readout is due to the fact that a spatially modulated space-charge field is destructed on homogenous illumination by a single Bragg beam because of a photoexcitation and a spatial uniform redistribution of the trapped electrons. The rate of this erasure is proportional to $\sigma_{ph} \sim I (\sigma_{ph} \gg \sigma_d)$. Even when reading with an attenuated beam, a recorded grating is erased rather quickly. For example, in as-grown LiNbO$_3$:0.03%Fe $\sigma_{ph} \approx 2 \times 10^{-13}$ Ohm$^{-1}$ cm/W $I$. Therefore for $I = 1$ mW/cm$^2$ a hologram is efficiently erased during less than 5 hours of continuous reading. This is especially undesirable for using a crystal with the recorded grating as a narrow-band optical device. Therefore, a development of read-out techniques without erasure is the most important task for applications of the photorefractive holographic recording.

The most obvious way for solving this problem is the use of a wavelength longer than the recording one ($\lambda_{read} > \lambda_{rec}$) for the read-out.$^{92-95}$ Actually, this technique of controlling the grating behavior in the dark is applied for laboratory investigations. However, in a practical case of hologram multiplexing the use of this technique results in an increased cross-talk and strong loss of the holographic efficiency, because of the inability to achieve the exact phase Bragg matching. Additionally, a partial hologram erasure does occur anyhow, because $\sigma_{ph} \neq 0$ in the long-wave range, too.

For realization of a non-destructive readout several methods are proposed that can be conventionally divided into two groups according to the two underlying principles. The first group of methods, so-called fixing, is based on screening the recorded space-charge field $E_{sc}(z)$ by charge carriers having a sign opposite to those forming $E_{sc}$. A complementary screening charge pattern provides a stability of $E_{sc}(z)$ under the read-out. The thermal hologram fixing in LiNbO$_3$, which is discussed in details in the present review, belongs to this group and is caused by screening $E_{sc}$ by thermally excited positive ions (protons). A screening the photorefractive field by thermally excited protons was assumed in other oxides, too. Another possibility was demonstrated at room temperature in Bi$_{12}$TiO$_{20}$ (BTO)$^{96,97}$ where the grating fixation is caused by screening of the electronic $E_{sc}(z)$ by holes because of a bipolar conductivity. The field fixation of holograms in ferroelectric photorefractories such as SBN or BaTiO$_3$ may also be referred to this group, because it is owing to screening $E_{sc}(z)$ by a redistributed bound charge (spontaneous polarization $P_s(z)$). This redistribution occurs when an appropriate depolarizing field $E_{cd} \approx E_c \approx 10^3$ V/cm is applied to a crystal containing a recorded grating ($E_{sc} \approx 10^3$ V/cm, too). Under applying this field, $P_s$ within the grating is partially reversed to form a spatially distributed polarization grating $\pm P_s(z)$. The latter provides a stability against an optical erasure. The erasure may be now performed only electrically by applying a field $E_{cd} > E_c$. An alternative way of realization of a non-erasing read-out is provided by the method of so-called two-color holography or, what is the same, recording in the gating regime, (see, e.g., Refs. 91, 104–108). The basic idea is as follows. The crystal is pumped by a short-wave intensive light $\lambda_g$ (the gating wavelength usually belonging to the near UV), either to populate a shallow level, which is empty in the equilibrium state$^{91,104,107}$ or to repopulate deep levels with different activation energies.$^{108}$ Simultaneously (or directly after) a grating is recorded by a spatially modulated longer-wave radiation $\lambda_{IR}$ exciting the electrons from a non-equilibrium-populated level. The photoexcited electrons are then trapped by the same deep levels, as in the usual case (e.g., Fe$^{3+}$ in LiNbO$_3$:Fe) to form a long-living $E_{sc}$. So, the grating is now recorded by $\lambda_{IR} > \lambda_g$, and its readout by the Bragg beam $\lambda_{IR}$ does not erase the space-charge formed by deeply captured electrons.

The principles underlying these two groups of methods of nonerasable readout, account for their fundamental drawbacks. The fixing methods cannot be realized in situ and do not permit a selective erasure and over-recording of an individual grating that sometimes is desired in hologram multiplexing. The gating methods do not provide a completely nondestructive erasure and long storage times$^{108,109}$ because a non-zero conductivity both under illumination and in dark always does exist.

III. BACKGROUND OF THE THERMAL FIXATION

The thermal fixation of holograms was discovered in LiNbO$_3$ and Ba$_3$NaNb$_5$O$_{15}$ and was observed later in a variety of similar and dissimilar materials (see Table 2). The procedure of
fixation typical for LiNbO₃ is applicable to related materials (LiTaO₃, Ba₂Na₂Nb₅O₁₅) in which the effect obviously finds the same explanation, as for LiNbO₃. The procedure of the thermal fixation in LiNbO₃ in general looks as follows. A holographic grating is recorded with the use of a two-beam scheme, the achieved diffraction efficiency being denoted as η. Then the crystal is heated up to temperatures in the range (usually 120 < Tfix < 200°C) and cooled down to room temperature. At room temperature the hologram is read by the Bragg beam, which shows η ≈ 0 at the very beginning; then η is growing to a saturation value ηsat ≲ η. Qualitatively similar results are obtained, when the recording is performed at higher temperatures in the range 120 < T < 200°C. After cooling to room temperature the behavior of η under the Bragg readout is the same, as described earlier. This behavior of η resembles qualitatively the chemical development of the usual photographic film. Therefore, the appearance of a stable hologram pattern at room temperature under illumination is called the development of a spatially charged structure (a latent image) formed at elevated temperatures and frozen on cooling. The development may be achieved under illumination by a non-Bragg beam and even under non-coherent visible light. In the latter case the dependence of η(t) does not contain a non-stationary component, which appears on developing by a Bragg beam and is related to a coupling of the reading and diffracted beams.⁶–⁹ For brevity, these two procedures of fixing (recording at room temperature → heating to Tfix → cooling → readout and heating to Tfix → recording at Tfix → cooling → readout) are referred to as post-fixing and simultaneous fixing, respectively. The authors of Ref. 110 proposed for multiplexed holograms a method of a local thermal fixation by means of heating an elementary grating by a focused CO₂-laser beam.

A fixed pattern may be erased either thermally by heating the crystal up to T > 300°C, or optically by uniform illumination at temperatures T > 120°C. Thermal fixing with slightly modified ranges of the optimum Tfix (in the range from 150 to 200°C) is the same in LiNbO₃, LiTaO₃, and Ba₂Na₂Nb₅O₁₅. Refs. 6–10, 13.

A qualitative general explanation of the fixing process proposed in Refs. 6–10 and underlying all the subsequent models,¹⁶,²²,²⁹,³³–³⁵,⁴⁶,¹¹⁴–¹¹⁶ is that at elevated temperatures certain mobile ions move under the field Eloc within the recorded grating to screen Eloc. A formed ionic pattern Ni(z) is a replica of the initial Eloc(z). On cooling, this ionic pattern becomes frozen, hence in the beginning of the development no spatially modulated internal field exists because of screening effects. Homogeneous illumination (the development) excites and spatially redistributes captured electrons, thus partially releasing the frozen backbone Ni(z). After the attainment of a steady state, a Ni(z) screened partially by Eloc(z) altogether dictate the properties (efficiency and temporal stability) of the developed hologram pattern. In photovoltaic crystals such as LiNbO₃:Fe, an additional factor exists related to a contribution from the photovoltaic current. This factor could not be taken into account in pioneering models developed before the era of the photovoltaic effect. According to a suggestion of the authors of Ref. 114 experimentally proved by the authors of Refs. 18, 117, the formation of an ionic pattern Ni(z) at elevated temperatures is accompanied by a spatial redistribution of the electron donors Fe³⁺ and traps Fe⁵⁺ so that on cooling the redistributed patterns [Fe²⁺](z) and [Fe³⁺](z) are frozen. As a result, the photovoltaic current under uniform

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Doping</th>
<th>Comments on the principles of the method and mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₂Na₂Nb₅O₁₅</td>
<td>Fe, Mo</td>
<td>The same as in LiNbO₃</td>
<td>[6]</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>Fe</td>
<td>The same as in LiNbO₃</td>
<td>[13]</td>
</tr>
<tr>
<td>Sr₀.₇₅Ba₀.₂₅Nb₂O₁₂</td>
<td></td>
<td>Cooling from the para- to the ferroelectric phase, a</td>
<td>[160]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>domain mechanism</td>
<td></td>
</tr>
<tr>
<td>BaTiO₃</td>
<td></td>
<td>Cooling from the para- to the ferroelectric phase, a</td>
<td>[163]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>domain mechanism</td>
<td></td>
</tr>
<tr>
<td>KNbO₃</td>
<td>Fe</td>
<td>A temperature treatment within the ferroelectric phase</td>
<td>[162]</td>
</tr>
<tr>
<td>La₃Ga₅SiO₁₄</td>
<td>Pr</td>
<td>A qualitative general explanation of the fixing process</td>
<td>[169]</td>
</tr>
<tr>
<td>KTa₉Nb₁₋ₓO₃(KTN)</td>
<td></td>
<td>Cooling from the para- to the ferroelectric phase, a</td>
<td>[111, 166]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>domain mechanism</td>
<td></td>
</tr>
<tr>
<td>KTN:Li</td>
<td></td>
<td>Room temperature, complementary electron, and hole</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>charge patterns</td>
<td></td>
</tr>
<tr>
<td>Bi₁₂SiO₂₀(BSO)</td>
<td></td>
<td>Heating and cooling, a screening by ions (similarly to LiNbO₃)</td>
<td>[113, 167]</td>
</tr>
<tr>
<td>Bi₁₂SiO₂₀(BSO)</td>
<td></td>
<td>Heating with a simultaneously applied ac-field</td>
<td>[168]</td>
</tr>
<tr>
<td>Bi₁₂TiO₂₀(BTO)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*A* Table 2: Thermal fixation of holograms in materials other than LiNbO₃.
illumination is permanently spatially modulated. In summary, in LiNbO₃ and its analogues a nonerasing readout of thermally fixed gratings is due to a block of interrelated factors.

