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"PHASE HOLOGRAPHIC STUDIES OF THE
CONDUCTIVITY OF Fe-DOPED LiNbO₃"

by

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ABSTRACT

The writing process involved in volume phase holographic storage in LiNbO₃ has been extensively studied, but no quantitative work exists concerning the decay of holograms. Since direct electrical conductivity measurements are difficult, if not impossible, decay rate measurements can provide an accurate figure for the material's conductivity.

A coupled-wave theory developed by Kogelnik is presented describing diffraction by a phase grating with unslated fringes in a lossy medium. Next, a dynamic theory of hologram grating developed by Kim is presented. Using classical E-M theory, the hologram decay is predicted to be a sum of exponentials.

Experimental data on writing and decay processes is presented which agree well with Kim's theoretical predictions, but which differ markedly from the expected decay behaviour. An excellent fit to the experimental
decay curves was obtained by assuming a time dependent conductivity of the form

\[ \sigma(t) = \sigma_0 + \sigma_1 e^{-t/\tau}. \]

The data show that \( \tau \), the time constant involved, varies with the iron doping level in the crystal. A model is proposed to explain the phenomenon, involving metastable trapping centers releasing electrons into the conduction band.
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CHAPTER I

INTRODUCTION

In the field of computer technology, one of the ever present requirements is for higher speed, more compact memory systems. The evolution of computer memory has gone from the core systems of the 1950's to the monolithic multi-thousand bit integrated circuits of the 1970's. This represents an improvement in bit density of many orders of magnitude, but there exist situations and applications which call for even more speed and capacity than these latest developments can provide. Library, or archival, storage requires an extremely stable, compact memory, yet it must also be somewhat non-volatile, i.e., it must not require a constant power supply to retain its information. On the other hand, certain information processing applications require similar high densities, but with the added feature of extremely high speeds.

And so we are faced with the following requirements: a stable, high density memory that will retain data without drawing power, yet can operate at high speeds when
needed. It should also be cyclable, that is, it can have its data erased and replaced repeatably with little degradation in performance. One system which can provide these qualities is phase holography in ferroelectrics.

Volume phase holographic data storage is the most promising solution to these requirements, since it offers a combination of high bit density and speed. The process makes use of the technique of storing two dimensional arrays of binary coded data in the ferroelectric crystals using holographic techniques. Many materials, such as KTN, PLZT, and BaTaO₃, are known to be usable as storage mediums, but the largest class are the ABO₃ ferroelectrics, such as LiNbO₃, LiTaO₃, and BaTaO₃. All of these crystals are photoelectric, and linearly electro-optic. In most of the materials, doping with transition metal impurities will increase the photocurrent process, and it is believed that the impurities act as electron donors. Many of these crystals are also piezo- and pyro-electric.

In this crystal class, one of the most promising is lithium niobate, LiNbO₃. Its advantages are a very low intrinsic conductivity, which can be increased several orders of magnitude by doping, and a high photo-
refractive sensitivity. The low intrinsic conductivity is important to insure long storage lifetimes, since lifetime is inversely proportional to conductivity, and a high sensitivity is desired so that the data can be recorded with a minimum expenditure of energy. Both of these attributes can be significantly altered by the concentration of metal dopants, allowing the crystals to be tailored to specific purposes. For example, archival storage requires a long storage time, and would best be suited by the use of undoped crystals. Here the slow recording process would not be a serious drawback. Other situations involving real time information processing could sacrifice the long lifetime for the ability to record and read massive amounts of data rapidly by making use of a highly doped crystal.

Most of the past work in this field has used lithium niobate as a subject material, usually doping the crystals with iron. This gives the medium a good sensitivity, and the absorption responsible for the photo-voltaic conversion takes place at approximately 4900 Å, conveniently near the laser lines of the argon ion laser. Iron-doped lithium niobate has been chosen for the work here.
Aims of this Research.

Recent work has closely examined the hologram formation process, and in particular, the electron transport phenomenon acting during hologram formation. However, very little work has been done on the hologram decay process. Decay rates should be a simple means of determining crystal conductivities, and hence, storage lifetimes. With this goal in mind, and in the hope of gaining more information on the energy band structure active in holographic storage, the following experiments in holographic decay in Fe:LiNbO$_3$ have been conducted.
CHAPTER II

EXPERIMENTAL PROCEDURE

A. Equipment and Set-Up

The main laser light source was a Spectra Physics Model 52B Argon Ion Laser operated single line at \( \lambda = 4880 \ \text{Å} \). The laser incorporated an étalon which gave a bandwidth of 50 MHz and restricted frequency jitter to 10 MHz. The beam was divided by a beamsplitter to form the two "writing beams", which intersected to form the interference pattern responsible for the grating formation. The intersection angle between the two writing beams is 12°. The diffraction efficiency monitor beam is generated by a Spectra Physics Model 212 Helium-Neon Laser at a wavelength of 6328 Å. The monitor beam is aligned at the proper Bragg angle, but this angle changes depending upon the polarization of the monitor beam. A sketch of the experimental set-up appears in Fig. II-1.

To insure mechanical stability, the entire experiment, including both laser sources, was mounted on a air-isolated optical bench. The experiment was also
Fig. II-1: Experimental Layout
enclosed in a protective box to eliminate thermal air currents which could have affected the relative phases of the two writing beams. The box enclosed all components from the beamsplitter to the crystal holder.

The optic axis of the lithium niobate, called the c-axis, is aligned so that it lies in the plane formed by the writing beams. The polarization of the writing beams is perpendicular to the c-axis. The crystals used measure one centimeter square by one millimeter thick. The front face of the crystal is normal to the angular bisector of the writing beams. The crystals were manufactured by Crystal Technology, and were doped with iron to different concentrations. None of the crystals were annealed and they had no optical coatings. In addition to the iron dopants, our crystals contained other metal impurities.\(^1\)

The writing beams had a beam diameter of 3 mm at the crystal, and the beams had a gaussian profile. The beams were controlled by three remote controlled electronic shutters. The shutters were inside the enclosure, yet were mechanically isolated from the experiment. The shutters could be controlled by an automatic sequencer that allowed the taking of data points at periodic intervals.
B. Experimental Procedures

Before any experiment was conducted, the crystal to be used was completely erased by exposing it to the white light of a high intensity lamp for several hours. The crystal was then allowed to relax for at least one day to allow it to reach charge equilibrium.

The crystal was then placed at the common intersection of the three beams. The beam diameters of the writing beams were 3 mm, and the diameter of the monitor beam was 1 mm.

The writing process was initiated by switching on both writing beams simultaneously. The diffraction efficiency was continually monitored by a probe beam of $\lambda = 6328 \, \text{Å}$ aligned at its Bragg angle. The intensity of the probe beam was kept at least two orders of magnitude lower than the writing intensity to avoid affecting the writing process. Considering the fact that $\alpha$ at $\lambda = 6328 \, \text{Å}$ is considerably less than at $\lambda = 4880 \, \text{Å}$, then the energy absorbed from the probe beam can be considered negligible compared to the energy from the writing beams.

During decay measurements, both writing beams were, of course, off, and the probe beam was periodically
switched on for 2 seconds to determine the diffraction efficiency. Several periods were available for use, varying from 30 seconds to 1 hour.
CHAPTER III

THEORY

In this section, the existing theories concerning holographic storage in LiNbO$_3$ are presented. First, the theory concerning diffraction by a static holographic grating is presented, including several special cases applicable to this work. Then, the basic electron transport method which leads to grating formation is considered. This leads to the theory of long term grating formation, and naturally, grating decay.

A. Diffraction by a Transmission Phase Hologram

The major work on the theory of diffraction by thick holographic gratings was published in 1969 by Kogelnik$^2$. In his calculations, he utilizes a coupled wave theory to derive the diffraction efficiency of several types of gratings. The coupled wave theory makes use of a wave coupling coefficient to find the energy transferred to the signal beam from the input beam. Of particular interest in our case, he considers
diffraction by a thick transmission grating consisting of a spatial variation in the refractive index. He further elaborates these calculations by considering the case of a lossy medium, (with a constant grating), and the condition of a slanted grating.

