Photorefractive gratings: fixing and recording in the visible and ultraviolet

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GERMANO LUIGI MONTEMEZZANI

Dipl. phys. ETH
born June 21, 1963
citizen of Magadino (TI)

accepted on the recommendation of
Prof. Dr. P. Günter, examiner
Prof. Dr. H. Melchior, co-examiner

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Abstract

The photorefractive effect can be used to record the optical information carried by a light wave by a phase hologram. The read-out is done by illuminating the crystal at the Bragg angle. This step can occur either simultaneously with the recording or at a later time. The grating read-out, however, normally deteriorates and erases the stored information.

In this work we investigate two approaches to avoid this unwanted erasure. The first is a hologram fixing procedure that allows reading out the hologram with the same wavelength used for recording. The second is to use different wavelengths for read-out and recording. The wavelengths can be selected in such a way that the read-out beam does not affect the phase-grating. Both approaches are experimentally and theoretically investigated, the possibility to use ultraviolet (UV) light for the recording of photorefractive gratings is studied in detail.

Two new theoretical models extend the conventional band models to include the case where ions can move in the crystals and the case where the incident photons induce phototransitions from the valence to the conduction band. The models are discussed in detail and their predictions are verified and used for the interpretation of the experimental results.

The experimental investigations are performed in crystals of potassium niobate (KNbO₃) and bismuth germanate (Bi₄Ge₃O₁₂). KNbO₃ is particularly suited for all photorefractive applications because of its large electro-optic coefficients, photoconductivity and photosensitivity in the visible. Bi₄Ge₃O₁₂ is particular interesting for applications in the ultraviolet because of its transparency range extending to the wavelength of 300 nm.

We demonstrate the fixing of holographic gratings in KNbO₃ using a thermal cycling procedure. The underlying charge transport process is found to be the drift of non-photoexcitable ionic (secondary) charges in the internal electric field formed by photoexcitable electronic (primary) charges.

In Bi₄Ge₃O₁₂, the competition between primary and secondary carriers is also observed. Only a partial fixing is obtained because the secondary carriers are not of ionic nature. Additional investigation shows that Bi₄Ge₃O₁₂ is well suited for coherent image amplification or for dynamic holography in the UV because of its efficient charge transport.

A novel kind of photorefractive experiment is performed in KNbO₃. Recording with ultraviolet light which induces interband phototransitions produces large free carrier concentrations and the charge modulation can be stored rather in one of the bands than in deep traps. Since a visible read-out beam cannot induce interband transitions it does not strongly influence the space-charge grating and large read-to-write intensity ratios can be used. Interband effects prove to be very promising because large diffraction efficiencies and short response times in the µs range are observed.
Riassunto

L'effetto fotorifrangente può essere utilizzato per memorizzare in un cristallo l'informazione portata da un'onda luminosa sotto forma di ologramma di fase. La lettura dell'informazione avviene illuminando il cristallo sotto l'angolo di Bragg, questo processo può avvenire simultaneamente con la fase di registrazione, oppure in una fase successiva. La lettura induce però un deterioramento e spesso la cancellazione dell'informazione memorizzata.

In questo lavoro si investigano due metodi per conservare intatta l'informazione. Il primo è un fissaggio dell'ologramma che permette la sua lettura con la stessa lunghezza d'onda usata per la registrazione. Il secondo è un metodo che usa due differenti lunghezze d'onda per la registrazione e la lettura. La loro selezione è fatta in modo che il raggio di lettura non disturbi il reticolo di fase. I due metodi sono studiati sia sperimentalmente che teoricamente e la possibilità di usare raggi ultravioletti per registrare reticoli fotorifrangenti è studiata in dettaglio.

Due nuovi modelli teorici estendono i modelli convenzionali includendo il caso in cui i cristalli contengano cariche ioniche mobili e quello in cui i fotoni incidenti inducano transizioni di elettroni dalla banda di valenza a quella di conduczione. I modelli sono discussi dettagliatamente e le loro predizioni sono verificate e usate per interpretare i risultati sperimentali.

Gli esperimenti sono eseguiti su cristalli di niobato di potassio (KNbO₃) e di germanato di bismuto (Bi₄Ge₃O₁₂). Il primo è particolarmente adatto per applicazioni dell'effetto fotorifrangente essendo i suoi coefficienti elettro-ottici, la sua fotoconduttività e la sua sensibilità alla luce visibile alquanto elevati. Il secondo si presta particolarmente ad applicazioni nell'ultravioletto essendo trasparente fino alla lunghezza d'onda di 300 nm.

Si dimostra il fissaggio di reticoli olografici nel KNbO₃ usando un metodo basato sulla variazione della temperatura. Il processo che ne stà alla base è il movimento di cariche ioniche (secondarie) spinte nel campo elettrico indotto dalle cariche elettroniche (primarie) eccitate dalla luce.

Cariche secondarie interagiscono con quelle primarie anche nel Bi₄Ge₃O₁₂. Le prime non sono di natura ionica e si ottiene perciò solo un fissaggio parziale dell'informazione. Si stabilisce che questo cristallo è adatto per l'amplificazione coerente di raggi luminosi o per l'olografia dinamica nell'ultravioletto essendo il trasporto delle cariche molto efficiente.

Un nuovo modo di registrare reticoli olografici alla superficie del KNbO₃ produce grandi efficienze di diffrazione e tempi di risposta di pochi microsecondi. Gli ologrammi sono registrati con luce ultravioletta che induce transizioni da banda a banda e produce grandi concentrazioni di cariche libere. Raggi visibili di intensità anche molto superiore di quella del raggi di registrazione ultravioletti non influenzano fortemente il reticolo spaziale di cariche.
Zusammenfassung


Zwei neue theoretische Modelle erweitern die konventionelle Bandmodelle. Der erste betrachtet den Fall wo die Kristalle bewegliche ionische Ladungen enthalten, der zweite den Fall wo die einfallenden Photonen induzieren Übergänge vom Valenz- zum Leitungsband. Die Modelle werden gründlich diskutiert und deren Vorhersagen sind nachgeprüft und werden gebraucht zur Interpretation der experimentellen Resultate.


Eine thermische Fixiermethode für holographische Gitter wird demonstriert für KNbO₃. Das unterliegende Prozess ist das Driften von (sekundären) ionischen Ladungsträger im Raumladungsfeld gebildet durch primären elektronischen Ladungen. Im Gegensatz zu den Ionen können diese optisch angeregt werden.

Eine Kompetition zwischen primären und sekundären Ladungsträger wird auch in Bi₄Ge₃O₁₂ beobachtet. In diesem Fall sind die Hologramm nur teilweise fixiert, weil die sekundäre Ladungsträger nicht ionischer Natur sind. Weitere Untersuchungen zeigen, dass, wegen den effizienten Ladungstransport, Bi₄Ge₃O₁₂ ist geeignet für kohärente Bildverstärkung und für dynamische Holographie im UV.

1. Introduction

The miniaturization of electronic circuits is approaching the point where electromagnetic interactions between neighbouring elements affects their reliability. Optical waves are fast and do not interact with each other in linear media, thus optical based components are ideal candidates for expanding the frontier of computation. After the invention of the first laser by T. H. Maiman in 1960 this field of research dealing with optical information processing (photonic) has grown considerably. It is nowadays one of the principal areas of development in science and technology. Among others, the major advantages of optics with respect to electronics are the intrinsic potential for parallel computation and the much larger bandwidth of optical signals. For the construction of all-optical switching elements the use of nonlinear-optical materials is necessary. Among these, photorefractive materials combine the advantages of low-power operation, real time writing-erasure and storage possibility.

Optical storage devices are already widely used in the computer technology and entertainment electronics due to the larger storage capability with respect to conventional magnetic media [1]. These devices include WORM's (Write Once Read Many times), CD-ROM's (Compact Disc Read Only Memory) and rewritable optical discs, the latter being based on magneto-optical materials. In general, in all these devices the information is recorded by the thermally induced modifications of the optical properties of the medium produced by an incident laser beam. The principle underlying the retrieval of the data is the change in light reflectivity caused by these modifications. Optical discs are typical bit-by-bit storage media (Fig. 1.1(a)), and, due to their two-dimensional character, their information storage capacity is limited to about $10^8$ bits/cm$^2$. In contrast, as demonstrated by Van Heerden [4], three-dimensional optical storage media may store up to $10^{12}$ bits/cm$^3$, that is one bit per cube of edge equal to the light wavelength. Thus, due to the higher resolution, three-dimensional media or devices sensitive to shorter wavelengths (towards the ultraviolet) may attract future interest for memory applications.

Among the potential candidates for three-dimensional storage there are volume holographic memories (Fig. 1.1(b)). Their advantages are (a) auto-correction of defects, because a defect in the recording medium does not obliterate the stored information, but only lowers the overall signal-to-noise ratio; and (b) high speed operation, because each block of data can be recorded and retrieved in parallel. Optical computers, which are for the moment rather a vision than a well defined goal of research, would take advantage of their intrinsic parallel information retrieval. In contrast, the sequential bit by bit read-out of today's optical storage devices is non-parallel in nature. At present, rather than optical computers, more specialized

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† Recent laboratory research proposes to use a stack of 2-D bit arrays to increase the storage capacity by up to two orders of magnitude. Crosstalk between different planes is avoided by using the intensity thresholding characteristics of two-photon absorption in photochromic media. The spatial site of the bit is selected either by the intersection of two or more beams [2] or by using a single highly focused beam [3].