The scenario of post-fixing is schematically illustrated by Figure 2, taken from Refs. 33, 34. The initial efficiency of the grating \( \eta_0 \) achieved during recording (phase 0) corresponds to the space-charge field \( E^{(0)}_1 \). In phase I (properly fixing process) the heating activates positive ions, which are moving under a driving field combined of the diffusion \( E_D \) and the photovoltaic \( E_{pv} \) fields. Simultaneously, the captured electrons are thermally excited, thus decreasing the initial \( E^{(0)}_1 \). The result of these complicated evolutions is the formation of a compensated grating, which is represented by the net space charge field amplitude \( E^{(1)}_1 \) (at a limiting complete compensation of electronic charge by ions, \( E^{(1)}_1 = 0 \)). In phase II, which characterizes the storage time of the latent image, the grating is left in dark. This stage corresponds to a slow dark decay of both the electronic grating and the ionic compensating grating, which adiabatically follows the former. An exposure to a reading light (the development) is shown by phase III. This light causes a partial redistribution of trapped electrons due to the photoexcitation, culminating in a quasi-stable field \( E^{(2)}_1 \). Because of possible ionic transport, the field \( E^{(2)}_1 \) may decay both in dark and under illumination (phase IV).

There are three parameters of special importance for a practical application of the thermal fixing.

First, the ratio of \( \eta_{fix}/\eta_0 \) depending on \( E^{(2)}_1 \) of Figure 2, second, the storage time of the developed pattern in dark; third, the stability of the developed grating under continuous illumination, or, what is the same, under multiple cycles of the Bragg readout.

One may a priori deduce an impact of some factors on these parameters. A necessary condition for a successful completion of phase I is that the screening of the space charge field by movable ions would occur faster than the thermal excitation of the captured electrons, otherwise \( E^{(0)}_1 \) would disappear before being screened. This requirement gives an upper limit for the fixing temperatures \( T_{fix} \). In LiNbO₃ \( T_{fix} \leq 200°C \), because at \( T > 200°C \) the thermal excitation of traps seems to compete with a migration of ions. The low limit of \( T_{fix} \) is governed by the requirement of a reasonably high mobility of the screening ions. In LiNbO₃ after fixing at \( T_{fix} = 100°C \), a residual \( \eta \neq 0 \) was detected at the beginning of the development,¹² which was indicative of a non-complete screening by ions; the achieved \( \eta_{fix} \) was very low. Another requirement of the fixation is a reasonable concentration \( N_I \) of screening ions, which, from the other hand, should be not too large, because with increasing \( N_I \) the ionic conductivity \( \sigma_i \) increases resulting in a decreased storage time.

For practical applications it is important to emphasize, that the procedure of a simultaneous fixing gives higher \( \eta_{fix} \) than the post-fixing, because in the latter case an obvious loss in \( \eta_0 \) occurs during heating from room temperature to the temperature of fixing. At the same time, recording at elevated temperatures provides additional experimental difficulties. This may be overcome using sophisticated procedures, for details see, for example Ref. 118.

IV. THEORETICAL APPROACH

All the models developed are based on the qualitative picture described earlier, namely on the assumption of two types of competitive species (electrons and ions) participating in the transport process. The first attempt of a model¹¹⁵ assuming \( E_{pv} \gg E_{dif} \) and a spatially uniform \( E_{pv} \), neglected the thermal decay of the space-charge, as well as the next, more rigorous charge transport model.¹⁶ The next step was done in Ref. 22 by taking into account the thermal decay of the recorded pattern. This refinement is of fundamental importance in view of insight to the fixing kinetics. The model¹¹⁹ proposed a description of the development for nonphotovoltaic medium. A complete
description of the fixing process was developed in recent advanced models.29,33—35,46,116,120 The models start from the coupled set of material equations describing the electron transport and grating formation (10 a–e) and incorporate additionally the continuity equation for ions and the ionic charge in the Poisson equation. The set of equations now takes the form:

\[
\begin{align*}
\frac{\partial n_e}{\partial t} &= \frac{\partial N^+}{\partial t} + \frac{1}{e} \frac{\partial j_e}{\partial z} \\
\frac{\partial N^+}{\partial t} &= (s_{ph} I + s_T)(N - N^+) - s, N^+ n_e \\
\frac{\partial H}{\partial t} &= -\frac{1}{e} \frac{\partial j_h}{\partial z} \\
\varepsilon e D \frac{\partial E}{\partial z} &= e(N^+ - N_o + H - H_o - n_e)
\end{align*}
\]

[33a]
[33b]
[33c]
[33d]

where

\[
\begin{align*}
j_e &= e \mu_e n_e E + e D_h \frac{\partial n_e}{\partial z} + k_G I (N - N^+) s_{ph} \\
j_i &= e \mu_h HE - e D_h \frac{\partial H}{\partial z}
\end{align*}
\]

[33e]
[33f]

Here the complementary screening ions are assumed to be protons, which is valid for LiNbO₃, as shown later. The notations corresponding to the added ionic terms are as follows: \( H \) is the proton density \( \mu_h \) and \( D_h \) are the diffusion and mobility coefficients of protons, respectively; \( D_h = \mu_h k_B T / e \) accordingly, the Einstein relation. Recall that \( N^+ \) and \((N - N^+) \) as applied to LiNbO₃:Fe are \( Fe^{3+} \) and \( Fe^{2+} \), respectively. In all the models three approximations are assumed: the linear approximation in the contrast \( m \) (that is a neglect of the higher Fourier harmonics of the variables), the so-called adiabatic approximation (a smallness of the free electron lifetime compared to the relaxation times of the variables) and the assumption of the smallness of free electron concentration in comparison to the concentrations of filled and empty traps. We now shortly outline the conclusions concerning the practically important fixing parameters (the decay rates of a fixed hologram and the value of \( \eta_{ph}) \) deduced from the model.22,29,31,34 In Ref. 29 one may find a detailed previous bibliography on theoretical models of the thermal fixing in LiNbO₃.

We shortly dwell on the work by Ref. 29 that presents a complete description of the high-temperature recording (denoted earlier as the simultaneous fixing). An involvement of two types of species (two mutually screening gratings) leads to existence in fixing phases of two kinetics—fast and slow.29,34 Accordingly to the model,29 the fast process is the dielectric relaxation depending on the conductivity. The slow kinetics is caused by an interaction between charge carriers of opposite signs (photo- or thermally excited electrons and thermally activated positive ions) and may be imagined as slowing-down the dielectric relaxation because of the charge compensation. Correspondingly, in the model of Ref. 29 the recording and decay of a space-charge field are presented in a pictorial view:

\[
E_K = E_f (1 - e^{-\Gamma f t}) + E_S (1 - e^{-\Gamma s t}) \quad [34]
\]
\[
E_K = E_f e^{-\Gamma f t} + E_S e^{-\Gamma s t} \quad [35]
\]

where \( E_K \) is the field amplitude, \( \Gamma_f \) and \( \Gamma_s \) are, respectively, the fast and slow relaxation rates. The presentation34 of the recording means that the value of \( E_K = E_f \) achieved by the end of the fast stage, is then decreasing during the subsequent slow stage due to a slow build-up of the protonic grating. Obviously, at low-temperature recording, \( \Gamma_s \rightarrow 0 \), the expression34 is transformed to the usual one for the photorefractive recording. The presentation35 describes the decay in dark (phase II) or under illumination (phase IV); the result of the slow decay stage is the disappearance of any inhomogeneity of the charge distribution.

The fast rate depending on the conductivity involves the ionic and electronic components

\[
\Gamma_f = 1/\tau_d = \gamma_h + \gamma_e \quad [36]
\]

where \( \gamma_h = \sigma_h / \varepsilon_0 \varepsilon H_0 \) and \( \gamma_e = \sigma_e / \varepsilon_0 \varepsilon H_0 \). In dark and under illumination, \( \gamma_e \) is equal to \( \sigma_d \) and \( \sigma_{ph} \), respectively. The slow relaxation rate is given by the expression

\[
\Gamma_s = \frac{\gamma_e \gamma_h}{\gamma_e + \gamma_h} (\xi_e + \xi_h) \quad [37]
\]

where dimensionless parameters \( \xi_e \) and \( \xi_h \) are

\[
\xi_e = \frac{E_D}{E_q} - i \frac{F_{pv} N_A \gamma^{ph}}{E_q N} \gamma^d_e \quad [38]
\]
\[
\xi_h = \frac{E_D N_s}{E_q H_0} \quad [39]
\]

Here \( E_D \), \( E_q \), and \( E_{pv} \) are diffusion-, saturation-, and photovoltaic fields presented, respectively by the Eqs. 9, 13, and 6. The authors of Ref. 29 analyzed the temperature dependencies of the fast and slow rates in LiNbO₃:Fe in the range from 20 to 300°C. In dark, \( I = 0 \), in as-grown LiNbO₃ \( \sigma_h \gg \sigma_d \), so the fast rate

\[
\Gamma_f = \gamma_h \quad [40]
\]

and the slow rate37 takes the form

\[
\Gamma_s = \gamma_e^{ph} K^2 l_{D} (1 + N_i / H_0) \quad [41]
\]

where \( l_{D} = (\varepsilon \varepsilon_0 k_B T / e^2 N_i)^{1/2} \) is the Debye screening length. Under illumination, \( I \neq 0 \), Eq. 37 for the slow rate additionally to the real part (denoted later as \( \Gamma_s' \)) contains an imaginary component (denoted as \( \Gamma_s'' \)) related to the existence of the photovoltaic field. In LiNbO₃ at high temperatures \( \sigma_h \gg \sigma_d \gg \sigma_{ph} \), so \( \Gamma_s'' = 0 \), and \( \Gamma_f \) and \( \Gamma_s' \) take the same forms, as at \( I = 0 \) [40, 41], respectively. For the low-temperature limit \( \sigma_{ph} \gg \sigma_h, \sigma_d \), then

\[
\Gamma_f = \gamma_e^{ph} \quad [42]
\]
\[
\Gamma_s' = \gamma_h K^2 l_{D} (1 + N_i / H_0) \quad [43]
\]
\[
\Gamma_s' = -K \mu_h E_{pv} H_0 / N_i \equiv -\gamma_h E_{pv} / E_q \quad [44]
\]
Fig. 3. Temperature dependencies of the fast and slow relaxation rates. Curves 1 and 1', as well as 2 and 2' characterize the fast rate $\Gamma_{f1}$ under illumination and in dark, respectively; the coincident curves 2 and 2' show the real part of the slow rate $\Gamma_{s1}$ irrespectively of illumination; curve 3 corresponds to the imaginary part $\Gamma_{s1}''$ under illumination, taken from Ref. 29.