Kogelnik's coupled wave theory assumes monochromatic light incident on the grating at the Bragg angle and polarized perpendicular to the plane of incidence. Fig. III-1 shows the model under consideration. The variables introduced in the figure are: $\bar{K}$, the grating vector; $\theta$, the angle of incidence (measured in the medium); $\Lambda$, the grating period; $\phi$, the grating slant angle; and $d$, the grating thickness. Kogelnik develops an equation for the coupling constant, $\kappa$, which determines the rate of energy transfer from the incident reference beam ($R$) to the diffracted output beam ($S$).

$$\kappa = \frac{\pi \Delta n}{\lambda} - j\frac{\Delta \alpha}{2}. \quad \text{III-1}$$

Here, $\Delta n$ is the refractive index variation, and $\Delta \alpha$ is the absorption modulation. In our case, it is assumed $\Delta \alpha = 0$. Inside the grating, the electric field vector, which must satisfy the wave equation, can be represented as the sum of the input and output beams.

$$E = R(z)e^{-j\rho x} + S(z)e^{-j(\rho-K)x}. \quad \text{III-2}$$
Fig. II-1: Model used in Kogelnik's Calculations: A Thick Hologram Grating with Slanted Fringes.
where \( \rho \) is the propagation vector of the input beam. The coupled wave equations linking the input beam to the diffracted beam are

\[
\cos \theta \frac{\partial R}{\partial z} + \alpha R = -j \kappa S
\quad \text{III-3a}
\]

and

\[
\left( \cos \theta - \frac{\kappa}{\beta} \cos \phi \right) \frac{\partial S}{\partial z} + (\alpha + j \nu) S = -j \kappa R
\quad \text{III-3b}
\]

where \( \beta \) is the free propagation constant, and \( \nu \) represents a dephasing measure and is given by

\[
\nu \equiv (\beta^2 - \sigma^2) / 2 \beta
\quad \text{III-4}
\]

The solution to the coupled wave equations is

\[
R(z) = r_1 e^{\gamma_1 z} + r_2 e^{\gamma_2 z}
\quad \text{III-5a}
\]

and

\[
S(z) = s_1 e^{\gamma_1 z} + s_2 e^{\gamma_2 z}
\quad \text{III-5b}
\]

where \( r_i \) and \( s_i \) depend upon the boundary conditions and

\[
\gamma_{1,2} = -\frac{1}{2} \left( \frac{\alpha}{\mathcal{C}_R} + \frac{\alpha}{\mathcal{C}_S} + j \frac{\nu}{\mathcal{C}_S} \right)
+ \frac{1}{2} \left[ \left( \frac{\alpha}{\mathcal{C}_R} - \frac{\alpha}{\mathcal{C}_S} - j \frac{\nu}{\mathcal{C}_S} \right)^2 - 4 \left( \frac{\kappa^2}{\mathcal{C}_R \mathcal{C}_S} \right) \right]^{1/2}
\quad \text{III-6}
\]
with

\[ C_R = \cos \theta \]  
\[ C_S = \cos \theta - \frac{K}{\beta} \cos \phi . \]

For the case of a lossy dielectric grating, this solution for the diffracted beam becomes

\[
S = -j \left( \frac{C_R}{C_S} \right)^\frac{1}{2} \exp\left[-\frac{1}{2} D_o (1+c)\right] \sin \left(\frac{\nu \xi}{1 - \xi^2/\nu^2}\right) \]

with the parameters

\[ \nu = \pi d \Delta n / \lambda (C_R C_S)^\frac{1}{2} \]
\[ \xi = \frac{1}{2} D_o \ (1-c) \]
\[ D_o = \alpha d / \cos \theta_o \]
\[ c = \frac{C_R}{C_S} \]

For our applications, \( C_R = C_S \), so that Eq. III- reduces to

\[
S = -j \exp^{-D_o} \sin \left(\pi d \Delta n / \lambda \cos \theta \right) \]

III-10
The diffraction efficiency, \( \eta \), is calculated as

\[
\eta = SS^* \tag{III-11}
\]

where \( * \) represents the complex conjugate. Thus the solution for \( \eta \) reads as

\[
\eta = \sin^2 \left( \frac{\pi d}{\lambda \cos \theta} \Delta n \right) e^{-2ad/cos \theta} \tag{III-12}
\]

This result deserves careful attention. Note that for small values of \( \Delta n \), such that \( \frac{d\Delta n}{\lambda \cos \theta} << 1 \), the \( \sin^2 \) term may be approximated as

\[
\sin^2 \left( \frac{\pi d}{\lambda \cos \theta} \Delta n \right) \approx \left( \frac{\pi d}{\lambda \cos \theta} \Delta n \right)^2 \text{ for } \frac{d\Delta n}{\lambda \cos \theta} << 1 \tag{III-13}
\]

This is commonly referred to as the "quadratic region," i.e., the range of \( \Delta n \) for which the statement

\[
\eta \approx (\Delta n)^2 \tag{III-14}
\]

is approximately valid.
B. Electron Transport Phenomena

in Lithium Niobate

When doped lithium niobate is exposed to visible radiation of approximately 500 nm, a photo voltage or photo current appears between the (+) and (−) c-axis ends of the crystal. For the intensity range used in this paper, the photo current density is proportional to the absorbed power density.

Chen\(^3\) proposed that photoexcited electrons drifted towards the +c end of the crystal under the influence of an intrinsic internal field. He estimated that this field, the origin of which he did not specify, was of the order of 70 kv/cm. This theory did explain his data, but later research produced data inconsistent with it, and it is no longer seriously considered.

Glass, von der Linde, and Negran proposed that the photocurrents were due to a bulk photovoltaic effect.\(^4\) They found that the photocurrent densities were proportional to the absorbed power densities according to the relation

\[ J = \kappa_1 \alpha I \]  

III-15

where \( I \) is the light intensity, \( \alpha \) is the absorption,
and $k_1$ is a constant which depends upon the nature of the absorbing center and the wavelength of the light, but was independent of the impurity concentration. They also found an intensity dependence in the applied electric field necessary to reduce the photocurrent to zero.

$$E_{\text{SAT}} = k_1 \alpha I^{1/2}$$  III-16

The bulk photovoltaic effect was explained by resorting to an asymmetry in the local crystal potential near the donor ion. Previous to this work, the donor ion had been identified as being the Fe$^{2+}$ ion, and the conduction band as being composed basically of Nb-$d\varepsilon$ orbitals. Hence, the absorption transition giving rise to the effect was the Fe$^{2+}$ - Nb$^{5+}$ intervalence transfer. Also, the Fe ion was concluded to occupy the lithium site. Glass, et al., stated that the different Nb-Fe distances in the $\pm c$ directions gave rise to a difference in the intervalence charge transfer probabilities in these directions. Hence, the initial excitation of a large number of electrons would result in a net current in the $+c$ direction. They calculated a mean free path for the electrons of
0.8 Å. This is significantly smaller than one lattice constant in LiNbO₃, indicating that the probabilities in the + c directions are roughly of the same order of magnitude.

Von der Linde and Glass, later modified the theory to incorporate the fact that the Fe ion did not occupy exactly the same location in the lattice before and after photoexcitation.⁶ They presented the following configuration coordinate diagram (Fig. III-2) to illustrate the process. The iron ion is in the divalent state while moving from point B to point C, but is in its trivalent state while moving from point C to point A. Thus we have a net charge movement of 1 electron a distance Δ in the + Q direction. The current density is then given by

\[ J = \frac{F}{h\omega} e^{-\Delta + p_+ l_+ - p_- l_-} \]  

III-17

where \( p_+ \) = probability of intervalence charge from Fe²⁺ to Nb⁵⁺ in the + c direction.

\( l_+ \) = mean free path of photoexcited electron in the + c directions.
Fig. II-2: Configuration Coordinate Diagram Showing Schematically the Energy of a Fe Donor as a Function of Some Representative Vibrational Coordinate
C. Electron Transport in LiNbO$_3$: Fe

In order to form a phase grating in a ferro-electric crystal, the interference pattern resulting from two intersecting writing beams must exist within the crystal. This situation is illustrated in Figure III-3. The intensity pattern is invariant in the y-direction, and its x-dependence is given by

$$I(x) = I_0 (1 + m \cos Kx)$$  \hspace{1cm} \text{III-18}$$

where $m$ is the modulation index, $K = \frac{2\pi}{\Lambda}$ and is the grating vector, and $\Lambda = \frac{\lambda}{2\sin\theta}$ is the fringe spacing of the interference pattern. In the regions of nonzero intensity, photoexcited electrons will be generated at a rate, $g$, given by

$$g(x) = \kappa_2 \alpha I(x)$$  \hspace{1cm} \text{III-19}$$

Since we must concern ourselves with a lossy dielectric medium, the z-dependence is accounted for by the inclusion of a factor of $e^{-az/cos\theta}$ into the equations for intensity. We assume that the photovoltaic conversion constant $\kappa_2$ is not time- or intensity-dependent.
Fig. III-3: Schematic Diagram of Hologram Formation.
This may be restated as an assumption that the density of excitable traps is not significantly affected during hologram formation. If we also assume that the mean free path for an excited electron is much less than a grating wavelength, $\lambda$, then we may state that the free electron distribution will closely follow the light intensity pattern.