‡ Practical limitations on the optical system and on material resolution limit this number by up to two orders of magnitude.
optical processors like image storage devices for optical associative memories [5-6] and optical correlators [7] are attracting the interest in volume hologram memories.

Photorefractive crystals belong to the materials which are suitable for recording volume holograms. The refractive index of such materials is locally changed as a result of an inhomogeneous illumination, creating a *volume phase hologram*. Real time write-erase operations (*dynamic holography*) can be realized without the need of a developing step. For long storage time applications there is an important drawback of such materials, the stored information is erased by the read-out light. The physical process responsible for this *erosure* is the same underlying the recording mechanism, that is a light-induced redistribution of electrons within impurity centers in the material. Basically, there are two ways to avoid this unwanted erasure. The first is to find a *fixing* procedure so that the hologram can be read-out (quasi-)nondestructively with light of the same wavelength used for recording. The second is to use two different wavelengths, one for recording and the other for read-out. The wavelength at which the crystal is more sensitive (normally the shorter one) is used for recording while the other is used for the read-out beam. If the read-out light intensity can be made much larger that the recording intensity one can say that the grating is *robust* [8]. The first method has some advantages because the read-out is made under the same angle that was employed for recording, avoiding distortions of the information. With the second method two different approaches can be taken. The first is to perform the recording and read-out steps at two different times. This is possible if the thermal decay time of the hologram is large enough. The second is to perform recording and read-out simultaneously. In this case the strong read-out beam can be controlled by weak recording beams (optical transistor).

The aim of this thesis is twofold. First, the possibility to use photorefractive KNbO3 crystals for long term hologram storage is investigated. Among the nonlinear materials, KNbO3
belongs to the ones having the largest electro-optic and nonlinear-optic responses. Together with photoconductive sillenite crystals like Bi$_{12}$SiO$_{20}$ and Bi$_{12}$GeO$_{20}$ it shows the largest sensitivities for photorefractive holographic recording. In this work, a thermal fixing procedure for KNbO$_3$ is developed and a detailed theoretical analysis of the underlying physical mechanisms of charge carrier redistribution and compensation is performed. The influence of the material properties (doping) and of the experimental arrangement (grating spacing, applied electric field) on the fixing mechanism are investigated. With our thermal fixing procedure, an increase of the storage time of volume holograms by a factor of $10^7$ is achieved with a diffraction efficiency $\eta = 0.05 - 1\%$.

The second approach taken in this work is the use of continuous ultraviolet laser light for grating recording. As discussed above, this has the advantages of an increased resolution and of a larger sensitivity for recording. To the best of our knowledge only preliminary studies of photorefractive effects in the ultraviolet (UV) have been reported, e.g. in KH$_2$PO$_4$ [9], RbZnBr$_4$ [10], and in LiNbO$_3$ [11-13] and LiTaO$_3$ [14] in the near UV spectral range. In KH$_2$PO$_4$ and RbZnBr$_4$ photogalvanic currents and light induced changes of the refractive index were detected by homogeneous illumination of the crystals with spectral lamps. The phenomena were observed only in the low temperature ferroelectric phase of these materials ($T < 122$ °K for KH$_2$PO$_4$, $T < 187$ °K for RbZnBr$_4$) and the recording of phase gratings using these effects was not demonstrated. In LiNbO$_3$ and LiTaO$_3$ phase holograms were recorded at the Kr-ion laser wavelength $\lambda = 350.7$ nm with $\eta \approx 30\%$, corresponding roughly to the efficiencies obtained in the visible. The hologram recording in these materials is slow (recording time $> 100$ s for an incident intensity $I = 1$ W/cm$^2$). The absorption of LiNbO$_3$ and LiTaO$_3$ below $\lambda = 350$ nm increases strongly, precluding their use for volume hologram recording in the further UV. In general, the lack of suitable highly nonlinear materials being transparent far in the UV has probably been the reason for the limited number of investigations in this spectral range. For our investigations in the UV two different materials are used. The first is Bi$_4$Ge$_3$O$_{12}$, which is transparent in the UV down to a wavelength of about 300 nm. Good quality, large size and low cost single crystals of this material can be grown, making it a good candidate for applications in optical signal processing. We present detailed investigations of the electro-optic and fundamental photorefractive properties of this material. We show that phase gratings can be recorded with time constants in the ms range for intensities $I = 1$ W/cm$^2$. The maximum diffraction efficiencies $\eta = 1\%$ are smaller than in LiNbO$_3$ because of smaller electrooptic coefficients. Effective amplification of ultraviolet laser beams, as well as quasi nondestructive read-out in the UV are demonstrated in this crystal.

As the second material for the UV investigations we use again KNbO$_3$. KNbO$_3$ is not transparent to UV light so that photon absorption causes phototransitions of charge carriers from the valence to the conduction band. We call the related mechanism of space-charge grating formation interband photorefractive effect. A simplified band scheme for this novel situation is shown in Fig. 1.2b. No theoretical analysis and experimental investigations of this kind of photorefractive effects has been reported previously. In this thesis the experimental investigations are accompanied by theoretical calculations of a simple band
model for interband photorefractive effects. It should be noted that photorefractive experiments recently performed in epitaxially grown semiconductor multiple quantum well (MQW) structures [8, 15, 16] are similar in nature to ours. There, resonant effects like the Franz-Keldysh effect or the quantum-confined Stark effect are used for increasing the amount of light diffracted from the thin (= 2 μm) MQW structures. In our bulk KNbO₃ crystals the thickness of the grating depends on the UV-wavelength used and varies between approximately 10 μm and 200 μm. The magnitude of the refractive index modulation produced by the normal electro-optic effect is large enough for generating diffracted beams exceeding 1% efficiency. By optimizing the experimental geometry in order to increase the interaction region, larger efficiencies (60-70 %) are obtained. The response time of the phase grating formation is approximately 10 μs for intensities of $\approx 1$ W/cm² and read-out intensities in the visible being more than a factor of $10^5$ larger than the recording intensity can be used without strong erasure of the hologram. Interband photorefractive effects open many possibilities for practical applications. These include applications needing high speed, and high resolution real-time processing in relatively thin nonlinear devices (spatial light modulators, optical correlators) and optical switching elements for waveguides.

| Conventional Photorefractive Effect  
<table>
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<th>(hv &lt; band gap energy)</th>
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| Interband Photorefractive Effect  
| (hv > band gap energy) |

Fig. 1.2: Simple band scheme underlying the charge redistribution in the conventional and interband photorefractive effect. Not all the possible transitions are shown. In the interband case a below band gap read-out laser beam does not influence strongly the charge redistribution.

This thesis is organized in the following way. Chapter 2 contains a review of different theoretical band models for the photorefractive effect. Two new models are presented.

(a) A model including charge redistribution by photoexcitable electrons and non-photoexcitable ionic defects. This model is presented in detail in section 2.3. The conventional model of Kukhtarev which is used to describe the photorefractive properties of most materials is derived as a special case.

(b) A model for interband photorefractive effects including three different situations is presented in section 2.5.
These theoretical models lead to novel predictions. The differences to the conventional case are discussed throughout chapter 2. In addition to the mentioned models, in Appendix B the case of electron-hole bipolar charge transport is shortly revised. One of the models previously reported in literature is modified to include the case where photoexcited electrons and thermally excited holes build-up nearly independent charge modulations (B.2).

In chapter 3, the effect of the photorefractive space-charge field on light waves is shortly discussed. This leads to the concepts of Bragg-diffraction and beam coupling between light waves. The experimental set-ups and the performed experimental investigations are contained in chapter 4. In section 4.1 the investigations on charge compensation and thermal hologram fixing in KNbO₃ are presented and interpreted with the help of electron-ion model of section 2.3. Section 4.2 contains the measurements performed in Bi₄Ge₃O₁₂ in the UV spectral range while section 4.3 is devoted to the investigations of interband photorefractive effects in KNbO₃. The results are summarized at the end of each section and final conclusions are made in chapter 5.
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2. The Photorefractive Effect

2.1 Introduction

A photorefractive material in a general sense is a material whose refractive index can be changed by light illumination. There are a number of physical mechanisms which can lead to this effect [17-21]. Among these there is one effect which is normally referred to in literature as the photorefractive effect. In this classical case the refractive index changes arise from internal space-charge electric fields via the linear electro-optic effect. The origin of the internal electric fields is the migration of photoexcited charge carriers from the illuminated to the dark sites of the crystal. Throughout this chapter only this kind of photorefractive effect will be treated.