Figure 3 illustrates the calculated temperature dependences of $\Gamma_{f1}$, $\Gamma_{s1}$ and $\Gamma_{s1}''$ for LiNbO$_3$ crystals. The calculations were made for $\Lambda = 1 \mu$m and with account for conventional material parameters of LiNbO$_3$. $E_{ph} = 60$ kV/cm, $N_i = 5 \times 10^{17}$ cm$^{-3}$, $H_0 = 3 \times 10^{19}$ cm$^{-3}$, the activation energies of the protonic conductivity, dark- and photoconductivity $E_a = 1.2$ eV, 1.4 eV, and 0.15 eV, respectively, the proton diffusion coefficient $D_{ph} = 0.3$ cm$^2$/s, $\sigma_{ph} = 2.5 \times 10^{-10}$--$10^{-11}$ Ohm$^{-1}$. From Figure 3 one may analyze qualitatively a competition of the involved processes in different temperature ranges.

The following conclusions concerning the kinetics of the different fixing phases may be drawn from this set of equations. The slow decay rate in the whole temperature range both in the dark (Eq. 41) and under illumination (Eq. 43) is proportional to the square of the grating spatial frequency. The larger the grating period, the longer the lifetime of the fixed grating. This fundamental relation to the diffusion mechanism was deduced in all models. As seen from a comparison of Eq. 41 to Eq. 43, $(\Gamma_{s1})_{dark} \gg \Gamma_{s1}^{hight}$ due to $\sigma_{h} > \sigma_{d}$, thus the decay under illumination (phase IV) should be faster than in the dark (phase II). A slow decay rates (Eq. 41) and (Eq. 43) in a given crystal is strongly controlled by the ratio $H_0/N_i$. The slowest decay $\Gamma'' = \gamma_h K^2 D_{ph} = D_h K^2$ may be achieved whenever decreasing the ratio $H_0/N_i$. So, in LiNbO$_3$:Fe, where $N_i = [Fe^{3+}]$, the highest lifetime of a fixed grating would require $[H_0] \ll [Fe^{3+}]$.

A necessary requirement of the successful accomplishment of a fixing procedure is the full compensation of electron and proton charges. The model$^{33}$ gives a lower limit for the screening proton concentration:

$$H \gg \frac{\varepsilon k_B T K^2}{e^2} \quad [45]$$

A lower limit means that a further increase of $H_0$ is a negative factor, because it enhances the dark decay rate $\Gamma_{f}$ (Eq. 40) and does not improve the fixing efficiency. Note that in LiNbO$_3$ not subjected to special treatment (not de-hydratated one) the proton concentration always satisfies the condition (Eq. 45). A complete compensation requires definite time periods estimated in Ref. 29 for LiNbO$_3$. Under high-temperature recording in the temperature range approximately $>130^\circ$C, $\gamma_h \gg \gamma_{e,ph}^h$, so the compensation occurs during $t \gg \Gamma_{f1}^{-1} = \gamma_h^{-1}$. However, in the low-temperature range, where $\gamma_{e,ph}^h \gg \gamma_e$ (approximately $<130^\circ$C) the duration of recording would be too large in comparison with $\Gamma_{f1}^{-1}$, what practically excludes the possibility of a full compensation. This implies a lower limit to the fixing temperature. Additionally, the consideration of Ref. 29 finds a critical temperature $T_{crit}$ at which the kinetics $E(t)$ become nonmonotonous with a maximum at $t = \Gamma_{f1}^{-1}$ and whose value depends on the ratio of the electron and proton conductivities. Practically this gives the highest temperature limit of the fixing procedure; in LiNbO$_3$ it is estimated to be in the range of $T_{crit} \approx 200^\circ$C.

So, summarizing this consideration, we see that in the end of the fixing process, two mutually screening gratings (electronic and ionic) are formed and no charge inhomogeneity exists. The lifetime of the gratings obeys the Eq. 41 and the amplitudes governing subsequently the value of $\eta_{fix}$ are controlled mainly by temperature conditions of the fixing procedure.

The next deciding stage determining $\eta_{fix}$ is the developing process. We now briefly considered conclusions of the models of Refs. 22, 31--34, concerning the amplitude of the developed field. The developing is performed usually at low (room) temperature when $\sigma_{ph} \gg \sigma_{d}$, so its kinetics may be presented by Eq. 42. Electrons are uniformly photo-excited, move (drift and diffuse) both in the electric field of a present spatially distributed ionic charge and photovoltaic field $E_{ph}$, wherupon they are re-trapped. So, the charge compensation achieved in the end of the fixing stage is now violated and the equilibrium distribution of trapped electrons is not uniform. The degree of this non-uniformity achieved in the end of the developing stage governs the value of $\eta_{fix}$: the higher the charge non-uniformity, the higher $\eta_{fix}$. In photovoltaic crystals one of the factors controlling this ultimate charge non-uniformity is the amount of the photovoltaic field under the uniform illumination during developing. The solutions for the maximum developed field $E_{1}^{(2)}$ in phase III in the short-circuit conditions deduced in Refs. 33, 34, looks as like:

$$E_{1}^{(2)} = \frac{i e \eta_{i1}(t)}{\varepsilon K} \frac{E_d - i E_{ph} N^+/N}{E_d + E_q - i E_{ph} N^+/N} \quad [46]$$

Physically, Eq. 46 means that the value of $\eta_{fix}$ controlled by $E_{1}^{(2)}$ may approximate $\eta_0$, if in the end of phase III the ionic
pattern \( N_c(z) \) is not screened or screened very slightly by trapped electrons. According to Eq. 46 this may occur, when

\[ |E_d - i(N^+/N)E_{ps}| \gg E_q, \tag{47} \]

which means that screening should be suppressed either by a strong photovoltaic field \( E_{ps} \gg E_q \), or by a strong diffusion field \( E_{diff} \gg E_q \). In as-grown LiNbO\(_3\):Fe, where \([\text{Fe}^{3+}] \approx 0.2 \) \([\text{Fe}^{3+}] \) (see e.g., Ref. 121), \( E_q \approx e[\text{Fe}^{3+}] / \kappa K \approx 5 \times 10^3 \text{ V/cm} \), so the fulfillment of the inequality \( E_{diff} \gg E_q \) would require too small hologram periods. The inequality \( E_{ps} \gg E_q \) requires a strong enhancement of \( E_{ps} \), which according to Eq. 32 may be achieved by increasing \([\text{Fe}^{3+}] \), for example, by a strong oxidation of LiNbO\(_3\):Fe transforming \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \) (Ref. 71). Under open-circuit conditions the photovoltaic field acts analogously to the applied external field, and the general conclusions are qualitatively the same.

In the model\(^{22,31}\) the developing process is discussed in more details with an emphasis on the role of the photovoltaic field. The consideration is based on taking into account the presence of a steady ionic grating of amplitude \( E_h \) in the kinetics equation of the electronic grating arising under developing. Not going into the details of this consideration, we demonstrate its important conclusions. The analysis shows that the specificity of a photovoltaic crystal is a shift of the developed electronic grating with regard to the fixed ionic grating. This effect is similar to applying an external dc-field. As a result of this shift, the value of the diffraction efficiency is temporally oscillating in the course of developing as \( \eta_{fix} \) approaches the saturation value. The phase shift between the electronic and the ionic gratings is given by the expression

\[ \varphi = \arctg(E_{ps}/(E_q + E_D)), \tag{48} \]

where \( E_{ps} = E_{ps}[N^+/N^+ + N^-] \). The parameters \( E_{ps}, E_q, E_D \) are the photovoltaic, saturation-, and diffusion fields presented, respectively, by Eqs. 6, 13, and 9. Assuming \( E_D \ll E_q, E_{ps} \) the authors deduce the following simplified relation between the amplitudes of the developed \( E_{dev} \) and ionic \( E_h \) gratings\(^{31}\):

\[ \eta_{fix} \approx D_r = \frac{E_{dev}}{E_h} \cdot \left[ \frac{(E_{ps}/E_q)^2}{1 + (E_{ps}/E_q)^2} \right]^{1/2}, \tag{49} \]

As seen from this expression, as well as in the model reported in Ref. 34, \( \eta_{fix} \) depends on the ratio \( E_{ps}/E_q \) and increases in the oxidized crystal because of an increase of \( N^+ \) (i.e., of \([\text{Fe}^{3+}] \) as applied to LiNbO\(_3\):Fe). The value of \( \eta_{fix} \) (Eq. 49) is controlled by the grating spatial frequency \( K \). In reduced crystals, where \( E_{ps} \ll E_q \), the dependence \( \eta_{fix}(K) \) is close to the linear, whereas in oxidized ones in which \( E_{ps} \gg E_q \), it is super linear. So the saturation value of \( \eta_{fix} \) in oxidized crystals is expected to be higher than in reduced ones at the same \( K \). Note that the condition of a high \( \eta_{fix} \) again comes into conflict with the requirement of a long lifetime of a fixed grating: the lesser is the grating period, the higher the value of \( \eta_{fix} \) (Eq. 49); however, the faster the decay both in dark (Eq. 41) and under illumination (Eq. 43).

In the end of this section we should note that the oxidation procedure changes principally the charge transport scheme (28) and the type of the photocarriers in LiNbO\(_3\):Fe \(^{122}\); therefore, it may happen that the presented microscopic models of the fixing process are not valid for a strongly oxidized crystal.