There are two separate mechanisms which govern the movement of the free electrons. One is diffusion, a thermal randomization process, and the other is drift, movement due to an applied (or internal) electric field, $E$. In addition, the electrons may experience movement during the photoexcitation process, as described in the previous section.

During writing, the electrons in the high intensity regions are continually being excited and reexcited while gradually moving in the +c direction. Electrons in dark regions of the intensity pattern are not excited, and so the electrons are moving from regions of high intensity to regions of low intensity. However, increasing charge buildup tends to retard further charge movement, and eventually, an equilibrium condition is reached where no further net charge transport is accomplished. This condition is referred to
as 'saturation', and corresponding to the saturation value of charge modulation, there exists a saturation value of electric field, and a saturation value of $\Delta n$, the refractive index variation. These saturation values are dependent upon the photocarrier generation rate, $g$, as given in Eq. III-19, and consequently dependent on intensity, $I$.

**D. Characteristics of Lithium Niobate:**

**The Linear Electro-Optic Effect**

Lithium niobate is a birefringent, uniaxial crystal exhibiting the linear electro-optic effect. The linear electro-optic effect refers to the phenomenon in which the refractive index has a component which is linearly dependent upon the applied electric field. The complete index of refraction may be written as

$$n = n_1 + \Delta n(E) \quad \text{III-20}$$

where $n_1$ is constant, and $\Delta n$ represents the field dependent term.

Since LiNbO$_3$ is birefringent, the refractive index must be represented by two components, one for the electric fields polarized perpendicular to the
c-axis, (the ordinary wave, with refractive index $n_0$), and another for electric fields polarized parallel to the c-axis (the extraordinary wave, with refractive index $n_e$). The relationship between the vector electric field and the anisotropic refractive index consists of a tensor equation, but for the particular application here, one need only be concerned with two of the scalar equations making up the tensor equation. The electric field, $E$, has components only in the c direction, and we look for a $\Delta n$ component in either the ordinary or extraordinary index of refraction. The $\Delta n$ component solved for depends upon the polarization of the probe beam being used. For probe beams with $E \parallel \hat{c}$ we have

$$\Delta n = \frac{1}{2} (n_0)^3 (3.8 \times 10^{-10} \text{ cm/v}) E$$

III-21

and for the probe beams with $E \perp \hat{c}$, we have

$$\Delta n = \frac{1}{2} (n_e)^3 (8.6 \times 10^{-10} \text{ cm/v}) E.$$

Substituting in values for $n_0$ and $n_e$, which are in general frequency dependent, we find, for $\lambda = 6328 \text{ Å},$

$$E \parallel \hat{c} : (\Delta n)_0 = 1.7 \times 10^{-8} E$$
and

\[ \vec{E} \perp \hat{c} : (\Delta n)_{e} = 5.2 \times 10^{-9} E \]

(E in \( \text{v/cm} \))

Thus, it can be seen that for a given value of space-charge field, a much larger value of \( \Delta n \) may be detected by using a probe beam with polarization aligned parallel to the \( \hat{c} \)-axis.

The absorption spectra of \( \text{LiNbO}_3 \) has been extensively studied and documented. (see Appendix 2). The reader is referred to the work of Clark, et al,\(^5\) and Henry and Lange\(^10\) for an in-depth study of the energy band structure of \( \text{LiNbO}_3 \).

E. The Time-Development of the Space Charge Field and the Refractive Index Variation

The solution for \( \Delta n(t) \) can be found from a coupled solution involving the electron density and the space charge field. Working from the general framework laid down by Amodei,\(^7\) a continuity equation for the electron density \( n \) was derived by Kim et al,\(^11\)

\[
\left( \frac{\partial}{\partial t} + \frac{1}{\tau} - D \frac{\partial^2}{\partial x^2} + \mu E \frac{\partial}{\partial x} + \mu \frac{\partial}{\partial x} E \right) n = g(1+m \cos Kx)
\]

III-23
where \( \tau = \) electron trapping time
\( D = \) electron diffusion coefficient
\( \mu = \) electron mobility
\( E = \) internal and bulk photovoltaic field
\( E = \) space charge field due to transported charge

The generation rate \( g \) is

\[
g = \frac{i_0 N}{\hbar \omega}
\]

where \( \sigma = \) absorption cross section
\( \dot{N} = \) donor concentration,

the modulation ratio is \( m \), and \( K = 4\pi \sin \theta / \lambda \) is the grating vector with \( \theta \) the writing half angle.

Note that the last term on the left side of Eq. III-23 is the electron drift arising from the space charge field. This equation can be solved by choosing a solution for \( n \) and \( E \) of the form of an infinite series of exponential terms

\[
\dot{n} = \sum_{p=-\infty}^{+\infty} \dot{n}_p(t) e^{ipkx} \quad \text{III-24a}
\]

and

\[
E = \sum_{p=-\infty}^{+\infty} E_p(t) e^{ipkx} \quad \text{III-24b}
\]
Kim then considers only the fundamental modes of \( \hat{n} \) and \( \xi \), and introducing the following quantities

\[
\tau_g = \frac{\varepsilon}{\mu g' r} \quad \text{III-25a}
\]

\[
f = \frac{(1+K^2 L')^2}{[(1+K^2 L')^2 + K^2 L^2]} \quad \text{III-25b}
\]

\[
f' = KL/[(1+K^2 L')^2 + K^2 L^2] \quad \text{III-25c}
\]

the amplitude \( A(t) \) and the phase \( \phi_g(t) \) of the space charge field can be written as

\[
A(t) = m[F_C^2(t) + F_S^2(t)]^{\frac{1}{2}} \quad \text{III-26a}
\]

\[
\phi_g(t) = \tan^{-1}\left[\frac{F_S(t)}{F_C(t)}\right] \quad \text{III-26b}
\]

where \( F_C(t) \) and \( F_S(t) \) are the in-phase and quadrature amplitude components

\[
F_C(t) = E[1-e^{-ft/\tau_g} \cos(f't/\tau_g)] - (D K/\mu)e^{-ft/\tau_g} \sin(f't/\tau_g) \quad \text{III-27a}
\]
\[ F_s(t) = E e^{-ft/\tau_g} \sin(f't/\tau_g) \]

\[ + (D K/\mu) [1-e^{-ft/\tau_g} \cos(f't/\tau_g)] \]

The space charge field asymptotically approaches its saturation value, while, \( \phi_g \), the phase angle between the light intensity pattern and the space charge field decreases approximately exponentially in time, approaching its saturation value.

An expression for the diffraction efficiency \( \eta \) can be arrived at using series of Bessel functions,\(^{12}\) and the expression derived by Uchida, is quite complex (see his Eq. 8b). Kim et al, have adapted his theoretical result to their particular application, and have published graphs of the time dependence of \( \eta \).\(^{13}\) Figure III-4 is a repeat of Figure 1-c from Ref. [13]. The diffraction efficiency is seen to execute a fast initial rise followed by damped oscillations of increasing period about a saturation value.

1. Decay of \( \Delta n \).

When the writing process terminates, the photocarrier generation rate becomes zero. The continuous photogeneration of carriers is no longer available
Fig. III-4: Theoretical Diffraction Efficiency Curves Plotted as a Function of Time for Four Intensities: $I_1 = 2I_2 = 4I_3 = 8I_4 = 12 \text{ mW/cm}^2$. [from Ref. (13)].
to the charges. The situation can be reduced to a non-uniform charge distribution in a dielectric medium. If the refractive index variation, $\Delta n$, is equal to some $\Delta n_0$ at the end of the writing period, then the time behavior of $\Delta n(t)$ during the decay period should be given by $^4,^{14},^{15}$

$$\Delta n(t) = \Delta n_0 e^{-t/\tau}, \tag{III-28a}$$

where $\tau$ is the dielectric relaxation constant, and is given by

$$\tau = \frac{\varepsilon}{\sigma}, \tag{III-28b}$$

$\varepsilon$ and $\sigma$ being the permittivity and dark conductivity, respectively. This may be substituted into a $\Delta n$ dependent equation for $\eta$, and with $I=0$, we will have a description of $\eta$ during decay. However, interpretation of the resulting formula is not trivial, especially if one begins with Uchida's Bessel function expression (Eq. 8b in Ref. 12), or Kim's results (Eq. 5 in Ref. 13).