In the mid-sixties Ashkin and coworkers [22] first found that intensive laser radiation focused on ferroelectric LiNbO$_3$ and LiTaO$_3$ crystals induced local semipermanent index changes. As this phenomenon was unwanted for their measurements, they referred to it as "optical damage". The potential of this new effect for use in high density optical storage of data was realized by Chen and coworkers in the late sixties [23]. Chen published in 1969 the first theoretical model for the photorefractive effect [24] based on the drift of spatially inhomogenously photoexcited charge carriers. This model has been the basis for further work over the last twenty years. In 1971, Amodei showed that charge redistribution by diffusion may play an important role in holographic recording at small grating spacing [25]. His model lead to a general model for charge migration in insulators. In 1974, Glass [26] introduced the bulk photovoltaic effect for explaining the fact that in some materials photocurrents can arise without the presence of any applied electric fields. Since then, its contribution to the photorefractive charge transport mechanism in some materials (as for instance in LiNbO$_3$) has been widely accepted. All these early works have been the basis for Kukhtarev and coworkers who published in 1979 their theory that considers the coupling between the wave equation and the charge transport equations [27]. Although later refinements have been made to this model [28-30], the Kukhtarev model remains the reference theoretical work for all researchers in the field.

In parallel to the cited theoretical works, a number of potential applications of the photorefractive effect have been demonstrated in the last twenty years, including hologram storage and fixing [31], real time holography [32], real time image processing [33], edge enhancement [34], image amplification [35], phase conjugation [36], spatial light modulators [37] and all optical associative memories [38].

In this chapter, we describe theoretical models used to explain experiments performed under different conditions. After a short description of the basic mechanisms leading to the photorefractive effect (section 2.2), we present in detail in section 2.3 a new model where an ionic conduction process leads to compensation of the light induced electronic space-charge field. The predictions of this model will be used in Chapter 4.1 for explaining the experiment on thermal hologram fixing in KNbO$_3$. The conventional results obtained in the one-center Kukhtarev model are derived as a special case and are compared with the predictions of our
model in section 2.4. Finally, models for the case of band to band carrier generation applying to oxide crystals illuminated at ultraviolet wavelengths are presented in section 2.5. Extensions of the conventional model to the case of crystals showing bipolar charge transport are presented in Appendix B because these models are only indirectly related with the experimental work of this thesis.

2.2 Basic concepts of the band transport model

To show the photorefractive effect a material should fulfil three different conditions. It should be electro-optic (the refractive index changes under the influence of an electric field), photoconductive (moving charge carriers are photogenerated) and should possess enough trap centers for retrapping the free carriers. The charge redistribution consists of three steps as well:

- Free electrons (or free holes) are generated through photon absorption.
- The photogenerated carriers tend to leave the illuminated region. Their movement occurs by drift in the resultant electric field or by diffusion. In some crystals, the bulk photovoltaic effect also contributes to the charge carrier motion.
- The charge carriers are retrapped at mid-gap trap centers and an electrical field builds-up because some of the carriers are retrapped at dark sites in the crystal and the charges of opposite sign are left behind in the illuminated regions.

A general band model for a hypothetical photorefractive material is shown in Fig. 2.1. Different defect levels 1, 2, 3, 4, ... may be present in the band gap region of the crystal. In thermal equilibrium only the levels lying below or few kT above the Fermi energy level of the material are occupied with electrons. Optical irradiation disturbs this thermal equilibrium and photon assisted electron transitions from the occupied levels to the conduction band, and from the valence band to unoccupied levels (generation of holes) may occur. Besides, there are spontaneous transitions from conduction band electrons into empty levels and of holes into filled levels.

Each photoexcitation process is described by photon energy dependent cross sections $\sigma_{i\rightarrow n}(h\nu)$ and $\sigma_{p\rightarrow i}(h\nu)$, where $\sigma_{i\rightarrow n}(h\nu)$ is the cross section for the transition of an electron from the level $i$ to the conduction band, and $\sigma_{p\rightarrow i}(h\nu)$ is the one for electron phototransition from the valence band to level $i$. The recombination processes are described by the recombination constants $\gamma_{ni}$ and $\gamma_{pi}$. In addition to the photoinduced transitions, also thermal excitation processes given by temperature dependent emission rates $e_{ni}(T)$ and $e_{pi}(T)$ may occur. Since in thermal equilibrium the charge carriers are distributed following Fermi-
The Photorefractive Effect

Dirac statistics, the thermal emission rates and the recombination cross sections depend on each other. For more details on the statistical theory of doped semiconductors see Ref. [40].

A general situation like the one shown in Fig. 2.1 cannot be easily described by a self consistent mathematical model. The number of possible transitions is too large and the related probabilities are normally not all known. In addition, upon illumination, transition channels which are inactive in thermal equilibrium may be activated. For instance, if all the centers of level 1 are filled with electrons, the thermal emission from the valence band to this level (through \( e_{p1} \)) does not occur. However, if photons of high enough energy can excite some electrons from level 1 to the conduction band, this thermal emission channel opens.

The above considerations show the complexity of the mechanisms governing the charge redistribution in photorefractive materials and the difficulties of an exact mathematical description. In order to make the theory tractable we resort to simplified models appropriate to particular cases. By doping the crystal one of the impurity centers may get a much larger concentration than all the others. In general, the Fermi level is then pinned close to this level, and the level will be partially filled with electrons. In their band model theory, Kukhtarev et al. [27] considered only electron excitation and recombination between such a unique donor level and one of the two bands. Besides the different involved cross sections and the charge carrier mobility, the donor concentration \( N_D \) and the concentration of empty donors
(acceptors) $N_{D0}^+$ in the dark † are the main parameters of their model. It is remarkable that, in spite of his simplicity, this model has been able to explain experimental results in a number of photorefractive crystals [35]. In the next section we follow the same approach as Kukhtarev with some modifications to include the contributions of secondary charge carriers.

† In Ref. [27] a number of acceptor $N_A$, which are not active in the photorefractive process is introduced. Their presence is postulated for means of conservation of charge neutrality in the crystals. In our work we do not postulate the presence of such inactive acceptors. However, for compatibility with the current formalism we define throughout this work the density $N_A$ by the equation $N_A = N_{D0}^+ - n_0$, where $n_0$ is the electron concentration in the conduction band in the dark.
2.3 The electron-ion model

We present here a model for the photorefractive effect that considers photoexcited electrons as primary charge carriers and additional optically inactive ionic secondary charges drifting in the space-charge field created by the electrons. With the help of this electron-ion model one is able to explain charge compensation and hologramfixing in KNbO₃.

Before starting with the description of the theoretical model we want to describe the terms of the problem and give some useful definitions with the help of Fig. 2.2. It shows schematically the dynamic behaviour of the space-charge field observed in KNbO₃ crystals performing photorefractive experiments at temperatures of about 100 °C.

![Fig. 2.2: Dynamic behaviour of the photorefractive space-charge field amplitude \( |E_1| \) observed in KNbO₃ crystals at elevated temperatures (= 100 °C). In part A and B the crystal is illuminated with two recording laser beams used for recording, in part C and D the crystal is in the dark or is illuminated by only one homogeneous beam. Charge compensation of a primary space-charge grating by secondary charge carriers and the subsequent revelation of the secondary grating are the underlying processes. The value of \(|E_1|\) at point 2 is not in scale.]

In the figure, four distinct regions A, B, C and D are indicated. In the first two regions, A and B, the sample is illuminated with two recording laser beams, we can thus consider these two parts together as the *hologram recording* process. The figure shows that the space-charge field \( E_1 \) reaches a maximum at point 1 and then decreases to a constant steady-state value at point 2. The value of \( E_1 \) at point 2 is very small. The usual tentative explanation for this behaviour is the following [41]. In part A photoinduced charge carriers create a primary photorefractive grating due to the inhomogeneous light illumination. We call this process the *writing* of the hologram. In part B the primary grating is compensated by secondary charge carriers which move by diffusion and drift in the field created by the primary charge carriers. In other words, the secondary charge carriers create a negative replica of the primary space-charge field. We call the process occurring in part B the *compensation* of the hologram. Of course, the strict distinction of the two processes occurring in part A and B is an idealization.
In reality, the writing of the hologram continues also after point 1 and the compensation begins already before this point. Nevertheless, the above definitions are useful because the dynamics shows clearly distinct features in the two parts.

Part C and D represent the hologram erasure process. In these two parts the crystal is either left in the dark or is illuminated in a homogeneous way. When the recording beams are switched off, the space-charge field increases, reaches a maximum at point 3 and decreases then to zero. This behaviour is observed in KNbO₃ independent of whether the crystal is in the dark or is illuminated homogeneously. The process occurring in part C can be assigned to the partial erasure of the primary space-charge grating by diffusion of the primary charge carriers. We call this process the revealing of the hologram. The process in part D is governed mainly by the secondary charge carriers which slowly redistribute themselves until a homogeneous distribution is reached. We can look at the process occurring in part D in two different ways depending on the experimental conditions. If the crystal is in the dark the process is related to the storage time of the hologram. If the crystal is illuminated for recovering the original information it is related to the handling time of the hologram. The reason for this distinction will become clear later.