V. EXPERIMENTAL STUDIES OF THE THERMAL FIXING IN LINBO\(_3\) CRYSTALS

Summarizing the qualitative considerations and outlined models described earlier, one may conclude that optimization of the parameters of fixed gratings, that is reaching longest storage times \( \tau \), in the dark, slowest decay rates \( 1/\tau_{\text{decay}} \) under illumination and highest \( \eta_{fix} \), requires certain compromise between the concentrations of ions and electron traps. Their ratio should be rather low to give a high \( \eta_{fix} \) provided by a low degree of screening the ionic frame by electronic carriers, and at the same time large enough to provide a partial screening of the ionic frame in order to slow down its decay. Of course, slowing down the decay may be achieved by decreasing the ionic conductivity, however, in this case the concentration of ions might become deficient for a complete screening of the initial space-charge field. In other words, benefiting from \( \tau \), one loses partially \( \eta_{fix} \) and vice versa. In LiNbO\(_3\) this compromise may be achieved by picking up the ratio between concentrations of \( \text{Fe}^{3+} \)-like electron traps and protons.

In this section we exemplify experimental studies of the thermal fixing in LiNbO\(_3\) crystals. Here we omit the origin of the screening ions, which will be discussed in section VI. It should be noted that in spite of a more than 30-year-old story of these experiments, the mechanism of fixing seems to be incompletely understood. Particularly, there is no full consensus regarding the origin of the complex kinetics of decaying gratings at elevated temperatures. The most uncertain question is the storage time at ambient conditions that cannot be obtained directly and is estimated either by direct extrapolating experimental \( \tau_c(T) \) from elevated temperatures or by calculations on the base of \( \sigma(T) \). A scatter in the values of the activation energies makes these estimates not very reliable.

Note, that the thermal fixing in principle may be caused not only by a screening of the space-charge field \( E_{sc} \) by complementary charge carriers, but as well by a partial switching of \( P_2 \), under \( E_{sc} \), as it takes place in SBN or BaTiO\(_3\). Actually, the coercive field \( E_c \) in LiNbO\(_3\) strongly falls down at \( T > 120^\circ \text{C} \), where a partial \( P_2 \) switching under external fields of about \( 10^4 \text{ V/cm} \) was detected in LiNbO\(_3\):Fe \(^{123}\). However, so far no experimental evidences of a contribution from \( P_2 \) switching to the thermal fixing have been obtained, although such a possibility was repeatedly discussed (see e.g., Refs. 17, 115). For example, oscillations of \( \eta \) at a long high-temperature recording the authors of Ref. 115 interpreted as an evidence of a polarization reversal. Clearly, this mechanism even though it does exist, is secondary.
The pioneering works on thermal fixing were performed in Fe, Mo-doped Ba$_2$NaNb$_5$O$_{15}$ (Ref. 124), undoped LiNbO$_3$ (Refs. 6, 10), and LiNbO$_3$:Fe (Ref. 11) (Figure 4).

In this basic scope of studies the authors characterized the fixing and developing processes on a whole, particularly, they established the activation energy of the fixing, the lowest temperature of the fixing $T \approx 100^\circ C$ (Figure 5), the temperature of erasure of fixed gratings $T \approx 300^\circ C$, and so on. The proposed explanation of the effect assuming the mechanism of the ionic compensation was based on the following reasons: the activation energies of the thermal fixing and of the dark conductivity in LiNbO$_3$ are close (of about 1 eV) and the value of a high-temperature $\sigma_d$ estimated from the temperature dependence of the fixing was in a good agreement with $\sigma_d$ obtained by direct measurements (Ref. 125). As the high-temperature $\sigma_d$ in LiNbO$_3$ was proved to be predominantly ionic (Ref. 126), so the authors of (Ref. 10) arrived at their explanation of the fixing via moving thermally excited ions. The effects of the thermal decay of the electronic space charge were neglected and the events were interpreted as moving mobile ions within a stable space-charge field formed by the diffusion mechanism. Recall that these results were obtained before the photovoltaic era has started. The maximum value obtained for the developed $\eta_{fix}$ was about 50% of the initial $\eta_0$. The storage time seemed to be very encouraging because only a very slight decay of $\eta_{fix}$ in the dark was detected during 5 months (Ref. 7). The authors of Ref. 11 succeeded in recording 500 holograms in LiNbO$_3$ at high temperatures. An increase of the storage time with the grating period was observed.

FIG. 5. The kinetics of the diffraction efficiency under read-out at room temperature after heating a LiNbO$_3$ sample to different temperatures; taken from Ref. 10.
In Ref. 115 studies of a high-temperature (180°C) recording grating were performed in LiNbO$_3$:Fe. The authors detected two steps (fast and slow) in the increasing diffraction efficiency with $\tau_1$ of the order of seconds and $\tau_2 \approx 100$–120 min. In the framework of the proposed model ignoring the thermal excitation of electrons, $\tau_1$ and $\tau_2$ were interpreted as the dielectric relaxation and thermal diffusion of ions, respectively. In terms of advanced later models the slow process may be attributed to a thermal releasing of traps.

In Ref. 15 the thermal fixing of holograms in LiNbO$_3$:Cu was demonstrated with an activation energy of $E_a = 0.95$ eV. In Ref. 17 a micro photometric method was used for studies of the developing of holograms recorded in LiNbO$_3$:Cu at 180°C. When approaching $\eta_{fix}$ to a saturation value, the phase of the grating shifts almost by $\pi$, which supported the mechanism of a mutual screening of two complementary gratings. This shift is related to a contribution from the photovoltaic effect (Ref. 25).

In Refs. 23, 24, 26 detailed studies in the grating behavior at elevated temperatures were performed. It was found that a decay of holograms in the range from 50 to 165°C in LiNbO$_3$:Fe may be fitted to a sum of several exponents (Ref. 23) the decay times show Arrhenius behavior $1/\tau = 1/\tau_0 \exp(-E_a/k_BT)$. A non-monoeXponential Xbehavior of the $\eta$ decay at elevated temperature was analyzed in several works. In Ref. 24 three exponents were detected with $E_a$ ranging from 1.0 to 1.3 eV. In Ref. 34 two kinetic types—fast and slow—were registered (Figure 6). The fast process was attributed to the compensation of the electronic space-charge by thermo-excited ions. The slow process with account for the thermal excitation of electrons (Refs. 22, 34) was interpreted as the decay of the electronic space-charge.

The authors of Ref. 26 compared the decay kinetics in the dark and under illumination (that is phases II and IV in Figure 2) at elevated temperatures. In agreement with Eqs. 41 and 43 these kinetics are different. In the range from 90 to 120°C a dark decay of $\eta$ is due to the screening process, the ionic skeleton being almost preserved. This conclusion was drawn due to the fact that the developing procedure after coming $\eta$ to zero could be performed repeatedly. By contrast, after a light-induced decay of $\eta$ the grating could not be developed. Therefore, a decay under illumination is caused by a thermal erasure of the released ionic skeleton, whose thermal stability is not more supported by a mutually screening electronic space-charge. A decay under illumination may be fitted to a single exponent with $E_a = 1.03$ eV. Starting from this amount one may estimate the decay rate of a fixed grating under read-out at room temperature.

Studies of the decay rate versus the grating period were performed at elevated temperatures in Refs. 24, 26, 30, 34. The decay rate is inversely proportional to $\Lambda^2$ in consistence with the model22 and later ones29,34 see Eq. (43) and Figure 7. An example gives a crystal with a dependence $\tau_s \sim 5.7\Lambda^2$ Ref. 30 that promises surprisingly large difference in $\tau_s$ for patterns with periods only slightly different. The proportionality of storage times to $\Lambda^2$ is provided mainly by the slow stage of the decay (i.e., electron thermoexcitation), whereas the ionic decay, as expected, is practically independent of $\Lambda$. Consequently, the dependence $\tau_s \sim \Lambda^2$ is more pronounced in crystals with a higher Fe concentration (of about 0.15%), in which a contribution from electronic charge is stronger on a whole.

Experimental studies of the developing process were performed in Refs. 27, 31, 34, 120, 127. The authors of Refs. 34 and 31, 32 investigated the dependence of $\eta_{fix}$ on the oxidation (transforming Fe$^{2+}$ → Fe$^{3+}$) or, which is the same, on the value

![FIG. 6. An example of the temporal dependence of the diffraction efficiency at elevated temperatures (taken from Ref. 34).](image-url)
of $E_{pv}$, (see Eqs. 46 and 47). In order to provide the slowest decay by means of reducing the ionic (protonic) conductivity these experiments were performed in dehydrated LiNbO$_3$:Fe.

In Ref. 34 the gratings were recorded at elevated temperatures with the subsequent developing at 50°C. The value of $\eta_{\text{fix}}$ in oxidized LiNbO$_3$: 0.01% Fe (with maximum Fe$^{3+}$ concentration) was almost by an order of magnitude higher than that in oxidized LiNbO$_3$:0.05% Fe ($\eta_{\text{fix}} \approx 0.8\eta_0$ and $\eta_{\text{fix}} \approx 0.1\eta_0$, respectively). Conversely, the decay time on developing in the low-doped crystal was by about an order of magnitude shorter than in the highly doped one (about 2 and 20 hours, respectively, at 90°C). As the activation energy of protons $E_a \approx 1.2$ eV predicted storage times of a naked protonic backbone at room temperature in the range of 50–70 days only, so the authors of Ref. 34 attempted to reduce the ionic conductivity in order to increase $\tau_{\text{decay}}$ and conserve simultaneously a reasonable value of $\eta_{\text{fix}}$. They tried either a very strong oxidation, which led to a significant reduction of the H-content, or a preparation of a stoichiometric sample using a VTE technique, which resulted in a decrease of the Li-vacancy concentration. Both techniques caused an increase of the activation energy of the ionic conductivity to $E_a \approx 1.4$ eV. This permitted the authors to speculate on an enhancement of $\tau_\text{fix}$ at room temperature up to 2 years.

Qualitatively similar results of oxidizing on the value of $\eta_{\text{fix}}$ in LiNbO$_3$:Fe were obtained in Refs. 31, 32. Additionally, the authors of Ref. 32 demonstrated an increase of $\eta_{\text{fix}}$ with $K$ predicted by them (Eq. 49); this effect is especially pronounced in oxidized crystals where this dependence is super linear.