The only easily manageable function that is available is Kogelnik's $\sin^2$ expression. This has been
widely accepted as accurate during the early stages of hologram formation, and results in the familiar quadratic beginning of the $\eta$ vs. $t$ writing curve. The quadratic effect occurs primarily for $\eta < 10\%$. If the hologram formation is halted during this quadratic period, the decay of $\eta$ will be described by

$$\eta(t) = \sin^2 \left( \frac{\pi d}{\lambda \cos \theta} \Delta n_o e^{t'/\tau} \right). \quad \text{III-29}$$

Here $t'$ represents time measured from the beginning of the decay period.

We first make the substitution

$$A = \frac{\pi d \Delta n_o}{\lambda \cos \theta}, \quad \text{III-30}$$

and then implement the McClaurin series for the sine function

$$\sin x = \sum_{K=1}^{\infty} \frac{(-1)^K x^{2K-1}}{(2K-1)!}. \quad \text{III-31}$$

The result is

$$\eta(t') = \left[ \sum_{R=1}^{\infty} \frac{(-1)^{K-1} (\Delta e^{-t'/\tau})^{2K-1}}{(2K-1)!} \right]. \quad \text{III-32a}$$
\[
\sum_{R=1}^{+\infty} \frac{(-1)^{K-1}(Ae^{-t'/\tau})^{2K-1}}{(2K-1)!} \\
\sum_{m=1}^{+\infty} \frac{(-1)^{m-1}(Ae^{-t'/\tau})^{2m-1}}{(2m-1)!} \\
= \sum_{R=1}^{+\infty} \sum_{m=1}^{+\infty} (-1)^{K+m-2} \frac{A^{2n+2m-2}}{(2K-1)!(2m-1)!} \\
X e^{-(2K+2m-2)t'/\tau}
\]

The resulting sum of exponential terms for \( \eta \) are in even powers of \( e^{-t'/\tau} \). Table III-2 shows an example of the relative magnitudes of the coefficients for these powers of \( e^{-t'/\tau} \).

It can be seen that for a given experimental decay curve, meeting the restrictions of Kogelnik's equation, we can fit the above exponential expression to the data using a Graham-Schmidt technique, and so determine the characteristic relaxation time to a high degree of accuracy. The dark conductivity, \( \sigma_D \), may be determined to an accuracy dependent on the exactness of \( \varepsilon \).

When \( \Delta n \) is allowed to develop to saturation, the expressions governing its time-development become rather complex, and the substitution \( \Delta n_0 e^{-t'/\tau} \) for
<table>
<thead>
<tr>
<th>Power of $e^{-2nt/\tau}$</th>
<th>Indices $(k,m)$ involved</th>
<th>Amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 \ (n=1)</td>
<td>(1,1)</td>
<td>+ 0.098796...</td>
</tr>
<tr>
<td>4 \ (n=2)</td>
<td>(1,2)*</td>
<td>- 0.003247...</td>
</tr>
<tr>
<td>6 \ (n=3)</td>
<td>(2,2)</td>
<td>+ 0.000027...</td>
</tr>
<tr>
<td></td>
<td>(1,3)</td>
<td>+ 0.000016...</td>
</tr>
<tr>
<td>8 \ (n=4)</td>
<td>(2,3)</td>
<td>- 2.63x10^{-7}</td>
</tr>
<tr>
<td></td>
<td>(1,4)</td>
<td>- 3.76x10^{-9}</td>
</tr>
<tr>
<td>10 \ (n=5)</td>
<td>(3,3)</td>
<td>+ 6.5 x 10^{-10}</td>
</tr>
<tr>
<td></td>
<td>(2,4)</td>
<td>+ 6.2 x 10^{-10}</td>
</tr>
<tr>
<td></td>
<td>(1,5)</td>
<td>+5.2 x 10^{-10}</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td></td>
<td>+0.095592</td>
</tr>
</tbody>
</table>

*Note that a pair $(i,j)$ implies the reverse order $(j,i)$ as well. Amplitude given above is the sum of the amplitudes for the 2 crossterms.
Δn does not lead to any immediate conclusions.

Graphically, the history of Δn(t) through writing and decay may be shown as in Figure III-5.

In the above diagram, let Δn₁₋₄ represent the values of Δn which result in maxima and minima in the n vs. t curve. It can be seen that these extrema will occur at times t₁₋₄ during the writing process.

Now, as Δn(t) decays, it reaches, in reverse order, each of the values Δn₁₋₄ where extrema occurred during writing. These values, Δn₄₋₁, will be reached at decay times t'₄₋₁, respectively. At each point in time, an extrema of the decay curve will occur. Thus, the decay curve will trace the same pattern of oscillations shown in the writing curve, but with a reversed and modified time scale.
Fig. III-5: Schematic of Time Development of $\Delta n$ During Writing and Decay.
CHAPTER IV

EXPERIMENTAL DATA

In this chapter, the experimental data are presented and described. Part A describes the effects due to the HeNe beam monitoring technique. Part B describes the writing curves and their dependence on intensity and crystal doping. In Part C, the decay curves are presented and examined. Finally, the results are compared to the theory and other researchers' data in Part D.

A. Accuracy of 6328 Å Probe Beam Technique

Nearly all of the data collected for this work consists of measurement of $\eta$ by means of a low intensity 6328 Å beam from a helium-neon laser. The accuracy of this technique is crucial to the validity of all the data taken using this method.

Repeated experiments on the absorption factors of our crystals at 4880 and 6328 Å have given the following results:
### TABLE IV-1

Transmittances of crystals at $\lambda = 4880$ Å and 6328 Å as a function of iron concentration. For all crystals, the thickness is 1.0 mm.

<table>
<thead>
<tr>
<th>Crystal #</th>
<th>Doping Concentration+ (cm$^{-3}$)</th>
<th>Transmittance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$4 \times 10^{18}$</td>
<td>$74.1$ $75.0$</td>
</tr>
<tr>
<td>9</td>
<td>$2 \times 10^{19}$</td>
<td>$8.6 \pm 1.4$</td>
</tr>
<tr>
<td>12</td>
<td>$4 \times 10^{19}$</td>
<td>$6.7 \pm 0.4$</td>
</tr>
<tr>
<td>6</td>
<td>$4 \times 10^{19}$</td>
<td>$5.6 \pm 0.3$</td>
</tr>
</tbody>
</table>

*These values were supplied by the manufacturer, and are approximate.*
Table IV-1 shows what has been found before, i.e., that LiNbO$_3$: Fe is highly absorbing near the argon ion laser lines, and less so for longer wavelengths. During experiments, the intensity of the 6328 Å read beam was kept below the single writing beam intensity by at least two orders of magnitude. The energy density absorbed by the crystal from each of the two beams for a constant time interval, T, may be calculated as

$$ IT \left(1-e^{-\alpha d}\right) $$

where $I$, and $\alpha$ are the power density, and absorption coefficient for the radiation in question. The crystal thickness is $d$.

Typical experimental values for the writing and reading beam power densities are 10 mW/cm$^2$ and 100 $\mu$W/cm$^2$, respectively. The resulting absorbed energy densities in a 0.1% Fe doped crystal for a one second interval are 9.33 mJ/cm$^2$ and 56.2 $\mu$J/cm$^2$, respectively. It can be seen from this that less than 1% of the total energy absorbed by the crystal is due to absorption of 6328 Å radiation. This is within the experimental error, and so from a strict energy input viewpoint, the presence of the reading beam should not affect the accuracy of the experimental data.
Two photon absorption has been seen in LiNbO$_3$, but does not occur for such low intensities ($I < 1 \text{ W/cm}^2$). The 6328 Å radiation cannot affect the performance of the crystal through this process.

Finally, experiments with and without the 6328 Å beam were performed. The results agree to within experimental accuracy and the data curves are shown in Figure IV-1.

B. Experimental Data on the Writing Process

The experimental writing curves are presented in Figures 2-5 in terms of $\eta$ vs. exposure time, with the parameter, $I$, beam intensity. The polarization of the reading beam is also varied from $\vec{E} \perp \hat{c}$ to $\vec{E} \parallel \hat{c}$.

The diffraction efficiency at the first maxima has been predicted to be approximately 80%. However, not all of the data curves shown depict this. Many curves execute oscillations without ever reaching an $\eta$ value greater than 50%. This problem of chronically low $\eta$ values cannot be attributed to the writing process, for the curves progress through the extrema of $\eta$ to saturation with typical time scales. One possible cause of this effect is a symptomatic problem in the beam alignment process.
Fig. IV-1: Writing Curves $\eta$ vs. $t_{\text{writing}}$, with and without HeNe probe beam.
Fig. IV-2: $\eta$ vs $t$, Crystal 9, Writing Process Stopped at $3^{rd}$ Maxima.
Fig. IV-3: $\eta$ vs $t$, Crystal 12, Writing Process Stopped After 2\textsuperscript{nd} Maxima.
Fig. IV-4: $\eta$ vs $t$, Crystal 6, Writing Process Stopped After 1st maxima.
Fig. IV-5: \( n \) vs \( t \), Crystal 9. Writing Process Stopped Before 1st Maxima.
are all important, and must be constantly kept in adjustment. Also, it must be realized that here one is interested in rates of decay, so that this problem will not affect the information extracted from the curves.