For our calculations, we consider the case where free electrons can be photoexcited from a single donor level situated in the band gap into the conduction band. No contribution of optically excited holes is considered. The photoexcited electrons move by diffusion and drift and are then retrapped generating a concentration grating. At the same time, ions (which are assumed to have a single positive charge) drift under the effect of the total internal electric field and diffuse in their concentration gradient. We neglect the contribution of photovoltaic currents to the motion of electrons and we consider the usual one-dimensional problem with the modulation along the x-axis. The complete set of initial equations is then written as

\[
\frac{\partial n}{\partial t} = (s_e I + \beta_e) (N_D - N_D^+) - \gamma_e n N_D^+ + \frac{1}{e} \frac{\partial J_e}{\partial x}, \quad (2.1a)
\]

\[
\frac{\partial N_D^+}{\partial t} = (s_e I + \beta_e) (N_D - N_D^+) - \gamma_e n N_D^+, \quad (2.1b)
\]

\[
\frac{\partial N_I}{\partial t} = - \frac{1}{e} \frac{\partial J_I}{\partial x}, \quad (2.1c)
\]

\[
J_e = e\mu_e n E + \mu_e k_B T \frac{\partial n}{\partial x}, \quad (2.1d)
\]

\[
J_I = e\mu_I N_I E - \mu_I k_B T \frac{\partial N_I}{\partial x}, \quad (2.1e)
\]

\[
\varepsilon \varepsilon_0 \frac{\partial E}{\partial x} = \varepsilon \varepsilon_0 \frac{\partial E}{\partial x} + \varepsilon \varepsilon_0 \frac{\partial E}{\partial x} = e(N_D^+ - n - N_A) + e(N_I - N_{I0}) \quad (2.1f)
\]

† In the case where charge compensation does not take place the complex dynamics of Fig. 2.2 is not observed. A rise of \(E_1\) to a stable level is normally observed during the recording process, this is followed by a monotonic decay during the erasure.
The symbols in the above equations are: \( n \), the free electron concentration in the conduction band; \( N_D \), the donor concentration; \( N_D^+ \), the concentration of ionized donors; \( N_{Io} \), the average concentration of ionic charges; \( N_I \), the concentration of ions; \( N_A \), the concentration of ionized donors in the dark; \( J_e \), the electronic current density; \( J_I \), the ionic current density; \( E_e \), the electronic contribution to the space-charge field; \( E_I \), the ionic contribution to the space-charge field; \( E \), the total electric field; \( \lambda \), the light intensity; \( \sigma _e \), the photoionization constant for electrons; \( \beta_e \), the dark generation rate for electrons; \( \gamma_e \), the recombination constant for electrons; \( \mu_e \), the electronic mobility; \( \mu_I \), the ionic mobility; \( \varepsilon_0 \), the permittivity of vacuum; \( \varepsilon \), the effective dielectric constant; \( e \), the absolute value of the elementary charge; \( k_B \), the Boltzmann-constant; and \( T \), the absolute temperature.

The set of equations (2.1a-2.1f) correspond to the one first put forward by Kukhtarev et al. [27] but is extended with the continuity equation for the ionic charges (2.1c)+(2.1e) and the contribution of the ion distribution to the Poisson equation (2.1f). We explain first the physical meaning of the above set of equations. Equation (2.1a) is the continuity equation with sources for the free electrons in the conduction band. The first term on the right-hand side gives the rate of photo- and thermally excited electrons from filled donors with density \((N_D-N_D^+)\), the second term gives the recombination rate from the band to ionized donors and the third term considers the charge conservation when electrons migrate in the conduction band. The photoionization constant \( \sigma_e \) in Eq. (2.1a) is related to the cross section for photoexcitation given in section 2.2 by \( \sigma_e = \sigma_0 - \sigma e \lambda \), with \( \lambda \) being the Planck constant and \( \nu \) the light frequency, while the dark generation rate \( \beta_e \) corresponds to the emission rate \( \gamma e \) found in the statistical theory of doped semiconductors. Eq. (2.1b) is the rate equation for the immobile empty donor centers, while Eq. (2.1c) is the continuity equation for the background conducting ions. The expressions for the current densities of electrons and ions (Eqs. (2.1d) and (2.1e) respectively) contain a term describing the drift in the total electric field and a term describing the statistical diffusion process of the charge carriers. Finally, (2.1f) is the Poisson equation describing the modulated part of the electric field which is generated by the inhomogeneous charge distribution in the crystal.

For solving the set (2.1a-2.1f) we consider the usual case of a sinusoidally varying light intensity distribution of the form

\[
I(x) = I_o + \text{Re}(I_1 \exp(iKx)) \,
\]

where \( K = 2\pi / \lambda \) is the grating wave-vector associated to the grating spacing \( \lambda \).

Following the usual linearization procedure for small modulation \((I_1 << I_o)\) we can set the quantities \( N_D^+, N_I, n, E, J_e \) and \( J_I \) in a sinusoidal form\(^\dagger\) of the type

\[
F(x) = F_o + \text{Re}(F_1 \exp(iKx))
\]

\(\dagger\) In general, these quantities are periodic, but not exactly sinusoidal functions. With this linearization one considers only the first Fourier component. For small modulation it can be shown that this approximation is good [42].
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where only the real part has physical meaning. In (2.3) the modulated quantities $F_I$ for $N_{D^+}$, $N_I$ and $n$ are small compared to the space-averaged quantities $F_o$. Inserting (2.2) and (2.3) into the set of equation (2.1a-2.1f) one gets three coupled linear differential equations for the first order variables $n_I, N_{D^+}$ and $N_{II}$. They are

$$\frac{\partial n}{\partial t} = -(\Gamma_{Re} + \Gamma_{De} + \Gamma_{die} - i\Gamma_{Ee}) n + (\Gamma_{die} - \Gamma_{le}) N_{D^+} + \Gamma_{die} N_{II} + s_e(N_D - N_{D^+}) I_1$$

(2.4a)

$$\frac{\partial N_{D^+}}{\partial t} = -\Gamma_{Re} n - \Gamma_{le} N_{D^+} + s_e(N_D - N_{D^+}) I_1$$, and

(2.4b)

$$\frac{\partial N_{II}}{\partial t} = \Gamma_{di} n - \Gamma_{di} N_{D^+} - (\Gamma_{di} + \Gamma_{DI} + i\Gamma_{EI}) N_{II}$$

(2.4c)

where $s_e(N_{D^+} - N_{D^+}) I_1$ is a time independent inhomogeneous term. The time rates $\Gamma$ in Eq.(2.4a-2.4c) are defined as follows

dielectric rate for electrons, $\Gamma_{die} = \frac{e\mu_e n_o}{\varepsilon \varepsilon_o}$, (2.5a)

sum of production and recombination rate, $\Gamma_{le} = s_e I_o + \beta + \gamma n_o$, (2.5b)

recombination rate for electrons, $\Gamma_{Re} = \gamma_e (N_A + n_o)$, (2.5c)

diffusion rate for electrons $\Gamma_{De}$, $\Gamma_{De} = \frac{K_e k_B T \mu_e}{\varepsilon}$, (2.5d)

drift rate for electrons, $\Gamma_{Ee} = K \mu_e E_o$, (2.5e)

dielectric relaxation rate for ions $\Gamma_{di}$, $\Gamma_{di} = \frac{e\mu_i N_{Io}}{\varepsilon \varepsilon_o}$, (2.5f)

diffusion rate for the ions $\Gamma_{DI}$, $\Gamma_{DI} = \frac{K^2 k_B T \mu_i}{\varepsilon}$, (2.5g)

drift rate for ions, $\Gamma_{EI} = K \mu_i E_o$. (2.5h)

Here $E_o$ is the externally applied electric field. The average electron density under illumination with intensity $I_o$ is given by

$$n_o = \frac{(s_e I_o + \beta_e) \left(N_D - N_{D^+}^+\right)}{\gamma_e N_{D^+}}$$

(2.6)

### 2.3.1 Steady state solutions

We analyze first the solutions of the set of equations (2.4a-2.4c) in the steady state where all time derivatives are zero. The value of the total space-charge field $E_1$ is given by

$$E_1 = \frac{e}{\varepsilon \varepsilon_o i K \Gamma_{le} (\Gamma_{di} + \Gamma_{DI} + i\Gamma_{EI}) (\Gamma_{De} - i\Gamma_{Ee}) (\Gamma_{di} + \Gamma_{Di} + i\Gamma_{EI})}$$

(2.7)
For low intensity cw illumination of the crystal the concentration \( n_0 \) of free charges in the conduction band is small compared with the concentrations \( N_{D0} \) and \( N_A \). In this case it is reasonable to assume that the sum of production and recombination rate \( \Gamma_{re} \) is small compared to the recombination rate \( \Gamma_{Re} \) and that the dielectric rate for electrons \( \Gamma_{die} \) is small compared to the corresponding diffusion rate \( \Gamma_{De} \). The solution (2.7) can then be transformed into a more convenient form

\[
E_1 = \frac{-im' E_q \left( E_D^2 + E_o^2 \right)}{\left( E_{ql} + E_D + iE_o \right) \left( E_D - iE_o \right) + E_q \left( E_D + iE_o \right)},
\]

where we have introduced standard quantities like \( E_D = k_B T/e \) for the diffusion field, \( m' = s l_j (s e l_o + \beta e) \) for the effective modulation index, and

\[
E_q = \frac{e}{e e_0 K} \frac{N_A (N_D - N_A)}{N_D} = \frac{e}{e e_0 K} N_{eff}
\]

for the maximum space charge field that can be created by the electrons. The term \( N_{eff} \) in (2.9) defines an effective number of active centers. In analogy with \( E_q \), a new limiting field was introduced in (2.8), that is

\[
E_{ql} = \frac{e N_{l0}}{e e_0 K}
\]

representing the maximum space-charge field amplitude that can be created by the ionic charges with density \( N_{l0} \). The total modulated space-charge field \( E_1 \) of Eq. (2.8) is a superposition of an electronic component \( E_{e1} \) and an ionic component \( E_{I1} \);

\[
E_{e1} = \frac{-im' E_q \left( E_{ql} + E_D + iE_o \right) \left( E_D - iE_o \right)}{\left( E_{ql} + E_D + iE_o \right) \left( E_D - iE_o \right) + E_q \left( E_D + iE_o \right)}
\]

\[
E_{I1} = \frac{+im' E_q E_{ql} \left( E_D - iE_o \right)}{\left( E_{ql} + E_D + iE_o \right) \left( E_D - iE_o \right) + E_q \left( E_D + iE_o \right)}
\]