When measuring the developing kinetics of a grating recorded at elevated temperatures, the authors of Refs. 27 and 31 observed a passing of $\eta_{\text{fix}}$ over a maximum in accord with the theoretical predictions for photovoltaic crystals Refs. 25, 31. In principle, this permits controlling the value of $\eta_{\text{fix}}$ by means of varying the developing time.

An interesting example of studies in the microscopic origin of fixing mechanisms with an emphasis on the role of the photovoltaic mechanism was demonstrated in Ref. 18. The authors studied fixing and developing of the photorefraction induced by a narrow (1–2 mm in diameter) Gaussian beam rather than of a recorded grating. The photorefraction was induced in LiNbO$_3$:Fe and LiNbO$_3$:Cu at 160°C during extremely long times (from 50 to more than 300 hours). After developing at room temperature a scanning of the photorefractive region along the polar axis revealed a non-uniform distribution of Fe$^{2+}$ (in LiNbO$_3$:Fe, see Figure 8a) and Cu$^+$ (in LiNbO$_3$:Cu), namely a shift of these ions towards $+z$ borders of the damaged region, which is owing to the electron transfer in the $+z$ direction via the photovoltaic effect. Correspondingly, $-z$ borders were enriched by Fe$^{3+}$ or Cu$^{2+}$, so maxima of the induced photorefraction $\delta n$ were observed at $-z$ borders (Figure 8b) in line with Eq. 32. Non-uniformly distributed [Fe$^{2+}$], [Cu$^+$] and $\delta n$ were stable under illumination. These experiments proved the existence of a non-uniform distribution of a space-charge after developing. Note that in this case a thermally fixed phase grating coexists with the amplitude grating $\Delta \alpha(z)$ produced by [Fe$^{2+}$](z). Additionally, to a redistribution of [Fe$^{2+}$] and [Cu$^+$] the authors found a redistribution of protons discussed later. In the sequential work Ref. 21 a development without light in LiNbO$_3$:Fe was achieved by means of applying in the dark an external field of the order of several kV/cm to a crystal with a thermally fixed hologram. Under applied fields a reversible growth of the diffraction efficiency up to several percent was observed. This effect was attributed to a non-uniformity of the dark electronic conductivity $\sigma_d(z)$ following the distribution [Fe$^{2+}$](z).

Of course, in this section we present not an exhaustive enumeration of experiments on the thermal fixing in LiNbO$_3$. We dwell on those researches that demonstrate the most typical results in studying this problem. It should be emphasized again that the situation with the storage times is uncertain. In Table 3 we summarize the experimental data on $\eta_{\text{fix}}$ and experimental as well as calculated storage times $\tau_\text{fix}$ of fixed holograms. In the column called Comment extrapolation means estimates done by means of extrapolating experimental curves from elevated temperatures to room temperature, whereas calculations mean evaluations without experimental data.

VI. PROTONS AS IONS RESPONSIBLE FOR THE THERMAL FIXATION OF HOLOGRAMS IN LiNbO$_3$

Before discussing the role of hydrogen in thermal fixing of holograms we remind the reader of the basics of its incorporation into oxide lattices, particularly into LiNbO$_3$. The bibliography on OH$^-$ ions in oxides on a whole and on hydrogen in LiNbO$_3$ may be found in recent reviews. We briefly dwell on the main points of these problems with an emphasis to thermal fixing.

In synthetic oxides the incorporation mechanism of hydrogen is not well understood, but following the widely accepted concept, it enters the lattice from the ambient atmosphere during or after the growing process. Among the possible hydrogen-based defects the hydroxyl ion OH$^-$ attracts the attention by
FIG. 8. (a) Spatial distributions of the optical absorption coefficients at $\lambda = 477$ and 2870 nm along the polar axis $z$ after a prolonged recording of the photorefraction by a focused laser beam at $165^\circ$C in LiNbO$_3$: 0.07%Fe. The origin at 0.0 corresponds to the center of the recording Gaussian beam. An increase of $\alpha_{477}$ nm (upper curve) and $\alpha_{2870}$ nm (lower curve) at the right ($+z$) border of the photorefractive strip indicates the corresponding increases of the Fe$^{2+}$- and H-concentrations, respectively, in this region. The left ($-z$) border is Fe$^{2+}$-deficient, that is, enriched by Fe$^{3+}$.

its presence in a wide range of materials. In oxide crystals hydroxyl ions occupy oxygen sites. Its surplus positive charge with respect to the lattice ([OH$^-$]) compensates some other kinds of intrinsic or extrinsic defects, which allows one to probe the defect structure by studying the spectroscopic properties of the hydroxyl ions affected by their surroundings. A relatively low concentration of OH$^-$ permits to study them as an isolated diatomic molecule in the lattice. As the hydrogen impurity is much lighter than the host atoms, so it gives rise to a localized vibrational mode with a frequency much higher than the vibrational frequencies of the host. The vibrational modes of OH$^-$ are studied by IR absorption spectroscopy and Raman scattering and can be interpreted in the framework of an anharmonic oscillator model. The stretch mode frequency of the hydroxyl ion in various oxide crystals lies in the range between 3200 and 3700 cm$^{-1}$, the typical halfwidth of the OH$^-$ vibrational band being between 5–50 cm$^{-1}$. The main characteristics of the IR absorption band in LiNbO$_3$ were described for the first time in Refs. 131 and 132, where the authors assigned an increase of this band to an incorporation of hydrogen (Refs. 131) and analysed its polarization characteristics and the fine structure. A large number of experimental studies in the OH-stretch mode in LiNbO$_3$ (see Refs. 129, 130 and references therein) may be shortly summarized as follows. In congruent LiNbO$_3$ the usually observed broad IR band with a halfwidth of about 32 cm$^{-1}$ demonstrates a strong peak at 3482 cm$^{-1}$ (2.87 $\mu$m) and a weak one at 3467 cm$^{-1}$ ($\approx$2.88 $\mu$m) (Figure 9).

As well as in other oxides, in LiNbO$_3$ the band is strongly dichroic, namely the optical absorption for the ordinary light polarization ($\sigma$) significantly exceeds that for extraordinary ($\pi$) one, that is, hydrogen stretching vibration occurs in the plane perpendicular to the polar axis C. For a given composition of LiNbO$_3$ the IR band does not depend on temperature starting from the liquid helium, which is unlike in other perovskites. At the same time, the shape of the IR band in LiNbO$_3$ and its peak position noticeably depend on the composition, described by the [Li]/[Nb] ratio (Refs. 132, 133), and on the type and concentration of dopants. With increasing Li-content the peak position is shifted and the band is narrowing (Figure 9). The latter result facilitates the interpretation. Some types of doping, for example, with so-called optical damage resistant impurities Mg, Zn, In with rather high concentrations and their combinations with rare-earth and transition metal impurities also lead to a.

The curves were obtained for ordinary polarization of the scanning beams. (b) The scanning of the photorefraction along the polar axis in the same photorefractive region after the high-temperature recording (upper and lower curves correspond to extraordinary and ordinary polarization of the scanning light beam). A maximum of the photorefraction at the left ($-z$) border reflects the proportionality of $\Delta n$ to the Fe$^{3+}$-concentration, see Eq. 32.
TABLE 3
Numerical characteristics of gratings thermally fixed in LiNbO₃ crystals

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$\eta_{fix}$</th>
<th>$\tau_s$, experim.</th>
<th>$\tau_s$, estimate</th>
<th>Temp.</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure crystal</td>
<td>0.5 $\eta_0$</td>
<td></td>
<td></td>
<td>RT</td>
<td></td>
<td>[6]</td>
</tr>
<tr>
<td>0.01% Fe</td>
<td>Several %</td>
<td>5 months</td>
<td></td>
<td>RT</td>
<td>A slow decay during 5 months</td>
<td>[7]</td>
</tr>
<tr>
<td>0.01% Fe</td>
<td>(0.1–0.01)$\eta_0$</td>
<td>5–15 years</td>
<td>0°C</td>
<td>RT</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>0.001% Fe</td>
<td>0.3$\eta_0$</td>
<td></td>
<td></td>
<td></td>
<td>Recorded and fixed simultaneously 500</td>
<td>[11]</td>
</tr>
<tr>
<td>0.01–0.02% Fe</td>
<td>5–35%</td>
<td>$\gg$2 years</td>
<td>$10^5$ years</td>
<td>RT</td>
<td>gratings at $160^\circ$C, $\tau_s$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>grows with $\Lambda$</td>
<td></td>
</tr>
<tr>
<td>0.05% Fe</td>
<td></td>
<td></td>
<td></td>
<td>RT</td>
<td>Improvement after an oxidation</td>
<td>[15]</td>
</tr>
<tr>
<td>0.1% Cu</td>
<td></td>
<td>1 day</td>
<td>150°C</td>
<td>RT</td>
<td>$\tau_s$ grows with $\Lambda$</td>
<td>[24]</td>
</tr>
<tr>
<td>0.01–0.02% Fe</td>
<td></td>
<td>10 years</td>
<td></td>
<td></td>
<td>Calculations of experimental</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>data taken from [11]</td>
<td></td>
</tr>
<tr>
<td>0.1% Fe</td>
<td>0.25 $\eta_0$</td>
<td>1 hour</td>
<td>90°C</td>
<td>$a_{OH} = 0.035$ cm$^{-1}$</td>
<td>[34]</td>
<td></td>
</tr>
<tr>
<td>0.05% Fe</td>
<td>$\ll\eta_0$</td>
<td>$&gt;10$ hours</td>
<td>90°C</td>
<td>$a_{OH} \leq 0.01$ cm$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05% Fe</td>
<td></td>
<td>50–70 days</td>
<td></td>
<td>RT</td>
<td>Calculations from protonic</td>
<td></td>
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<td></td>
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<td>conductivity</td>
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<td>Calculations for a hydrogen</td>
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<td>less crystal, with a new</td>
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<td></td>
<td>type of ionic conductivity</td>
<td></td>
</tr>
<tr>
<td>Fe, Cu</td>
<td></td>
<td>15 years</td>
<td>RT</td>
<td></td>
<td>An extrapolation from</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>165°C</td>
<td></td>
</tr>
<tr>
<td>0.1% Fe</td>
<td></td>
<td>3.7 years</td>
<td>RT</td>
<td></td>
<td>An extrapolation from 145–</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>165°C for $\Lambda = 0.7$ $\mu$m</td>
<td></td>
</tr>
<tr>
<td>0.1% Fe</td>
<td>0.8 $\eta_0$</td>
<td></td>
<td></td>
<td>RT</td>
<td>Recording at 170°C</td>
<td>[27]</td>
</tr>
<tr>
<td>0.1% Fe</td>
<td>0.8 $\eta_0$</td>
<td>5.7 years</td>
<td></td>
<td></td>
<td>An extrapolation from</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150°C $CA = 1$ $\mu$m, $N_H = $</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$10^{19}$ cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>0.7$\eta_0$</td>
<td>200 years</td>
<td>RT</td>
<td></td>
<td>$\Lambda = 2$ $\mu$m, $N_H = 10^{17}$ cm$^{-3}$</td>
<td>[31]</td>
</tr>
</tbody>
</table>

$\eta_0$ is the initial diffraction efficiency of the recorded hologram, $\eta_{fix}$ is the diffraction efficiency of the fixed and developed hologram, $\Lambda$ is the grating period, RT means room temperature, $N_H$ is the hydrogen concentration, $a_{OH}$ is the optical absorption coefficient at 2.87 $\mu$m.

shift of this band (Refs. 129, 130, 134), which is subject of wide discussion beyond the scope of our review.