With this factor in mind, one can examine the writing sensitivities for these experiments. Sensitivity is calculated using the following formula:

\[ \text{P.R.S.} = I_o T_o \]

where \( I_o \) is the total energy density present in both writing beams as incident on the front crystal face, and \( T_o \) represents the time required to form a hologram with \( \eta_{6328\AA}^o = 1\% \). No effort is made to correct for energy lost through reflections on transmission, because the P.R.S. should indicate how much total energy is required to achieve diffraction. Note also that \( \eta \) at 6328 \( \AA \) is used, and not \( \eta \) at the writing wavelength, as is more common.

The time \( T_o \) is determined according to the following algorithm. Data points for \( \eta < 10\% \) are measured from the data strip chart and plotted against exposure time on a log-log plot to show the power dependence of \( \eta \) on \( t \).
This will graphically demonstrate the range over which Kogelnik's $\sin^2(t)$ expression is accurate. Figures 8-9 show these "quadratic" regions. We find that the behavior is still mainly quadratic up to 10%, and that below ~6%, the behavior can be considered only quadratic. Once a quadratic line is fit to the data points, $T_0$ can be found from the intercept of the quadratic line and the $n = 1\%$ line.

C. EXPERIMENTAL DATA ON THE DECAY PROCESS

The decay curves were obtained by periodically measuring the $n$ of grating by means of a 2 second pulse of 6328 Å laser light incident at the Bragg angle. The measurement interval was set at 1.25 minutes for the first 5-15 minutes of decay, and then set a ~15.25 minute interval for the remainder of the decay record.

In all cases, it is clear that the behavior of $n$ during decay is a time-reversed and distorted image of curve. The number and type of extrema in the writing curve are duplicated by the extrema of the decay curve. This is illustrated in Figure IV-9. In some cases, a slight enhancement effect can be seen, but the magnitude of such enhancement effects is small compared to the magnitude of a typical oscillation.
Fig. IV-6: $\ln \eta$ vs $t$, Crystal X9, Quadratic Region of the Writing Process. Initial Sensitivity = 91. mJ/cm$^2$.  

$T_0 = 4.2$ sec.
Fig. IV-7: ln \( n \) vs \( t \), Crystal X6, Quadratic Region of the Writing Process. Sensitivity = 98. mJ/cm\(^2\).
Fig. IV-8: In \( n \) vs \( t \), Crystal X12, Quadratic Region of the Writing Process. Initial Sensitivity = 110. mJ/cm\(^2\).
Fig. IV-9: Write-Decay Curve Pair Showing Retrace. (Note Differences in Time Scales).
This "retracing" is a direct result of the fact that \( \eta \) depends primarily on the value of \( \Delta n \), and has no dependence on the time derivatives of \( \Delta n \). That is, there is only a dependence on the instantaneous value of \( \Delta n \), with no concern for the past history of \( \Delta n \) in time. As \( \Delta n \) develops during writing, it increases through certain values corresponding to the extrema exhibited by \( \eta \) in the writing curve (Figure IV-10a,b). During decay, \( \Delta n \) must decrease through these same values, but now in reverse order (Figure IV-10c,d). In doing so, the entire writing history is traced out, only backwards, and with a nonlinearly modified time scale. The magnitudes of the two curves show complete agreement within experimental error.

The "enhancement" effect, as first mentioned by Amodei and Staebler,\textsuperscript{14} is usually seen only in holograms written to low value of \( \Delta n \). As they stated, enhancement occurs when the diffraction efficiency of a grating improves when the reading beam is incident on the hologram. The effect is due to constructive interference between the incident beam, the diffracted beam, and the grating present. The effect cannot cause large changes in \( \Delta n \), because it consists of only a small amount of charge transfer. Hence, when hologram gratings of medium
Fig. IV-10: Schematic Relating Time Development of $\Delta n$ to the Extrema in the $\eta$ Writing and Decay Curves.
to high $\Delta n$ initial values begin to decay, the large charge transference of the decay process effectively masks any enhancement effects. Also, the technique of intermittent reading during decay helps to maintain enhancement effects to a minimum by minimizing the time of interaction between reading beam and grating.

D. Comparison with Previous Work

(1) The writing curves agree well with previously published theories and experimental data. All curves show the predicted characteristics such as the initial quadratic region, and oscillations for long exposures. An example of the reproducibility of the curves may be seen in Figure IV-11. The agreement is well within experimental error. This reproducibility may be taken as firm evidence of the accuracy and repeatability of the experimental alignment technique described in Chapter III. The repeatability of curves extending beyond the initial quadratic region can be expected to be of slightly lower quality. Figure IV-12 compares several long exposure writing curves. This discrepancy is due to the extreme sensitivity of the writing process upon the beam alignment. This problem of critical alignment is aggravated by the low power and less than optimal
Fig. IV-11: Comparison of 2 Writing Curves to Show Reproducibility (Quadratic Region).
Fig. IV-12: Long Exposure Comparison of 2 Writing Curves.
beam pattern present in the output of the argon ion laser. Figure IV-12a shows a typical example of the consequences of misalignment. The two experiments were done with very similar writing intensities, and so the extrema should occur at near the same values of exposure. However, one curve has its first maxima at 0.8 J/cm$^2$, while the other is at 1.2 J/cm$^2$.

(2) Here is presented the data on the decay of holograms. The reproducibility of the data is within 20%. This is shown in Figure IV-13. All decay curves exhibit the "retrace" effect, where the decay curve is a reversed image of the writing curve, with a modified time scale.

As discussed in Chapter II for quadratic region holograms, the classical theory predicts an exponential decay of the hologram with a time constant proportional to the dark conductivity of the material. Hence it should be possible to determine the dark conductivity by measuring the slope of a plot of $\ln \eta$ vs. $t_{\text{decay}}$. Such a plot is presented in Figure IV-13. One cannot help but notice the sizable deviation from a constant slope function. The decay constant is initially very low, corresponding to a fast decay, but the rate of decay decreases continually to a much lower final value.
Fig. IV-12a: Two Long Exposure Writing Curves Showing Slight Beam Misalignment.
Fig. IV-13: $\ln \eta$ vs $t$ for 2 Experiments, Showing Non-Constant Decay Rate and Reproducibility.
This disagreement with classical theory also appears at the end of oscillatory decay curves.

Steps were taken to insure that this effect was a true effect caused by the hologram decay, and not some experimental artifact. The PM tube used for monitoring the diffracted beam was exchanged for a CRL Model 212 photodiode detector operating independently of the 120 VAC line in order to eliminate all possible external electrical effects on the output signal. No change in the forms of the decay curves was noted after repeated rotations of the detectors. Temperature was monitored and found to be within ± 5. degrees Centigrade of room temperature (23°C) during the decay period. On many experiments the temperature was constant to within 2°C.

This effect of a changing decay constant can be quantified by measuring the decay rate of each decay curve at a specific value of diffraction efficiency. In this manner, the decay rates as a function of crystal doping and of elapsed time to the measurement point may be calculated. If the decay constant of the material were truly constant, then the decay rate would be constant as a function of elapsed time. But if \( \tau(= 1/\text{calculated decay rate}) \) is plotted vs. decay time, \( \tau \) is initially
seen to increase very rapidly, and appears to show asymptotic behavior, with the value of the asymptote being dependent upon crystal doping (Fig. IV-14). Analysis of these results, and a proposed model to account for the effect, are presented in the next Chapter.
Fig. IV-14: $\tau(t)$, Decay Constant (Measured at $\eta = 10\%$) vs $t$, Decay Time, as a Function of Crystal Doping.
CHAPTER V

DISCUSSION

A. Introduction of Décaying Conductivity

From the classical model of hologram decay, we know that the decay constant, \( \tau \), can be found from the physical parameters of the material by the equation \(^4,15\)

\[
\tau = \frac{e}{\sigma} \quad \text{(V-1)}
\]

where \( e \) is the permittivity of the material and \( \sigma \) represents the conductance. If, however, \( \tau \) is found to be a function of time, then either the permittivity, the conductivity, or both quantities, must also be time-dependent. Permittivity has been found to be dependent on frequency and temperature, but for crystalline materials of this class, \( e \) is always considered constant, and it is assumed that \( e \) shows a negligible time dependence. Hence the decay constant may be written as

\[
\tau(t) = \frac{e}{\sigma(t)} \quad . \quad \text{(V-2)}
\]
So it can be seen that these decay curves show a decaying conductivity during the period after hologram writing.