We first discuss the results (2.8) and (2.11) in the simpler case where no field is applied to the crystal, that is, \( E_o = 0 \). The space charge fields \( E_1, E_{e1} \) and \( E_{I1} \) are then purely imaginary indicating a phase shift of \( \pm \pi/2 \) with respect to the light interference fringes. As will be shown later, this phase shift gives rise to energy transfer between the recording beams, and thus to beam amplification. For \( E_o = 0 \) we get

\[
E_1 = \frac{-im' E_{e1} E_q}{E_q + E_D + E_{ql}},
\]

\[
E_{e1} = \frac{-im' E_q (E_D + E_{ql})}{E_q + E_D + E_{ql}}
\]
The equation shows that, if the number of ions $N_{i_0}$ largely exceeds the effective number of traps $N_{\text{eff}}(E_{q_l} > E_q)$, the total space charge field $E_1$ in Eq. (2.12a) becomes small, well below the values of $E_D$ or $E_q$. This corresponds to the experimental observations in KNbO$_3$ crystals at high temperatures (Chapter 4.1).

### 2.3.2 Dynamic behaviour with no applied field

When we set $E_0 = 0$, the set of Eqs. (2.4a-2.4c) can be solved exactly giving the grating dynamics for small modulation. In this case, the time evolution of $N_{D1}^+, N_{I1}$ and $n_1$ takes a triple exponential form of the type

$$G_x(r) = G^1 \exp(-\Gamma_1 t) + G^2 \exp(-\Gamma_2 t) + G^3 \exp(-\Gamma_3 t) + G_{\text{sat}} \tag{2.13}$$

The $G_{1(r_i)}$ are nine real amplitudes for $N_{D1}^+, N_{I1}$ and $n_1$ and the constant terms $G_{\text{sat}}$ account for the inhomogeneity of the set of differential equations (2.4a-2.4c). The three time rates $\Gamma_1$, $\Gamma_2$ and $\Gamma_3$ are obtained from a cubic characteristic equation derived from (2.4). This is

$$\Gamma^3 - \left(\Gamma_{\text{tot}}\right) \Gamma^2 + \left(\Gamma_b\right)^2 \Gamma - \left(\Gamma_c\right)^3 = 0 \tag{2.14}$$

where the constant terms $\Gamma_{\text{tot}}$, $(\Gamma_b)^2$ and $(\Gamma_c)^3$ contain the characteristic time rates listed in (2.5a-2.5h) and will be defined below. Since the fields $E_1$, $E_{e1}$ and $E_{I1}$ are linearly related to the amplitudes of the modulated concentrations $N_{D1}^+, N_{I1}$ and $n_1$, they also have the form (2.13) but are purely imaginary, showing the expected $\pi/2$ phase shift. The amplitudes $G_{1(r_i)}$ are determined by the requirement that Eqs. (2.13) fulfill the appropriate initial conditions. The constant term $G_{\text{sat}}$ vanishes in the erasure process ($t_1 = 0$) and assumes the steady-state values (2.12a-2.12c) for the recording process.

We want now to formulate an analytical expression for the three time rates $\Gamma_1$, $\Gamma_2$ and $\Gamma_3$ involved in the dynamics of the space charge fields. In the case of no applied field they are all real and positive. The three coefficients in Eq. (2.14) which are used for obtaining the three solutions $\Gamma_1$, $\Gamma_2$ and $\Gamma_3$ are as follows. The first coefficient is equal to

$$\Gamma_{\text{tot}} = \Gamma_{\text{die}} + \Gamma_{le} + \Gamma_{Re} + \Gamma_{De} + \Gamma_{di} + \Gamma_{Di} \tag{2.15}$$

which represents a total rate given by the sum of all non vanishing rates in (2.5a-2.5h). The second coefficient is given by

$$\Gamma_b = \sqrt{\Gamma_{\text{die}} \left(\Gamma_{Di} + \Gamma_{le} + \Gamma_{Re}\right) + \left(\Gamma_{di} + \Gamma_{Di}\right) \left(\Gamma_{De} + \Gamma_{le} + \Gamma_{Re}\right) + \Gamma_{De} \Gamma_{le}} \tag{2.16}$$

and the third one is

$$\Gamma_c = \sqrt{\Gamma_{\text{die}} \Gamma_{Di} \left(\Gamma_{le} + \Gamma_{Re}\right) + \Gamma_{De} \Gamma_{le} \left(\Gamma_{di} + \Gamma_{Di}\right)} \tag{2.17}.$$
It can be checked that \( \Gamma_{\text{tot}} > \Gamma_b, \Gamma_c \) and the solutions of the cubic equation (2.14) can be developed in a series in terms of \( (\Gamma_b/\Gamma_{\text{tot}})^2 \) and \( (\Gamma_c/\Gamma_{\text{tot}})^3 \) leading in the first approximation to the following expressions

\[
\Gamma_1 = \Gamma_{\text{tot}},
\]

\[
\Gamma_2 = \frac{(\Gamma_b)^2}{\Gamma_{\text{tot}}} - \frac{(\Gamma_c)^3}{(\Gamma_b)^2} - \frac{\Gamma_{\text{tot}}(\Gamma_c)^6}{(\Gamma_b)^6} - 2 \frac{(\Gamma_{\text{tot}})^2(\Gamma_c)^9}{(\Gamma_b)^{10}} - \ldots = \frac{(\Gamma_b)^2}{\Gamma_{\text{tot}}} - \Gamma_3,
\]

\[
\Gamma_3 = \frac{(\Gamma_c)^3}{(\Gamma_b)^2} + \frac{\Gamma_{\text{tot}}(\Gamma_c)^6}{(\Gamma_b)^6} + 2 \frac{(\Gamma_{\text{tot}})^2(\Gamma_c)^9}{(\Gamma_b)^{10}} + 5 \frac{(\Gamma_{\text{tot}})^3(\Gamma_c)^{12}}{(\Gamma_b)^{14}} + \ldots.
\]

The time rate \( \Gamma_1 \) describes mainly the dynamics of the free electron grating in the conduction band. The experiments show that the related time constant \((\Gamma_1)^{-1}\) is normally in the \( \mu \)s region. For cw laser illumination it can be shown that the space-charge field amplitudes accompanying this time constant are small. Therefore, unless the grating has been formed by intensive laser pulses or using highly absorbed ultraviolet light, the term containing \( \Gamma_1 \) in the time evolution of the space-charge field (2.13) can be neglected.

We concentrate further on the two other time rates \( \Gamma_2 \) and \( \Gamma_3 \). In most of the cases, the leading terms in (2.18b) and (2.18c) dominate so that \( \Gamma_2 \) and \( \Gamma_3 \) can be written as

\[
\Gamma_2 = \frac{(\Gamma_b)^2}{\Gamma_{\text{tot}}},
\]

\[
\Gamma_3 = \frac{(\Gamma_c)^3}{(\Gamma_b)^2},
\]

and

\[
\Gamma_2 = \frac{(\Gamma_b)^2}{\Gamma_{\text{tot}}} + \frac{(\Gamma_c)^3}{(\Gamma_b)^2}.
\]

It is usually also true that the recombination rate \( \Gamma_{Re} \) and the diffusion rate \( \Gamma_{De} \) for electrons are much larger than all other time rates in (2.5a-2.5h) and the relations (2.19a) and (2.19b) can be put into more useful forms, which are

\[
\Gamma_2 = \Gamma_{\text{dil}} \left[ 1 + \frac{K^2}{K_{\text{tot}}^2} \right] + \Gamma_{\text{die}} \left[ \frac{1 + \frac{K^2}{K_{\text{die}}^2}}{1 + \frac{K^2}{K_e^2}} \right],
\]

\[
\Gamma_3 = \Gamma_{\text{dil}} \left[ 1 + \frac{K^2}{K_{\text{tot}}^2} \right] + \Gamma_{\text{die}} \left[ 1 + \frac{K^2}{K_e^2} \right] \left[ 1 + \frac{K^2}{K_{\text{tot}}^2} \right]
\]

\[
\Gamma_4 = \Gamma_{\text{dil}} \left[ 1 + \frac{K^2}{K_{\text{die}}^2} \right] + \Gamma_{\text{die}} \left[ 1 + \frac{K^2}{K_e^2} \right] \left[ 1 + \frac{K^2}{K_{\text{tot}}^2} \right]
\]
where

\[ K_{oe}^2 = \frac{e^2 N_A (N_D - N_A)}{\varepsilon \varepsilon_0 k_B T N_D} = \frac{e^2 N_{\text{eff}}}{\varepsilon \varepsilon_0 k_B T} \quad (2.22) \]

is the square of the Debye wavevector for the electrons, for this wave vector the diffusion field \( E_D \) equals the trap limited field \( E_q \).

\[ K_{ol}^2 = \frac{e^2 N_{lo}}{\varepsilon \varepsilon_0 k_B T} \quad (2.23) \]

is the square of the corresponding wavevector for ions, and

\[ K_{\varepsilon}^2 = \frac{e \gamma_e N_A}{\mu e k_B T} \quad (2.24) \]

is the square of the inverse diffusion length.