The proposed model of the OH$^-$ absorption band in LiNbO₃ may be shortly formulated as follows (see, e.g., Refs. 133, 135). Recall that LiNbO₃ belongs to the pseudo-ilmenite group composed by six planar rows of oxygen atoms in a distorted close-packed hexagonal structure. The chains of distorted facet-linked oxygen octahedra are oriented along the polar axis C, the oxygen planes lying normally to it. The stretching IR band is due to proton- coupling to six nearest O$^{2-}$ ions. A distortion of the oxygen octahedra results in different lengths of the available O-O bonds (Figure 10), that is, in six non-equivalent sites for the hydroxyl ions. The model assumes that the longest O-O bonds (positions 5 and 6 in Figure 10) are not occupied by OH-ions, so the OH$^-$ band should be formed by four different components corresponding to four different OH-bonds. Actually, a careful deconvolution of the band shapes of OH spectra for different Li/Nb ratio gives 4 or 5 lines; from a deconvolution of the band in nearly stoichiometric LiNbO₃ four Lorentzian components 3465, 3472, 3479, and 3488 cm$^{-1}$ were obtained, two former being well resolved. So, following this model in LiNbO₃ the hydroxyl ions (or, which is the same, hydrogens) are statistically distributed over four non-equivalent positions. The total area under the band is proportional to the whole OH concentration (e.g., Ref. 137) and the intensities of the individual (deconvoluted) lines are assumed to be proportional to amounts of OH$^-$.
FIG. 9. The shape of the IR absorption band in LiNbO₃ as a function of the [Li]/[Nb] ratio. A—congruent crystal, E, H—[Li]/[Nb] = 0.988 and 1, respectively (the congruent crystal was grown by the Czochralski method, Li-enriched samples by the top seeded solution method).

![Absorption Band Diagram](image)

FIG. 10. The scheme of the oxygen plane perpendicular to the polar axis in LiNbO₃. The presented hydrogen sites were proposed in Ref. 135.

![Oxygen Plane Scheme](image)
The conductivity in LiNbO$_3$ versus hydrogen and deuterium concentrations Ref. 137.

Simulations (e.g., Refs. 78, 147) led to the conclusion that in as-grown congruent LiNbO$_3$ the formation of V$_O$ is unlike. The currently accepted model of the LiNbO$_3$ defect structure is based on the fundamental assumption of the 100%-occupation of oxygen sites (Ref. 79), so V$_O$ as possible charge carriers may be disregarded. At the same time, $E_a$ of Li-transport in LiNbO$_3$ being of about 0.4 eV (Ref. 148) is inconsistent with $E_a$ $\approx$ 1 eV estimated from direct conductivity measurements. The ultimate decision was made in Ref. 149, where the proportionality between the hydrogen concentration and the conductivity was demonstrated in LiNbO$_3$ at temperatures from 400 to 1100$^\circ$C. This conclusion was supported in Refs. 137, 150 and extended to deuterium in D$^+$-enriched LiNbO$_3$ (Ref. 137) (Figure 11). Therefore, the protonic origin of the conductivity in LiNbO$_3$ may be taken as settled both at elevated and room temperature. Recall again that this conclusion is applicable to LiNbO$_3$, undoped or doped with low impurity concentrations. As shown earlier, in LiNbO$_3$:Fe or LiNbO$_3$:Mn with $[\text{Fe}] \geq$ 0.2–0.25% the activation energy of the dark conductivity is as low as 0.3–0.4 eV$^{90}$ being related to electron hopping over iron sites rather than to the proton movement.

The values of the transport characteristics (activation energy, diffusion coefficient $D_b$, mobility $\mu$) are noticeably scattered. The estimates of $D_b$ varied in the range from 4$^{151}$ to 0.01$^{152}$ and 0.0014 cm$^2$/sec.$^{32}$ Note that the data for $D$ were obtained both in bulk crystals and surface structures, such as proton exchanged optical wave-guides, which may somewhat account for this scatter. Table 4 exemplifies the dependence of $E_a$ on LiNbO$_3$ crystal compositions, deduced either from direct conductivity measurements at elevated temperatures $\sigma_d(T)$ or from the decay times $\tau_{\text{decay}}$ of recorded holograms.

As seen in Table 4, the most obvious reason for a $E_a$ spread is its dependence on the $[\text{Li}]/[\text{Nb}]$ ratio. Additionally, the scatter in $D$ and $E_a$ may be related to a non-equilibrium distribution of hydrogen over several non-equivalent O-sites (Refs. 136, 154).

On the whole, although the protonic conductivity in LiNbO$_3$ is studied insufficiently, one may conclude that its activation energy being in the range of about 1 eV coincides approximately with the activation energy of the thermal fixation of holograms in LiNbO$_3$ (see the previous section). On this ground it was reasonable to assume hydrogen (in the form of protons or hydroxyls) to be responsible for screening the electronic space-charge. The first attempt to relate the fixation to Si ions accidentally present in the crystal,$^{12}$ was ruled out by experiments in LiNbO$_3$ enriched by Si.$^{115}$

<table>
<thead>
<tr>
<th>$[\text{Li}]/[\text{Nb}]$</th>
<th>Impurity</th>
<th>$E_a$, (eV)</th>
<th>From $\sigma_d(T)$</th>
<th>From $\tau_{\text{decay}}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congruent</td>
<td></td>
<td>1.1</td>
<td></td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>Congruent</td>
<td></td>
<td>1.23</td>
<td></td>
<td></td>
<td>[137]</td>
</tr>
<tr>
<td>Congruent Fe</td>
<td></td>
<td>1.17</td>
<td></td>
<td></td>
<td>[137]</td>
</tr>
<tr>
<td>Congruent Fe</td>
<td></td>
<td>1.13</td>
<td></td>
<td></td>
<td>[153]</td>
</tr>
<tr>
<td>0.99 Mn</td>
<td></td>
<td>1.13</td>
<td>1.05</td>
<td></td>
<td>[153]</td>
</tr>
<tr>
<td>0.99 Mn</td>
<td></td>
<td>0.96</td>
<td>1.05</td>
<td></td>
<td>[153]</td>
</tr>
</tbody>
</table>

![Graph](image_url) FIG. 11. The conductivity in LiNbO$_3$ versus hydrogen and deuterium concentrations Ref. 137.
redistribution of hydrogen within the photorefractive region. From Figure 8a one may see that the H$^+$ concentration is increased in the region, where the concentration of Fe$^{2+}$ (and of Cu$^+$ in the case of LiNbO$_3$:Cu) is increased, or, in other words in the regions of electron accumulation. This means that protons are those mobile ions that screen the electronic space charge. The results of the neutron diffraction on a thermally fixed grating supported this conclusion. Since those experiments protons are generally accepted as the main ions responsible for fixing in LiNbO$_3$. The conclusion of a decisive role of protons in the fixing process was supported as well by investigations of characteristics of fixed holograms in LiNbO$_3$ crystals with different contents of hydrogen (Refs. 18, 32, 34). Note that the H-concentration in as-grown or slightly oxidized LiNbO$_3$ crystals always satisfies the requirement (Eq. 45) $N > 5 \times 10^{16}$ cm$^{-3}$ for the low limit of the ionic concentration providing the complete screening of $E_{xc}$.

At the end of this section it should be mentioned that there are evidences indicating a contribution from some ions other than protons to the thermal fixing. For example, in strongly oxidized (hydrogen-free) LiNbO$_3$:Fe crystals despite the absence of hydrogen and an increase of $E_{xc}$ up to 1.4 eV, a thermal fixing of holograms occurs nevertheless. It is worth noting that many properties of LiNbO$_3$ (dielectric permittivity, pyro- and coefficients, some optical parameters, electron emission, etc.) show certain anomalies in the temperature range between 120°C–150°C (e.g., Refs. 156–158); anomalies in the lattice parameters were also detected (Ref. 159). These peculiarities impelled some authors to conclude about a phase transition in this temperature range, which might initiate an ionic conductivity on the whole.

**VII. THERMAL FIXATION OF HOLOGRAMS IN OTHER PHOTOREFRACTIVE MATERIALS**

We now briefly mention the results on the thermal fixing of recorded gratings in crystals other than LiNbO$_3$. These are SBN (Strontium-Barium-Niobate), KNbO$_3$, KTaO$_3$, KTiO$_4$, Nb$_2$O$_5$, Bi$_{12}$SiO$_{20}$, Bi$_{12}$TiO$_{20}$, and Bi$_{12}$TiO$_{20}$, (BTO) (together with applying ac-fields), La$_3$Ga$_5$SiO$_{14}$:Pr (LGS).