1. Transient Conductivity

The expression for the conductivity should contain a monotonically decreasing term, $\sigma'(t)$, and a constant term due to dark conductivity, $\sigma_D$, i.e.,

$$\sigma(t) = \sigma_D + \sigma'(t).$$

It was found that by giving the transient term the form

$$\sigma'(t) = \sigma_1 e^{-t/\tau_T},$$

an excellent fit to the data could be achieved. $\tau_T$ represents the lifetime of the transient conductivity. Here, dark conductivity is defined as the intrinsic conductivity of the sample under no illumination, with the additional requirement that the sample must have been in dark conditions for a period sufficiently long such that all long term effects from past illumination have become negligible.
The decay of the electric field due to the decaying charge build up may be found from the relation

\[ E(t) = E_0 \exp\left[ - \int_0^t \frac{\sigma(t')}{\varepsilon} \, dt' \right] \tag{V-5} \]

The integral in the exponent may be easily solved by substitution of Equation V-3,4

\[
\int_0^t \frac{\sigma(t')}{\varepsilon} \, dt' = \frac{1}{\varepsilon} \int_0^t (\sigma_0 + \sigma_1 e^{-t'/\tau_T}) \, dt' \\
= \frac{1}{\varepsilon} \left[ \int_0^t \sigma_0 \, dt' + \int_0^t \sigma_1 e^{-t'/\tau_T} \, dt' \right] \\
= \frac{1}{\varepsilon} \left[ \sigma_0 t + (-\sigma_1 \tau_T) \left( e^{-et/\tau_T} - 1 \right) \right] \\
= \frac{\sigma_0}{\varepsilon} t + \frac{\sigma_1 \tau_T}{\varepsilon} (1 - e^{-t/\tau_T}) \tag{V-6}
\]

Returning to Equation V-5, we now have

\[ E(t) = E_0 \exp\left[ - \frac{\sigma_0}{\varepsilon} t - \frac{\sigma_1 \tau_T}{\varepsilon} (1-e^{-t/\tau_T}) \right] \tag{V-7} \]

If attention is restricted to the quadratic region, that is, when \( \Delta n \) (the refractive index change) is small enough such that \( \sin^2 (\Delta n) = (\Delta n)^2 \), then we
may also regard $\eta$ as proportional to $(\Delta n)^2$. We also find that $\Delta n$ is proportional to $E$, so that $\eta$ is proportional to $E^2$. Hence we can write the time development of $\eta$ during decay as

$$\eta(t) = \eta_0 \exp[-2 \left( \frac{\sigma_0}{\epsilon} t + \frac{\sigma_1 r}{\epsilon} (1 - e^{-t/r_T}) \right)]$$

Here, $\eta_0$ represents the initial value of the diffraction efficiency. Note here the implicit assumption that writing ends and decay begins all within the quadratic region.

2. Behavior of the Effective Decay Constant, $\tau_{\text{EFF}}(t)$

In Chapter 4, experimental data was shown in the form of $\tau_{\text{EFF}}$ vs. decay time. This effective decay time, $\tau_{\text{EFF}}$, is merely the reciprocal of the slope of the curve of $\ln \eta$ vs. decay time. In other words,

$$\tau_{\text{EFF}}(t) = \frac{1}{b(t)}$$

where $b(t)$ is defined by
Thus we have

\[ \frac{\partial}{\partial t} \left[ \frac{\sigma_0}{\varepsilon} t + \frac{\sigma_1 \tau_T}{\varepsilon} \left(1 - e^{-t/\tau_T}\right) \right] \]

\[= \frac{\sigma_0}{\varepsilon} + \frac{\sigma_1}{\varepsilon} e^{-t/\tau_T}. \tag{V-10} \]

\[\tau_{\text{EFF}}(t) = \left(\frac{\sigma_0}{\varepsilon} + \frac{\sigma_1}{\varepsilon} e^{-t/\tau_T}\right)^{-1}. \tag{V-11} \]

\textbf{B. Comparison of Model to Experimental Data}

Equations V-8 and V-11 are able to fit the experimental data quite well. Note here that the restriction that \( \eta \) be within the quadratic region is still valid. The theoretical fits to the experimental decay curves are shown in Figures V-1 through V-7. It is crucial to note here that the best fit values for \( \tau_T \) are larger for experimental decay curves spanning the larger decay time intervals. For curves reaching the longest values for decay time, the curve fits show that there is essentially no transient conductivity left. This may be interpreted as evidence of the time dependence of \( \tau_{\text{EFF}}(t) \). The implications here are that a single decay curve does not cover a broad enough time interval to accurately determine \( \tau_T \). One either has a short-time
Fig. V-1: $\ln \eta$ vs $t$, the Theoretical Fit, and the Coefficients Used.
Fig. V-2: $\ln \eta$ vs $t$, the Theoretical Fit, and the Coefficients Used.

\[
\frac{\sigma_1}{\xi_0} = 1.16 \times 10^{-2} \text{ (min)}^{-1}
\]

\[
\gamma = 122 \text{ min}
\]

\[
\frac{\sigma_0}{\xi_0} = 1.56 \times 10^{-3} \text{ (min)}^{-1}
\]
Fig. V-3: $\ln n$ vs $t$, the Theoretical Fit, and the Coefficients Used.

$\frac{\sigma}{\sigma_0} = 8.90 \times 10^{-3} \text{(min)}^{-1}$

$\tau = 125.9 \text{ min}$

$\frac{\sigma}{\sigma_0} = 1.83 \times 10^{-3} \text{(min)}^{-1}$
$\frac{\sigma_t}{\sigma_0} = 6.87 \times 10^{-3} \text{(min)}^{-1}$

$\tau = 167.3 \text{ min}$

$\frac{\sigma_0}{\sigma_t} = 1.41 \times 10^{-3} \text{(min)}^{-1}$

Fig. V-4: In $n$ vs $t$, the Theoretical Fit, and the Coefficients Used.
Fig. V-5: In $\eta$ vs $t$, the Theoretical Fit, and the Coefficient Used.

$$\frac{\sigma}{\epsilon_o} = 4.63 \times 10^{-4} \text{(min)}^{-1}$$

$$\tau = 952.2 \text{ min}$$

$$\frac{\sigma}{\epsilon_o} = 7.66 \times 10^{-4} \text{(min)}^{-1}$$
Fig. V-6: $\ln \eta$ vs $t$, the Theoretical Fit, and the Coefficients Used.

$\frac{\sigma_0}{\gamma} = 5.96 \times 10^{-4} (\text{MIN}^{-1})$
Fig. V-7: In $\eta$ vs $t$, the Theoretical Fit, and the Coefficient Used.
curve in the quadratic region which does not provide sufficient information about the true value of \( \sigma_0 \), or one obtains an oscillating curve, in which case one may determine \( \sigma_0 \), but all information about \( \sigma_1 \) is lost. The solution here is to utilize all of the decay curves to form a plot of the effective decay constant, \( \tau_{\text{EFF}} \), as a function of decay time. This may be done by finding the decay rate at a fixed value of \( \eta \) on each curve. These rates are then plotted versus the decay time applicable for each decay curve. For example, for the decay curve sketched in Figure V-8, we find the slope at a given value of \( \eta \). Since these equations have been calculated for the quadratic region, the data points must have some common value of \( \eta \) within the quadratic region. The common point is arbitrary, and \( \eta = 10\% \) has been chosen. A very good estimate of the slope at \( \eta = 10\% \) can be obtained by fitting a simple exponential to a few data points grouped around the \( \eta = 10\% \) point. The values of \( \tau_{\text{EFF}} (= 1/b \) from Figure V-8) are then plotted versus the values of decay time. The result is shown in Figure IV-14.

This plot shows a family of curves, each corresponding to a particular crystal. These curves are well fit by Equation V-17. The comparison between experimental
Fig. V-8: Sketch Showing Method of Determining Decay Constant at an Arbitrary Value (10%) of Diffraction Efficiency.
and theoretical curves is shown in Figure V-9. The fit to the data points is quite good. The asymptotic value can be seen to vary with crystal doping, which corresponds to dark conductivity varying with doping, as is proper. From the theoretical curve fits, we can find the physical parameters for each crystal. These values are tabulated in Table V-1.