The rate \( \Gamma_2 \), whose grating spacing dependence is explicitly given in (2.20), can be generally ascribed to the time evolution of the primary electronic grating and describes the dynamics during the writing (A) and revealing time (C) of the hologram. The ionic distribution is negligibly perturbed in a time scale given by this rate.

Equation (2.21) describes the grating spacing dependence of the time rate \( \Gamma_3 \). This time rate does not exist in the conventional one charge carrier Kukhtarev model. Thus, the dynamic evolution of the space-charge amplitude in crystals showing charge compensation is more complex than the one expected for the conventional case. The experiments show that \( \Gamma_3 \) is the rate describing the dynamics during the storage time (in the dark), the handling time (under homogeneous illumination) or the compensating time (under inhomogeneous illumination) of a grating in ionic compensating materials. In general, both ions and electrons can redistribute in a time scale given by \( \Gamma_3 \).

We discuss now the grating spacing dependence of the rate \( \Gamma_3 \). We consider the case where the crystal contains a number of ions \( N_{lo} \) which is large compared with the effective number of traps \( N_{\text{eff}} \), that is \( K_{ol}^2 >> K_{oe}^2 \). It will be shown later that this condition is necessary to explain the experimental observations in KNbO\(_3\) using our model. We assume further that the temperature is not too high so that \( F_{\text{dim}} << F_{\text{die}} \) is fulfilled. This can be easily realized by adapting the experimental conditions. Equation (2.21) can then be simplified to

\[ \Gamma_3 = \Gamma_{\text{dim}} \frac{K^2}{K_{oe}^2 + K^2} \quad (2.25) \]

\[ \dagger \] This time rate corresponds to the one found in the one charge carrier Kukhtarev model (section 2.3.4) augmented by the term containing \( \Gamma_{\text{dim}} \). For most experimental situations this term is small compared to the term proportional to \( \Gamma_{\text{die}} \).
Therefore, for small grating spacings \((K \rightarrow \infty)\) \(\Gamma_3\) is given by the dielectric relaxation rate for the ions \(\Gamma_{\text{diff}}\). This represents the dielectric limit. It is interesting that this is in contrast with the case of the time rate \(\Gamma_2\) related to the primary grating. There, the dielectric limit is found for large grating spacings. Equation (2.25) predicts for large grating spacings \((K \rightarrow 0)\) a quadratic dependence of \(\Gamma_3\) on \(K\), that is, compensating, storage, and handling time increase with the square of the grating spacing \(\Lambda\).

### 2.3.3 Dynamic behaviour with applied field

The case where the applied field \(E_0\) does not vanish can be treated in a similar way as the simpler case examined in the previous section. Eq. (2.13), which describes the time evolution of the amplitude \(F_1\) in (2.3), is still valid but the relaxation rates \(\Gamma_i\) are now complex and we designate them \(\Gamma_1^*, \Gamma_2^*\) and \(\Gamma_3^*\). Keeping the dependence on the space variable \(x\), Eq. (2.13) takes then the form

\[
E_1(x,t) = E_{1\text{sat}} \cos(Kx + \phi) - \frac{3}{2} \left\{ \exp(-\text{Re}(\Gamma_i^*) t) \right\} \left| E_{1o}(\Gamma_i^*) \right| \cos(Kx + \phi - \text{Im}(\Gamma_i^*) t) \right]
\]

(2.26)

for the grating build-up, and

\[
E_1(x,t) = \frac{3}{2} \left\{ \exp(-\text{Re}(\Gamma_i^*) t) \right\} \left| E_{1o}(\Gamma_i^*) \right| \cos(Kx + \phi - \text{Im}(\Gamma_i^*) t) \right]
\]

(2.27)

for the decay after switching off the illumination. The phases \(\varphi_i\) and \(\phi\) are defined with

\[
\tan \varphi_i = \frac{\text{Im} \left( E_{1o}(\Gamma_i^*) \right)}{\text{Re} \left( E_{1o}(\Gamma_i^*) \right)} \quad \text{and} \quad \tan \phi = \frac{\text{Im} \left( E_{1\text{sat}} \right)}{\text{Re} \left( E_{1\text{sat}} \right)} ,
\]

(2.28)

where the quantities \(E_{1o}(\Gamma_i^*)\) are the space-charge field amplitude related with each complex time rate \(\Gamma_i^*\). The imaginary parts of the three time rates produce a time dependent change of the phase shift between the light fringes and the three components of the grating. As long as the steady state is not reached, every component of the grating is running inside the crystal with velocity \(\text{Im}(\Gamma_1^*)/K\). Therefore, the imaginary part of the time rates produces oscillations in the dynamics. However, the observation of such oscillations is only possible if the oscillatory terms \(\text{Im}(\Gamma_1^*)\) are not too small with respect to the exponential decay rates \(\text{Re}(\Gamma_1^*)\).

We concentrate now on the three complex time rates \(\Gamma_1^*, \Gamma_2^*\) and \(\Gamma_3^*\). They are again the three solutions of the cubic equation (2.14), this time with complex coefficients \(\Gamma_{\text{tot}}^*, (\Gamma_0^2)^\ast\) and \((\Gamma_3^2)^\ast\). The first coefficient is defined as

\[
\Gamma_{\text{tot}}^* = \Gamma_{\text{tot}} + i \left( \Gamma_{E_l} - \Gamma_{E_e} \right) ,
\]

(2.29)
where $\Gamma_{EL}$ and $\Gamma_{Ee}$ are the drift rates for ions and electrons defined in (2.5h) and (2.5e) and $\Gamma_{tot}$ is given in (2.15). The second constant is

$$\left(\Gamma_b^2\right)^* = \Gamma_b^2 + \Gamma_{EL} \Gamma_{Ee} + i \left(\Gamma_{EL} \left(\Gamma_{die} + \Gamma_{le} + \Gamma_{Re} + \Gamma_{De}\right) - \Gamma_{Ee} \left(\Gamma_{dl} + \Gamma_{le} + \Gamma_{Di}\right)\right)$$

(2.30)

and the third is

$$\left(\Gamma_c^3\right)^* = \Gamma_c^3 + \Gamma_{le} \Gamma_{Ee} \Gamma_{EL} + i \left(\Gamma_{die} \Gamma_{EL} \left(\Gamma_{le} + \Gamma_{Re}\right) + \Gamma_{De} \Gamma_{le} \Gamma_{EL} - \Gamma_{le} \Gamma_{Ee} \left(\Gamma_{dl} + \Gamma_{Di}\right)\right)$$

(2.31)

The solutions $\Gamma_1^*$ of Eq. (2.14) can still be expressed in good approximation by Eqs. (2.18a-2.18c) by replacing all the real constants with the corresponding complex constants. As in the derivation of Eqs. (2.20) and (2.21) from (2.19a) and (2.19b), we consider the usual case with the diffusion rate $\Gamma_{De}$, the recombination rate $\Gamma_{Re}$, and the drift rate $\Gamma_{Ee}$ for electrons to be larger than the other rates defined in relations (2.5a-2.5h). We assume further that $\Gamma_{dl} > \Gamma_{Di}$. All the quantities $\Gamma_1^*$, $\Gamma_2^*$ and $\Gamma_3^*$ can then be obtained from (2.18a), (2.19a) and (2.19b) if the real coefficients $\Gamma_{tot}$, $\Gamma_2^*$ and $\Gamma_3^*$ in these three expressions are replaced by the corresponding complex coefficients. However, the expressions are rather lengthy and we give only the values for $\Gamma_2^*$. From Eq. (2.19a) we get

$$\text{Re}(\Gamma_2^*) = \Gamma_{dl} \left[1 + \frac{K^2}{K_{el}^2} + \frac{K^2 K_D^2}{(K^2 + K_{le}^2)^2 + K^2 K_D^2}\right] + \Gamma_{die} \left[\frac{K_e^2 (K^2 + K_{le}^2) \left(1 + \frac{K^2}{K_{oe}^2}\right) + \frac{K_e^2 K^2}{K_{oe}^2} - K_D^2}{(K^2 + K_{le}^2)^2 + K^2 K_D^2}\right]$$

(2.32)

for its real part, and

$$\text{Im}(\Gamma_2^*) = \Gamma_{dl} \frac{K K_D}{K_{el}^2} + \Gamma_{die} \left[\frac{K_e^2 \left(1 - \frac{K^2}{K_{oe}^2}\right) K K_D}{(K^2 + K_{le}^2)^2 + K^2 K_D^2}\right]$$

(2.33)

for its imaginary part, where

$$K_D = \frac{eE_o}{k_B T}$$

(2.34)

is the wavevector for which the applied field equals the diffusion field.