Note that in all these crystals the recording mechanism differs from that in LiNbO$_3$. In BaTiO$_3$, BSO and SBN it is purely diffusion, whereas in KNbO$_3$ it involves both photovoltaic and diffusion fields depending on the impurity state (see, e.g., Ref. 48). KTN at ambient conditions is in the centro-symmetric paraelectrical phase, so the photorefraction occurs via the quadratic electrooptic effect and the read-out of a photorefractive grating requires applying an external bias field. An interesting example of the orientation dependence of the recording mechanism is observed in the piezoelectric crystal LGS, where the properties of the photovoltaic tensor dictate a dependence of the photovoltaic current $j_{pv}$, that is, of the recording mechanism on the angle $\beta$ between the light polarization vector and the polar axis $x$. If $\beta = 0^\circ$, then $j_{pv} \neq 0$ and the hologram is recorded by the photovoltaic mechanism; for $\beta = 45^\circ$ we have $j_{pv} = 0$, so the recording proceeds by the diffusion mechanism.

Thermal fixing in these crystals has not been studied in detail due to their secondary role as storage media. The process of thermal fixing in them manifests itself as an unusual behavior of the diffraction efficiency $\eta(t)$ when recording at elevated temperatures ($T > 60$–70°C); the diffraction efficiency after saturating at $\eta_{max}$, starts to decrease and falls down to zero. When illuminating by a single Bragg beam at room temperature, a non-zero $\eta$ appears increasing to a certain value $\eta_{fix} < \eta_{max}$. The fixing means that an optical erasure of this developed grating under the read-out proceeds much slower than the original grating recorded at room temperature. A principal distinction of all these materials from LiNbO$_3$ is that in all of them the optical erasure does occur though relatively slow, whereas in LiNbO$_3$ a fixed grating practically is not optically erased at room temperature.

The behavior of $\eta(t)$ at elevated temperatures is exemplified by KNbO$_3$ (Figure 12), the inscription to this figure formulates the qualitative interpretation of the dynamics by the authors in (Ref. 162). In this crystal $\eta_{fix} = (0.1–0.5)\eta_{max}$. A similar scenario was reported for KTN, BaTiO$_3$, BSO, LGS. Passing $\eta(t)$ over a maximum at elevated temperatures in all cases was attributed to a formation of a complementary grating, which screens the original (recorded) one. The existence of a complementary grating was sometimes proved experimentally. For example, in KNbO$_3$ simultaneous measurements of $\eta$ and $\Gamma$ during developing found a coexistence of two gratings (original and screening ones) mutually shifted by $\pi$. In LGS the authors found a dependence of the phase shift between the original and complementary gratings on the polarization vector of the off-Bragg developing light beam. This dependence was in accordance with the orientation dependence of the recording.
mechanism mentioned earlier. In general, the interpretation of \( \eta(t) \) at elevated temperatures presented in Figure 12 as a manifestation of screening the photorefractive effect \( E_s \) by any charge carriers, does not raise doubts. However, the origin of the screening charges was determined in no one of these crystals.

The thermal fixing process in all crystals obeys an Arrhenius law with the activation energies \( E_a \approx 1 \text{ eV in KNbO}_3 \),162 1.44 eV in \( \text{BSO} \),167 0.89 eV in \( \text{LGS} \). Rather low values of \( E_a \) in \( \text{LGS} \) makes it possible to accomplish the fixing procedure at temperatures as low as 63°C. Several attempts were made to prove that fixing process is related to thermally excited ions rather than to thermally excited carriers of an electronic nature (electrons or holes). To prove it in \( \text{KNbO}_3 \), the experiments were performed in the crystals with different compositions.162 In strongly reduced undoped \( \text{KNbO}_3 \) the photoconductivity \( \sigma_{ph} \) is electronic and \( E_{sc} \) is formed by captured photo-electrons, whereas in doped crystals \( \text{KNbO}_3: \text{Fe} \) and \( \text{KNbO}_3: \text{NaLiFe} \), where \( \sigma_{ph} \) is of the p-type, \( E_{sc} \) is formed by captured photo-holes. In spite of the different origin of \( E_{sc} \), the activation energy of the thermal fixing in all these crystals is practically the same, which evidences of a common (ionic) origin of the screening carriers. As \( E_a \approx 1 \text{ eV of the thermal fixing in } \text{KNbO}_3 \) is close to the activation energy of the protonic conductivity in oxides, so the authors of Ref. 162 suggested the thermally activated protons as a reason of fixing. The screening complementary charge carrier in \( \text{KTN} \) are optically inactive,166 so more probably are ions rather than electrons or holes. An influence of an \( \text{H} \)-enrichment on the storage time of fixed gratings was found in \( \text{KTN} \),166 however, the results are ambiguous. In \( \text{BaTiO}_3 \) the authors only postulate that screening charge carriers are protons.163 Interestingly, to account for fixing mechanisms in \( \text{SBN} \),160 \( \text{BaTiO}_3 \),163 and \( \text{KTN} \)111 the authors engage to some extent the ferroelectric mechanism, because they perform fixing by means of cooling the crystals over the phase transition temperatures, thus involving possible domain redistribution under the space-charge field of the recorded gratings.

Summarizing these isolated data, one can conclude that a screening of the photorefractive space-charge fields by thermally activated charge carriers (of different origin) at elevated temperatures is evidently a common effect for photorefractive media on the whole. However, only a few cases of a real use of this effect for hologram fixing have been found so far. A principal difference of the thermal fixing characteristics in \( \text{LiNbO}_3 \)—like materials (\( \text{LiTaO}_3 \), doped \( \text{Ba}_2 \text{NaNb}_5 \text{O}_{15} \)) from those in other crystals is obviously related to the existence of the bulk photovoltaic effect.

VIII. PRACTICAL APPLICATIONS OF HOLOGRAM THERMAL FIXING IN \( \text{LiNbO}_3 \)

A first attempt of a practical application of thermal fixing has been performed by the RCA group11 immediately after the discovery of this effect. The authors recorded 500 holograms at 160°C, thus simultaneously fixing them, in \( \text{LiNbO}_3: (0.01–0.02) \% \text{Fe} \); the read-out after developing at room temperature revealed a set of gratings with diffraction efficiencies successively decreasing from 35 to 5% (following from the last recorded hologram to the first one, respectively), which showed no decay in darkness during 2 years. A development of the fundamentals of thermal fixing in the succeeding 30 years initiated a variety of investigations of applications. These studies may be separated into two groups. First, thermal fixing is used in traditional applications of photorefractive crystals for constructing non-volatile optical memory devices, which combine a high storage density with a fast random-access and high data transfer rate (e.g., Refs. 94, 95, 120, 171–182). A more recent direction of applications is based on the high angular selectivity of recorded phase gratings that may be used in devices requiring a narrow spectral bandwidth and a close spatial shift tolerance. We now briefly outline the available data on these two directions.

Note that for storage applications, an attractive feature of devices based on the photorefractive effect is a potentially very high diffraction efficiency (at the limit 100%), which provides a strong intensity of the transformed light wave. Another important feature is the possibility of multiplexing, that is the recording of many elementary holograms in the same photorefractive sample, which are not mixed and may be read separately. The best techniques giving the largest number of recorded holograms \( M \) is the angular multiplexing. The optimum configuration for a compact storage system using the angular multiplexing is the 90°-one178 in which gratings are recorded in a cubic-shaped \( \text{LiNbO}_3 \) crystal by mutually orthogonal signal and reference beams falling onto orthogonal faces of the sample, the polar c-axis lying in the diagonal plane at 45° to the faces. The main limitation of the angular multiplexing is a decreasing of the diffraction efficiency \( \eta \) of an elementary hologram with increasing \( M \), because all pre-recorded holograms are partially erased on recording of each sequential one. This obstacle requires a search for rather sophisticated schedules of multiplexing (a matching of successive recording times to erasing times), whose aim is to provide whenever possible equality of diffraction efficiencies of stored holograms (e.g., Ref. 172). Mention should be made of the characterization of multiplexed holograms, which can be done in the language of averaging. For a large number of holograms \( M \), the dependence of the diffraction efficiency \( \eta \) on the number of holograms \( M \) is close to the activation energy of the thermal fixing in all these crystals is practically the same, which evidences of a common (ionic) origin of the screening carriers. As \( E_a \approx 1 \text{ eV} \) of the thermal fixing in \( \text{KNbO}_3 \) is close to the activation energy of the protonic conductivity in oxides, so the authors of Ref. 162 suggested the thermally activated protons as a reason of fixing. The screening complementary charge carriers in \( \text{KTN} \) are optically inactive,166 so more probably are ions rather than electrons or holes. An influence of an \( \text{H} \)-enrichment on the storage time of fixed gratings was found in \( \text{KTN} \),166 however, the results are ambiguous. In \( \text{BaTiO}_3 \) the authors only postulate that screening charge carriers are protons.163 Interestingly, to account for fixing mechanisms in \( \text{SBN} \),160 \( \text{BaTiO}_3 \),163 and \( \text{KTN} \)111 the authors engage to some extent the ferroelectric mechanism, because they perform fixing by means of cooling the crystals over the phase transition temperatures, thus involving possible domain redistribution under the space-charge field of the recorded gratings.

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\[
\eta = \frac{([A_0 \tau_{rec}](\tau_e/M))^2}{[M/\#M]^2} \quad [50]
\]

where \( M/\# = (A_0/\tau_{rec}) \tau_e \). The convenience of the Mok-factor for characterizing a system of multiplexed holograms is due to the fact that the values of \( A_0 \) and \( \tau_{rec} \) themselves are difficult to measure, whereas \( A_0 \tau_{rec} \) and \( \tau_e \) can be obtained from the slopes...
of $\eta(t)$ and $\ln[\eta(t)]$ during recording and erasure, respectively, which immediately gives $M/\eta$. So, $M/\eta$ measured from the kinetics of a single hologram can predict with a good accuracy the value of $\eta$ for $M$ holograms (with the use of a suitable schedule of recording, see earlier). In other words, this is the Mok-factor which may be an indicator of the average diffraction efficiency of multiplexed holograms; an improvement of $M/\eta$ is a direct improvement of the system performance as a whole.