As can be seen from the table, the value for the transient conductivity lifetime varies from crystal to crystal. The lifetime, \( \tau_T \), as well as the magnitude of the effect, as measured by \( \sigma_1 \), increase with doping concentration. Note also that the values for \( \sigma_0 \), the dark conductivity, vary even between crystals 6 and 12, which are supposedly of the same doping. We can see then that the doping concentrations supplied by the manufacturer are only approximate. Instead, if we use \( \sigma_0 \) as a rough measure of doping concentration, we may plot \( \tau_T \) and \( \sigma_1 \) versus \( \sigma_0 \) to get an idea of how these two quantities vary with doping level. These plots are shown in Figure V-10. One can see here that \( \tau_T \) increases with doping, while \( \sigma_1 \) decreases with doping. Even though \( \sigma_1 \) decreases with doping, its minimum value (9.0 \( \times \) \( 10^{-15} \) (ohm-cm)\(^{-1} \) for X6), is still three times larger than the dark conductivity for that crystal.
<table>
<thead>
<tr>
<th>Crystal</th>
<th>Doping concentration</th>
<th>$\sigma_0$, dark conductivity (Ω-cm)$^{-1}$</th>
<th>$\sigma_t$, transient conductivity (Ω-cm)$^{-1}$</th>
<th>$\tau$, trap lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.1 4×10$^{19}$</td>
<td>3.5×10$^{-15}$</td>
<td>9.0×10$^{-15}$</td>
<td>5.8×10$^{4}$</td>
</tr>
<tr>
<td>9</td>
<td>0.05 2×10$^{19}$</td>
<td>2.1×10$^{-15}$</td>
<td>4.7×10$^{-14}$</td>
<td>6.7×10$^{3}$</td>
</tr>
<tr>
<td>12</td>
<td>0.1 4×10$^{19}$</td>
<td>2.6×10$^{-15}$</td>
<td>2.1×10$^{-14}$</td>
<td>2.2×10$^{4}$</td>
</tr>
</tbody>
</table>

**TABLE V-1**
Decay time to $\eta = 10\%$ point (minutes)

Fig. V-9: Log-log Plot of Measured Decay Rate $\tau_{\text{EFF}}$ (at $\eta = 10\%$) vs Decay Time $t$, and Calculated Curves from Eq. V-17.
Fig. V-10: Transient Conductivity, $\sigma_\perp$, and "Trap" Lifetime, $\tau_T$, vs Dark Conductivity $\sigma_0$. 

$\tau_T$, trap lifetime (seconds)

$\sigma_\perp$, transient conductivity (ohm-cm)$^{-1}$

$\sigma_0$, dark conductivity (ohm-cm)$^{-1}$
(3.5 \times 10^{-15} \text{(ohm-cm)}^{-1}). For crystal 9, the ratio of \( \sigma_1 / \sigma_0 \) is even larger, being approximately 22.

C. Proposed Model

1. Metastable Trapping Centers

If the change in conductivity is attributed to a change in the conduction electron density, then the relation between the conductivity \( \sigma(t) \) and the electron density \( n(t) \) is given by

\[
\sigma(t) = e \mu n(t)
\]

where \( e \) is the electronic charge and \( \mu \) is the electron mobility. This implies

\[
n(t) = n_0 + n'(t)
\]

where

\[
n_0 = \frac{\sigma_0}{e \mu}
\]

and

\[
n'(t) = \frac{\sigma_1}{e \mu} e^{-t/\tau_T}
\]
A possible model to explain this phenomenon involves a metastable (long-lifetime) electron trapping center. These trapping centers, which are at present unidentified, trap electrons from the conduction band during the hologram formation process, and after the writing process has terminated, begin to release their trapped electrons back into the conduction band with a characteristic lifetime $\tau_{\text{TRAP}}$.

It is assumed that the magnitude of the electron flow density into and out of these traps is negligible when compared to the electron flow due to photogeneration. However, in decay conditions, the contributions from these traps to the conduction electron density creates changes in the conductivity comparable in magnitude to the intrinsic dark conductivity. Assumptions about the magnitudes of these various components must be made because the conductivities are so small as to render direct measurements impractical for all but the largest photoconductivity measurements. Final results will be shown to be consistent with these assumptions.

The rate equations for the decay process may be developed in terms of the conduction band density $N_c$, and an associated decay constant $\tau_c$, and the filled trap density $N_T$, with its lifetime $\tau_T$. Since the traps
are hypothesized to excite into the conduction band, one may write

$$\frac{3N_c}{\partial t} = - \frac{N_c}{\tau_C} + \frac{N_T}{\tau_T} \tag{V-14}$$

for the conduction band, and

$$\frac{3N_T}{\partial t} = - \frac{N_T}{\tau_T} \tag{V-15}$$

for the trapping centers.

In order for the trapping centers to significantly affect the rate of hologram decay, the two terms on the R.H.S. of Eq. V-14 must be comparable in magnitude. This requires that $N_T$ be on the order of $10^{19}$ cm$^{-3}$, which is a bit high for a defect concentration. This point is the primary disadvantage of this model.

**D. Limitations of the Model**

The preceding model is, of course, an approximation. The rationale behind this usage is presented in this section.

1. **Origins of the Model**

Previous work has shown that the addition of metal impurities (Fe, Cr, Mn, etc.) to LiNbO$_3$ result in a more conductive material.$^{1,9,15}$ This is partially due to the addition of the "free" electrons associated with the metal.
ions. In the process of grating formation, the electrons are redistributed, forming alternating regions of high Fe$^{3+}$ or Fe$^{2+}$ ion densities. It is reasonable to expect that regions of high Fe$^{3+}$ density will display a smaller conductivity than regions of high Fe$^{2+}$ density. Hence, the conductivity terms appearing in Maxwell's equations must be assumed to be both time- and space-dependent. The time-dependency is required since the electron density, and hence the conductivity, eventually returns to a uniform equilibrium value. Also, for a strictly rigorous treatment, the time- and space-dependence of the permittivity, $\varepsilon$, must be accounted for.

Governing Differential Equations

An initial approximation of the decay process may be made by looking at the uniform grating as considered by Kogelnik. This grating is assumed constant in the $\hat{y}$ and $\hat{z}$ directions. One may then construct the differential equations from Maxwell's equations, including the time- and space-dependencies in $\sigma$ and $\varepsilon$, as mentioned above. The resulting equations are second-order and non-linear. The assumptions utilized are that $\varepsilon$ changes little in time in comparison to $\varepsilon_0$, so that derivatives of $\varepsilon$ with respect to time are negligible. The variations in $\sigma$ are not small enough to be neglected. The current density $\bar{J}$
is assumed to consist of a conduction term of $\sigma E$, but no convection ($\rho V$). It can be shown that the equations cannot be solved unless a time-dependent conductivity is assumed, and that the solution is not a simple exponential in any case.

The solution used in this chapter is a compromise of the exact solution and a simple exponential solution. The complete closed form solution has not yet been obtained.
E. Previous Work by Other Researchers

Prior to this work, very little work involving the decay of holograms has been done. Most references to decay processes merely state that the behavior is exponential. Glass, et al.,\textsuperscript{4} quoted an exponential behavior with a characteristic relaxation time of 200 seconds, corresponding to a dark conductivity of $1.4 \times 10^{-12} \text{ (ohm-cm)}^{-1}$. The crystal doping was not specified. This conductivity is two to three orders of magnitude higher than the measured values presented here. If metastable centers were active in his sample, a high value of conductivity could be found if the measurements were taken only a few minutes after exposure to light.

Research by Ishida, et al.,\textsuperscript{15} in the area of hologram erasure has shown that during erasure with an erasure beam at near normal incidence, the diffraction efficiency decays monotonically with exponential behavior. They do not quote any time constants. This result is not inconsistent with the present work in that in Ishida's case, the conductivity of the material would be dominated by the photoconductivity due to the erasure beam, and the transient conductivity effects would be masked. Hence, the decay would be exponential with a characteristic relaxation time given by

$$\tau = \varepsilon/\sigma_{ph}$$

where $\sigma_{ph}$ is the photoconductivity.
Exponential loss of $\eta$ by erasure has also been found by von der Linde and Glass.¹⁶ They found that the exponential time constant was approximately 1 second, with an erasure beam of intensity of 1 W/cm². Kurz¹⁷ also found exponential erase behavior.

Other researchers have made note of certain characteristics of hologram decay or erasure. Huignard, et al., have examined the degradation in signal-to-noise ratio occurring after many write-erase cycles.¹⁶ Their findings were that the writing and erasing processes were symmetric ($\eta$ was kept to within the initial quadratic and linear regions, and not allowed to reach the first maxima).
F. Conclusion

Through the study of hologram decay, a persistent conductivity effect has been found. The lifetime of this effect is of the order of $10^4$ seconds. The exact cause of the effect is unknown, and a brief model involving metastable trapping centers is presented. Additional studies are required for the phenomenon to be completely described.