The dependencies of the time rates on the grating spacing, the light intensity and applied electric field are discussed in section 2.4 where a comparison with the predictions of the conventional Kukhtarev model is made.
2.3.4 The conventional Kukhtarev model: A special case

In the conventional case presented by Kukhtarev et al. [27] a single charge carrier species is redistributed starting from a single donor level. The results applying in this case can be easily derived from the above equations. For this purpose we have to put the number of ions \( N_{10} \) and the ionic mobility \( \mu_i \) equal to zero.† From (2.8) or (2.11a) with \( E_q=0 \) one gets for the steady-state space charge field

\[
E_1 = \frac{-im' E_q (E_D - iE_o)}{E_q + E_D - iE_o},
\]

which can be rewritten as

\[
E_1 = -m' \frac{E^2_q E_o}{(E_q + E_D)^2 + E_o^2} - im' \frac{E_q E^2_D + E_q E^2_o + E^2_q E_D}{(E_q + E_D)^2 + E_o^2}.
\]

The first term in (2.36) gives the component of the space-charge field which is not shifted with respect to light interference fringes, while the second (imaginary) term represents the \( \pi/2 \) shifted component. In the diffusion case (\( E_o=0 \)), Eq. (2.36) reduces to the well known formula

\[
E_1 = -im' \frac{E_q E_D}{E_q + E_D}.
\]

In the derivation of Eqs. (2.8)-(2.12) and (2.35)-(2.37) electrons were assumed to be the redistributing primary charge carriers. In the opposite case where only holes are being redistributed through photoexcitation to the valence band all the above equations maintain their validity if one substitutes \( E_q \) with \(-E_q\) and \( E_D \) with \(-E_D\). Thus, in the diffusion case (Eq. (2.37)) the space-charge field changes sign, indicating an opposite phase shift for the hole and electron cases.

The space-charge field dynamics in the one center model is also given by Eq. (2.13) with \( E_1(t) = 0 \). As discussed in section 2.3.2, the amplitude \( E_1(t) \) is very small for cw-laser irradiation. Therefore, the Kukhtarev model predicts a single exponential time evolution of the kind

\[
E_1(t) = E_{sat} \left(1 - \exp(-\Gamma_2 t)\right),
\]

for the recording process, and

\[
E_1(t) = E_1(t = 0) \exp(-\Gamma_2 t)
\]

† The ions are still present in the crystal \( (N_{10} \neq 0) \), but because \( \mu_i=0 \) one would have to wait an infinite time for the steady state. To make the model realistic we therefore put \( N_{10}=0 \) as well.
for the optical or dark erasure process. The time rate $\Gamma_2$ follows from Eq. (2.20) inserting $\Gamma_{dif}=0$,

$$\Gamma_2 = \Gamma_{die} \left[ 1 + \frac{K^2}{K_{oe}^2} \right] \left[ 1 + \frac{K^2}{K_e^2} \right],$$

(2.40)

where it should be remembered that the dielectric rate $\Gamma_{die}$ depends on light intensity (Eqs. (2.5a) and (2.6)). For aim of completeness we give also the expression for the real and imaginary part of the time rate $\Gamma_2^*$ for the case where an electric field is applied. From (2.32) and (2.33) we get

$$\text{Re}(\Gamma_2^*) = \Gamma_{die} \left[ \frac{K_e^2 (K^2 + K_e^2) \left( 1 + \frac{K^2}{K_{oe}^2} \right) + K_e^2 K^2}{(K^2 + K_e^2)^2 + K^2 K_D^2} \right],$$

(2.41)

$$\text{Im}(\Gamma_2^*) = \Gamma_{die} \left[ \frac{K_e^2 \left( 1 - \frac{K^2}{K_{oe}^2} \right) K K_D}{(K^2 + K_e^2)^2 + K^2 K_D^2} \right].$$

(2.42)
2.4 Discussion of the electron-ion model

In this section, the predictions derived from the electron-ion model are compared with the ones of the conventional one-charge carrier model. We use the set of parameters listed in Appendix A to discuss our model. The values characterizing external conditions like the light intensities, the effective modulation index $m'$, and the temperature are arbitrary but correspond to usually applied experimental conditions. The other parameters have been chosen in such a way that the most important predictions of the theoretical model can be well identified in the different figures. In some cases the simplified analytical expressions are compared with exact solutions of the set of equations (2.4a-2.4c) obtained using the same set of parameters.

The mean density of free ions $N_{Io}$ is chosen to be large compared to $N_A$ and $N_D$. This is necessary in order to be able to simulate the observed compensation effects by the theory. Some of the remaining parameters which describe crystal properties are particularly referred to KNbO$_3$ crystals, but values being appropriate to BaTiO$_3$, Bi$_{12}$SiO$_{20}$, Bi$_4$Ge$_3$O$_{12}$ or other photorefractive crystals can be used without qualitative modifications in the theoretical predictions. The number $N_A$ of ionized donors in the dark corresponds to a typical value for slightly doped KNbO$_3$ crystals. The small ionic mobility $\mu_i$ is chosen in such a way that the product $\mu_i N_{Io}$ is consistent with our experimental observations in KNbO$_3$ [41]. The parameters $s_e$, $\beta_e$, $\gamma_e$ and $\mu_e$ are taken from Ref. [43] for KNbO$_3$. The relatively small electron mobility $\mu_e$ should be considered as a trap-limited mobility [44] and not as a true conduction band mobility. Finally, the density of donors $N_D$ is estimated from usual doping concentrations. It is chosen in such a way that its combination with $N_A$, $s_e$, $\beta_e$, $\gamma_e$ and $\mu_e$ through the equations (2.6) and (2.5a) gives dielectric relaxation rates consistent with observations in reduced KNbO$_3$.

2.4.1 Steady state space-charge fields

Fig. 2.3 and Fig. 2.4 show the grating spacing dependence of the steady-state space charge field $E_1$ and its electronic component $E_{e1}$ for the electron-ion model and for the conventional one-center model. In Fig. 2.3 the curves are drawn for the diffusion case while Fig. 2.4 shows the case where an electric field is applied.

In the conventional case (long dashed lines) the situation is the following. For no applied fields, the amplitude $E_1$ of the space-charge field first increases, reaches a maximum at a certain grating spacing and then decreases for larger $\Lambda$. $E_1$ decreases towards small grating spacing because of the limitations given by Poisson equation (2.1f). As the gradient of $E_1$ gets large for large spatial frequencies, the space-charge field itself is limited by the finite number of donors and acceptors. Thus, for small grating spacings the space charge field is limited by the field $E_q$, which is directly proportional to $\Lambda$ (Eq. 2.37). The situation at large grating spacings is different. In this regime there are enough donors and traps to create a large space-charge field. However, the charge carrier diffusion process, which takes place until the drift produced by the internal space charge field counterbalances it, limits the final
value of $E_1$. Thus, since for large $\Lambda$ diffusion is slow, the space charge field is limited by the value of $E_D$, explaining the linear decrease of $E_1$ towards large grating spacings.

![Graph](image)

**Fig. 2.3:** Grating spacing dependence of the total space-charge field amplitude $E_1$ and its electronic contribution $E_{e1}$ for the case of no applied field. The curves are drawn with Eqs. (2.12a), (2.12b) and (2.37) using the model parameter of Appendix A. The long-dashed line shows the conventional case of no ionic motion.

![Graph](image)

**Fig. 2.4:** Grating spacing dependence of the absolute values of the fields $E_1$ and $E_{e1}$ for an applied field $E_o=10$ kV/cm. Eqs. (2.8), (2.11a) and (2.35). Long-dashed line: conventional case.
An external electric field introduces an additional driving force helping charge separation at large grating spacing. Thus, the final value of $E_i$ is increased with respect to the diffusion case (Fig. 2.4, long dashed line). For large values of $\Lambda$ where $E_o << E_q$, the space charge field saturates to a value proportional to the external field $E_o$.

If moving ions are present, the situation discussed above is changed radically. From Fig. 2.3 we see that the total space-charge field $E_i$ is decreased considerably with respect to its electronic component $E_{ei}$. This component grows linearly with grating spacing and do not decrease for large $\Lambda$ like for the above discussed case. The compensation effect by the ions leads to a total space-charge field which is always much smaller than the diffusion field $E_D$. Thus, the diffusion process is not contrasted by a back-drift in the internal field and charge separation can proceed to its maximum, so that $E_{e1}$ and $E_{i1}$ are proportional to $E_q$.

For $E_o \neq 0$ the steady state value of the total space-charge field $E_i$ is no longer so strongly dependent on the grating spacing $\Lambda$ (solid line in Fig. 2.4). For large enough $\Lambda$, $E_i$ is proportional to $m' E_q E_0 / E_q$ and is essentially in phase with the light interference fringes. Note that the unshifted (that is real) component of the electronic and the ionic contribution to the space-charge field are still small compared with the $\pm \pi/2$ phase-shifted components. Nevertheless, the resulting field $E_i$ is formed by these unshifted components which have opposite signs and different magnitude for electrons and ions.