A high multiplexing capability in photorefractive media, particularly in LiNbO$_3$:Fe, was demonstrated; in 10 years the storage capability advanced from 500$^{95,120,173,176}$ to 5,000$^{94,174,179}$ and even 10,000–20,000 holograms$^{180–182}$ with a reliable fidelity of a retrieval of an elementary hologram. In Ref. 185 the authors succeeded in recording and storing of one thousand holographic data pages, each containing 1$^*10^5$ pixels (a density of about 250 G pixels/inch$^2$) in a LiNbO$_3$:Fe sample of $15*15*8$ mm$^3$ in size. It is clear, that for hologram multiplexing the fixing procedure is of special importance, taking into account very low diffraction efficiencies.

After the pioneering work$^{11}$ there were several attempts to fix thermally holograms multiplexed in LiNbO$_3$.$^{120,176–178,180,182}$ The authors of Ref. 120 who achieved a capability of 1 MB during recording and fixing of 530 digital holograms, performed the first regular study of fixing conditions for multiplexing, particularly of the thermal regime of fixing. Recall that recording at elevated temperatures (producing a simultaneous fixing) gives higher $\eta$, and lower noise$^{11}$ than the post-fixing. At the same time, the former procedure involves instabilities of the crystal parameters, an air convection and a consequent deterioration of the fixed hologram. To overcome this problem some authors propose to place the crystal into a vacuum chamber$^{23}$; the authors of Refs. 118, 186, 187 developed active stabilization systems. These methods may solve the problem only partially, because a deterioration of a fixed hologram at room temperature after recording at elevated temperatures is due also to fundamental reasons, such as the thermo-optical and piezo-optical effect (thermo- and strain-induced changes of the refractive indices), which cannot be avoided. So, the post-fixing procedure is preferable for multiplexed holograms, although it leads to a lowered $\eta$.

To demonstrate a practical realization of thermal fixing of multiplexed holograms, we briefly mention Ref. 182, in which the authors achieved thermal fixing of 10,000 holograms recorded in a LiNbO$_3$:0.015% Fe crystal $2*1.5*4$ cm$^3$ in size. To record this number of gratings, 5 fractal rows in the crystal bulk were used with 2000 angularly multiplexed holograms in each row. Holograms were recorded using the optimized schedule$^{172}$ providing an average (almost equal) diffraction efficiency of an elementary hologram of about $7*10^{-9}$. Multiplexing was performed at room temperature with a post-heating for fixing $T = 120^\circ$C, whereupon the fixed system was developed at room temperature with the use of a mercury lamp. The authors attempted two regimes of fixation: a fixation of the recorded holograms altogether in one act of heating and an incremental procedure of fixing, namely, a step-by-step heating the sample after recording each successive thousand holograms. The latter procedure required ten fixing (heating) acts and a sophisticated schedule of recording. The former procedure should provide under the used conditions a ratio $\eta_0/\eta$ of about 0.3; actually, it gave a close value 0.26. The latter procedure appeared to be more efficient, because it gave a $\eta_0/\eta$ of about 0.66, the average efficiency of fixed holograms being about 4.6$^{10^{-9}}$. A surprising result is that in agreement with Ref. 11 a system of thermally fixed holograms shows a lower noise compared to the initial non-fixed one.

Let us briefly run through the more recent, alternative applications of photorefractive gratings$^{188–194}$ based on their angular selectivity, which is strictly constrained by the Bragg conditions. First these are very-narrow-bandwidth interference filters required in a number of areas, such as solar astronomy, high-resolution spectroscopy, extra- or intra-cavity laser elements, and so on. Examples of these applications were demonstrated in Refs. 188, 190, where a Bragg-reflecting band filter was produced by means of recording a grating in a reflection geometry in a LiNbO$_3$:Fe plate with a few mm thickness. For $\lambda = 514.5$ nm the achieved parameters were a bandwidth (FWHM) of about 50 pm, reflectivity $T$ about 35%, and an angular aperture about 5$^\circ$. The values of FWHM and $T$ of this photorefractive interference filter are somewhat worse than of the most advanced narrow-band filters,$^{193}$ however, the great advantages are a much lower price and much smaller size and weight. An additional advantage is the possibility of temperature and field tuning of the peak wave-length, which is due, respectively, to the thermooptic and electrooptic (and piezooptic) effects. Tuning coefficients are $5$ pm$/^\circ$C$^{190}$ and 6 pm/kV$^{191}$.

Some researchers$^{192,193,196}$ tried the thermal fixing in wavelength-division multiplexers (WDM), which they develop on the base of superimposed phase gratings in a photorefractive medium. WDM serve to merge (multiplex) and separate (demultiplex) superimposed optical signals of different wavelengths, which are simultaneously transmitted by a single optical fiber in an optical communication network. These devices again use the high Bragg-angle selectivity, which provides a necessary condition that a given photorefractive grating should diffract only a single light-wave (thus being related to a certain single optical channel). In Ref. 196 the authors demonstrated eight- and sixteen-channel multiplexers based on LiNbO$_3$:Fe crystals with different Fe concentrations. To produce a multi-channel multiplexer, a corresponding number of gratings was recorded by means of varying the recording angles; the orientation and the spatial period of a grating determines the wavelength and propagation direction of the corresponding diffracted beam. The gratings were recorded by an Ar-ion laser at $\lambda = 514.5$ nm in a transmission geometry, whereas multiplexed (input) or demultiplexed (output) beams with the average wave-length $\lambda \approx 1.55 \mu$m were oriented approximately parallel to the polar axis, that is, operated in the reflection geometry. Figure 13 shows the configuration of the demultiplexing in the described case.$^{190}$ In these devices the authors tested non-fixed as well as thermally fixed
gratings recorded at elevated temperatures and developed under a mercury lamp at room temperature. Both types of multiplexers exhibited the bandwidths as low as 0.1 nm, a high cross-talk suppression (>25 dB) and low intensity losses, that is, high averaged diffraction efficiencies \( \eta \), however, in thermally fixed samples the latter was somewhat lower than in non-fixed ones.

Fixed holograms in LiNbO₃:Fe were also tried in an optical correlating system. The development of real-time correlators in photorefractive media may be found in Refs. 197, 198. Recall that an optical correlator serves to compare an unknown object to a known reference one. The principle is based on a correlation of the Fourier transform of an unknown object to the Fourier transform of the reference one. In the readout process the latter is incident on the correlator (in our case, a crystal with a thermally fixed reference image) at a Bragg angle, the diffracted beam intensity being proportional to the correlation function. In Ref. 194 a matched filter was created by means of recording a reference object in LiNbO₃: 0.1% Fe at 160°C (the grating spacing \( \Lambda = 1.35 \mu m \)). The fixed developed image was very stable, estimates predict its life time to be about 10 years. Authors analyzed the device using controlling tests (the recognition performance for different characters, an invariance with respect to a rotation or size-variations of a recorded object) and concluded that a correlator based on a fixed hologram is comparable by its characteristics to a correlator based on a non-fixed photorefractive grating. The former can provide an advantage of operating at the wave-length of recording, whereas the latter correlator permits operation in a long-wave range only.

Finally, thermal fixing of holograms may find applications in wave-guiding structures on LiNbO₃. A hologram fixation was demonstrated in planar waveguides, which is very attractive in view of signal processing and beam manipulations in integrated optics. Holograms were recorded in LiNbO₃:Fe:Ti and LiNbO₃: Ti crystals with planar waveguides Ti-undiffused on the y-cut; recording was performed either at room temperature (non-fixed) or at 180°C (fixed) by Ar-ion laser beams incident onto the y-cut of the crystal, a grating vector being parallel to the z-axis. At room temperature, a weak probing beam from a He-Ne laser was coupled into waveguides (in the fixed case after the development) in order to probe the modulation of the refractive index \( \Delta n(z) \) produced by the recorded grating. In both, the non-fixed and the fixed case a large modulation \( \Delta n(z) \) within waveguides was found that in saturation was close to the value of \( \Delta n(z) \) in the crystal bulk; after fixing it was even larger than in the non-fixed sample. A significant drawback of gratings recorded in the waveguides (both after fixing and without it) is a pronounced decrease of the measured modulations for the TE-modes guided near the surface.

IX. CONCLUSION

By now the procedure of thermal hologram fixation has found a more or less adequate description and is examined sufficiently in LiNbO₃ crystals, especially doped with iron and in related materials such as LiTaO₃. At the same time there is a deficiency of these investigations in other materials, although the experiments in other crystals (BaTiO₃, SBN, BSO, etc.) prove a commonness of this effect for photorefractive materials on a whole. In LiNbO₃ crystals the microscopic origin of the thermal fixing may be taken as settled; namely, it is caused by screening the electronic space-charge by protons thermally activated at temperatures \( T > 120–130°C \). In LiNbO₃ crystals the thermal fixing provides diffraction efficiencies \( \eta_{fix} \) comparable to those in non-fixed ones, rather long storage times of the recorded gratings in the dark, and their temporal stability under illumination. In line with the developed theoretical models optimization of characteristics of thermally fixed holograms, that is an increase of \( \eta_{fix} \) and of the decay time \( \tau_{deck} \) may be achieved in low-doped LiNbO₃:Fe crystals, particularly subjected to some treatments such as oxidation and dehydration. The maximum achieved experimental values of \( \eta_{fix} \) are 0.7–0.8 of the initial (non-fixed) \( \eta_0 \). In some experimental works no degradation of fixed holograms was revealed during a time as long as 2 years. Taking into account an increase of the decay time with the grating period \( \Lambda \approx \Lambda^2 \) one may expect the life time of a fixed grating with \( \Lambda = 1 \mu m \) not less than 70–100 years at room temperature. Similar estimates are obtained by extrapolation of \( \tau_{deck} \) observed at elevated temperatures. The available theoretical description directs the ways to a further improvement of these parameters. The method was successfully tested in non-volatile optical storage systems based on hologram multiplexing and is coming into use in narrow-band devices requiring a high angular selectivity. The thermal fixation does not increase the noise of the multiplexed gratings compared to the initial non-fixed system. Certain
fundamental draw-backs of the method is the impossibility of performing the fixing in situ and of a selective erasure and over-recording of an elementary hologram.

REFERENCES

42. J. J. Amodei, RCA Rev. 32, 185 (1972).