Since LiNbO$_3$ is to be used as an optical storage medium, its long term storage characteristics are of prime importance. The effect tends to accelerate loss of the hologram, and is therefore undesirable. To optimize storage characteristics, this phenomenon must be identified in order that methods may be found to eliminate or minimize the effect. If the effect is found to be associated with the Fe ion, then other metal dopants should be studied in an attempt to find one that does not form this type of center. If the effect is due to an intrinsic defect of LiNbO$_3$, such as a vacancy or shear plane, then this would indicate the use of high quality, carefully grown crystals in order to minimize the defect concentration.
References


APPENDIX 1
MATERIAL PROPERTIES OF LITHIUM NIOBATE

Formula Weight: 147.83

Mass Density [21]: 4.64 gm/cm³ (at 25°C)

Melting Point [23]: 1260 ± 10°C

Curie Temperature [21]: 1210 ± 10°C

Crystal Structure [23]: Rhombohedral, C₃ᵥ (R3c) (at 25°C)

Lattice Constants [23]:

\[ a_R = 5.14829 ± 2 \text{ Å} \]
\[ c_R = 13.861 ± 4 \text{ Å} \]

Corresponding to:
\[ a_H = 5.4944 \text{ Å} \]
\[ \alpha = 55.867° \]

Atomic Arrangement [20,23-25]: Constant from 0° to 1200°C

(i) Oxygen atoms arranged on planar sheets forming a network of distorted octahedra (based on hexagonal close-packing of oxygens)

(ii) The centers of the octahedra are occupied, in moving along the +c axis, by Nb, vacancy, Li, Nb, vacancy, Li.

(iii) Interatomic distances:

\[ \text{Nb - 0} \quad 1.889 ± 0.003 \text{ Å} \quad 2.112 ± 0.004 \text{ Å} \]

\[ \text{Li - 0} \quad 2.068 ± 0.011 \text{ Å} \quad 2.238 ± 0.023 \text{ Å} \]

Vacancy - 0 ~2.2 Å
<table>
<thead>
<tr>
<th>Formal Charge</th>
<th>Ionic Radius</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium +5</td>
<td>0.69 Å</td>
</tr>
<tr>
<td>Lithium +1</td>
<td>0.68 Å</td>
</tr>
</tbody>
</table>

(iv) Isotropic thermal vibrations for all atoms; Debye temperature of 503°K.

Defects

(i) [22]: Assuming substitutional impurities
+1, +2 ions enter lithium site
+4, +5, +6 ions enter niobium site
+3 ions enter either site

(ii) [32]: Evidence exists for an oxygen vacancy - metal dopant defect center with chemochromic properties.

Band Structure [29]: Oxygen 2pπ valence band and a niobium 3dε conduction band. Band gap 3.72 eV (≈ 3500 Å). Energy difference between band centers ≈ 5 eV.

Refractive Index 30: For pure LiNbO₃, the refractive indices are temperature and wavelength dependent:
(for T < 600°C)

\[
(n_o)^2 = 4.9130 + \frac{1.173 \cdot 10^5 + 1.65 \cdot 10^{-2} T^2}{\lambda^2 - (2.12 \cdot 10^2 + 2.7 \cdot 10^{-5} T^2)^2} - 2.78 \cdot 10^{-8} \lambda^2
\]
\[(n_e)^2 = 4.5567 + 2.605 \cdot 10^{-7}T^2 \]
\[+ \frac{0.970 \cdot 10^5 + 2.70 \cdot 10^{-2}T^2}{\lambda^2 - (2.01 \cdot 10^2 + 5.4 \cdot 10^{-5}T^2)^2} \]
\[- 2.24 \cdot 10^{-8} \lambda^2 \]

\[T = \text{temperature in °K} \quad \lambda = \text{wavelength in nm} \]

<table>
<thead>
<tr>
<th>(\lambda = 6328 , \text{Å} )</th>
<th>(4880 , \text{Å} )</th>
<th>(T = 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n_o )</td>
<td>2.2884</td>
<td>2.3504</td>
</tr>
<tr>
<td>(n_e )</td>
<td>2.2019</td>
<td>2.2544</td>
</tr>
<tr>
<td>birefringence</td>
<td>-0.0865</td>
<td>-0.0960</td>
</tr>
</tbody>
</table>

**Dielectric Constant [21]:** \(T = 25°C\)

(i) \( 78 \varepsilon_o = 6.91 \times 10^{-12} \, \text{F/cm} \) perpendicular to optic axis

(ii) \( 32 \varepsilon_o = 2.83 \times 10^{-12} \, \text{F/cm} \) parallel to optic axis

**Electro-Optic Tensor [8,27]:**

\[
\begin{pmatrix}
0 & -r_{22} & r_{13} \\
0 & r_{22} & r_{13} \\
0 & 0 & r_{33}
\end{pmatrix}
\]

with\[r_{13} = 8.6 \times 10^{-10} \, \text{cm/V} \]
\[r_{22} = 3.4 \]
\[r_{33} = 30.8 \]
Electro-Optic Tensor (Cont.):
\[
\begin{pmatrix}
0 & r_{42} & 0 \\
r_{42} & 0 & 0 \\
-r_{22} & 0 & 0
\end{pmatrix}
\quad \text{with} \quad r_{42} = 2.8
\]

Piezo-Electric Tensor [31]:
\[
\begin{pmatrix}
0 & -e_{22} & e_{31} \\
0 & e_{22} & e_{31} \\
0 & 0 & e_{33} \\
0 & e_{15} & 0 \\
e_{15} & 0 & 0 \\
-e_{22} & 0 & 0
\end{pmatrix}
\quad \text{with} \quad e_{15} = 3.7 \ (\text{c/m}^2)
\]
\[
e_{22} = 2.5
\]
\[
e_{31} = 0.2
\]
\[
e_{33} = 1.3
\]

Elastic Tensor [31]:
\[
\begin{pmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\
C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
-C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & C_{14} \\
0 & 0 & 0 & 0 & C_{14} & C_{66}
\end{pmatrix}
\quad \text{with} \quad C_{11} = 2.03 \ (\times 10'^{12} \ N/m^2)
\]
\[
C_{12} = 0.53
\]
\[
C_{13} = 0.75
\]
\[
C_{14} = 0.09
\]
\[
C_{33} = 2.45
\]
\[
C_{44} = 0.60
\]
\[
C_{66} = \frac{1}{2} (C_{11} - C_{12}) = 0.75
\]
For the equations concerning the above tensors, see Ch. 7, Ref. 31.

Pyro-Electric Coefficient [14]:

$\sim 10^{-8} \text{ C/(m}^2\text{-deg)}$  (at \( T = 100^\circ \text{C} \))

Mobility [28]:

15. \( \text{cm}^2/\text{V-sec} \)  (extrapolated from \( 1000^\circ \text{C} \))

Trapping Time [19]:

4 x \( 10^{-11} \) s  (using above mobility)

Inverse Susceptibility [21]:

\( (1/X) \) linear from 300 to 950\(^\circ\)C

Curie-Weiss intercept \( \sim 1080^\circ \text{C} \)

Conductivity [18]:

> \( 10^{-18} \) (ohm-cm\(^{-1} \))
APPENDIX 2

ABSORPTION SPECTRA FOR SEVERAL CRYSTALS

A2-1 Crystal X6; doping of 0.1% wt/mol Fe, reduced.
A2-2 Crystal X9; doping of 0.05% wt/mol Fe, reduced.
A2-3 Crystal X12; doping of 0.1% wt/mol Fe, reduced.
A2-4 Crystal X11; doping of 0.015% wt/mol Fe, reduced.

These spectra cover the wavelength range of 380 to 720 nanometers. The curves were taken with both $\sigma$- and $\pi$-polarized light. The measurements were taken with a Cary 17 spectrophotometer.

The spectrum for Crystal X11 is essentially that of a "pure" crystal, and the effects of Fe impurities may be seen by comparing the X11 spectra to the others.
Fig. A2-1: Absorption Spectra for Crystal X6.
(0.1% wt Fe Doping).
Fig. A2-2: Absorption Spectra for Crystal X9.
(0.05% wt Fe Doping).
Fig. A2-3: Absorption Spectra for Crystal X12. (0.1% wt Fe Doping).
Fig. A2-4: Absorption Spectra for Crystal X11. (0.01% wt Fe Doping).