### 2.4.2 Dynamic behaviour

#### 2.4.2.1 Grating spacing dependence

The grating spacing dependencies of the time rates $\Gamma_2$ and $\Gamma_3$ given by Eqs. (2.20) and (2.21) are shown in Fig. 2.5 and Fig. 2.6 respectively.

From Fig. 2.5 we see that $\Gamma_2$ approaches a constant value at large grating spacings, the asymptote being equal to the sum of the dielectric rates for electrons and ions. For very small $\Lambda$, however, $\Gamma_2$ does not depend on the ionic mobility, as can be seen by looking at the dashed lines which give exact solutions obtained by inserting numerical values in the initial equations. This is in disagreement with Eq. (2.20) which predicts a larger rate in this regime. This discrepancy is due to the higher order terms in Eq. (2.18b) that have been neglected in the derivation of Eq. (2.20). Such terms become important in the case where the dielectric rates for electrons and ions ($\Gamma_{die}$ and $\Gamma_{dil}$ respectively) become comparable in magnitude.

The functional dependence shown in Fig. 2.5 is valid also in the case of the one-charge carrier Kukhtarev model confirming the fact that the rate $\Gamma_2$ should be ascribed to the primary electronic charge carriers.

---

† Since $E_i = E_e + E_{i1}$ is small, the ionic component $E_{i1}$ of the space-charge field (not shown in Fig. 2.3) takes approximately the same values as $E_{e1}$, but with opposite sign.
Fig. 2.5: Grating spacing dependence of the time rate $\Gamma_2$ for $E_0=0$. The full lines show the approximate analytical expression (2.20) for the model parameters of Appendix A (lower curve) and a 10 times increased ionic mobility ($\mu_I = 2 \times 10^{-14} \text{m}^2/\text{Vs}$, upper curve). The dashed lines are exact solutions of Eq. (2.14) for the corresponding parameters.

Fig. 2.6: Grating spacing dependence of the time rate $\Gamma_3$ for $E_0=0$. The full lines show the approximate analytical expression (2.21) for the model parameters of Appendix A (lower curve) and a 10 times increased ionic mobility ($\mu_I = 2 \times 10^{-14} \text{m}^2/\text{Vs}$, upper curve). The dashed lines are exact solutions of Eq. (2.14) for the corresponding parameters. For the smaller value of $\mu_I$ the solid and the dashed line overlap also at small grating spacings.
Fig. 2.6 shows that the agreement between the approximated analytical solutions (2.21) and the exact solution is much better for the time rate $\Gamma_3$. Again, a small discrepancy due to the higher order terms in Eq. (2.18c) is observed for grating spacings smaller than one $\mu$m and comparable values of $\Gamma_{diff}$ and $\Gamma_{die}$. The quadratic decrease of $\Gamma_3$ for large $\Lambda$ discussed in the derivation of (2.25) can be easily recognized. For small $\Lambda$, $\Gamma_3$ is approximated by the value of $\Gamma_{diff}$. It will be shown in Chapter 4.1, that a fit of experimental data to (2.21) giving curves similar to the one shown in Fig. 2.6 proves to be very useful for getting information on parameters influencing the photorefractive effect.

We can give now some examples of the full dynamic evolution for the case $E_o = 0$. The usual simple exponential behaviour of the space-charge fields (Eqs. (2.38) and (2.39)) is replaced by an essentially double exponential behaviour. Fig. 2.7 and Fig. 2.8 show the exact solutions of the initial set of equations (2.4a-2.4c) for two different values of the grating spacing. The full dynamic evolution of the total space-charge field $E_1$ and of their electronic and ionic components is shown. The numerical values to be inserted in Eq. (2.13) are given in Table 2.1. The effect of compensation can be clearly recognized in the figures and correspond to the one observed experimentally (Fig. 2.2).

Table 2.1: Values for Eq. (2.13) which were used to generate Figs. 2.7, 2.8 and 2.9. The values are calculated from the set of equations (2.4a-2.4c) with the parameters of Appendix A except for the ones indicated explicitly in the figure captions.

<table>
<thead>
<tr>
<th></th>
<th>Recording</th>
<th>Erasure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fig. 2.7</td>
<td>Fig. 2.8</td>
</tr>
<tr>
<td>$\Gamma_1$ [s$^{-1}$]</td>
<td>$10^7$</td>
<td>$5\times10^6$</td>
</tr>
<tr>
<td>$\Gamma_2$ [s$^{-1}$]</td>
<td>23.3</td>
<td>16.3</td>
</tr>
<tr>
<td>$\Gamma_3$ [s$^{-1}$]</td>
<td>5.0</td>
<td>0.85</td>
</tr>
<tr>
<td>$E_{1(r_1)}$ [V/m]</td>
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<td>0.05</td>
</tr>
<tr>
<td>$E_{1(r_2)}$ [V/m]</td>
<td>-41784</td>
<td>-24271</td>
</tr>
<tr>
<td>$E_{1(r_3)}$ [V/m]</td>
<td>+41060</td>
<td>+24088</td>
</tr>
<tr>
<td>$E_{1sat}$ [V/m]</td>
<td>723</td>
<td>184</td>
</tr>
</tbody>
</table>

For a clearer demonstration of the compensation dynamics in Fig. 2.7 and Fig. 2.8 we have selected a set of parameters giving equal dielectric relaxation times for electrons and ions. Nevertheless, the time rate $\Gamma_3$ is smaller than $\Gamma_2$ because the fields driving the compensation and erasure processes are smaller than the compensating electronic and ionic contributions to the space-charge field. In addition, the figures show that the compensation is slower for $\Lambda = 2 \mu$m than for $\Lambda = 0.5 \mu$m. This is expected from the derived dependence of the time rate $\Gamma_3$ on grating spacing (2.21). It is interesting to note that, in case only ions contribute to the grating observed during the storage or handling time of the hologram, the time rate $\Gamma_3$ would never be smaller than the dielectric relaxation rate $\Gamma_{diff}$ [41]. Therefore, the experimental fact that $\Gamma_3$ decreases at large $\Lambda$ can only be explained by the simultaneous presence of the electronic charges. Similar effects where the interaction between different charges influences the time evolution have been observed in the field of thermoelectrets. It
was shown that a system of homo- and heterocharges decays much slower than a homocharge or a heterocharge alone [45].

Fig. 2.7: Exact solution of the dynamic equations (2.4a-2.4c) for the model parameters of Appendix A except for a 10 times increased ionic mobility ($\mu_I = 2 \cdot 10^{-14} \text{ m}^2/\text{Vs}$). Curves for the total space charge field $E_t = E_1 + E_{II}$ and the two components $E_1$ and $E_{II}$ are shown. The numerical values of all the parameters describing the solution for the field $E_1(t)$ following Eq. (2.13) are given in Table 2.1. $E_o = 0$.

Fig. 2.8: Same as Fig. 2.7, but for a grating spacing $\Lambda = 2 \text{ mrm}$. 
The information contained in Fig. 2.7, Fig. 2.8 and in Table 2.1 will also serve as a basis to discuss the behaviour of the amplitudes $E_{el}(r_1)$, $E_{el1}(r_1)$ and $E_{el1}(r_1)$ in Eqs. (2.13). By comparison of the two figures one can see that the steady-state values of the two components $E_{el}$ and $E_{el1}$ are larger for $\Lambda=2\ \mu m$. This is expected from Eq. (2.12) and from Fig. 2.3. One might suggest that the field $E_{el}$ would evolve in time only with the time rate $\Gamma_2$. In this case we would expect an increase of the height of the transient peaks of $E_1$ in Figs. 2.7 and 2.8 for larger grating spacings. However, this contradicts both the experimental observations and the calculated solutions of the problem. The reason is that at larger grating spacings an increasing part of the primary grating $E_{el}$ evolves with the time rate $\Gamma_3$ which is normally associated to the ionic grating. In other words, the amplitude $E_{el}(r_3)$ in (2.13) is increasing in magnitude with increasing grating spacing. For very large grating spacings the term $E_{el}(r_3)$ largely exceeds $E_{el}(r_2)$ and only a minor part of the electronic contribution to the space-charge field evolves with the faster rate $\Gamma_2$. In this limit, the total space-charge field $E_1$ is a sum of two large components evolving with the same time constant and cancelling each other to a large extent. Thus, for large grating spacings the field $E_1(t)$ is always small compared with $E_{el}(t)$ and $E_{el1}(t)$. However, for small grating spacings, the fields $E_{el}$ and $E_{el1}$ are almost independent with $E_{el}(r_3) \ll E_{el}(r_2)$ and $E_{el1}(r_3) \gg E_{el1}(r_3)$ (Fig. 2.7).

2.4.2.2 \textbf{Influence of the ionic concentration}

Fig. 2.9 shows the same behaviour as the one reported in Fig. 2.7, but for a 40 times smaller concentration of ions $N_{lo}$.

![Fig. 2.9](image_url)

Fig. 2.9: Exact solution of the dynamic equations (2.4a-2.4c) for $\Lambda=0.5\ \mu m$. The parameters are the same as in Fig. 2.7 except for a 40 times smaller number of ions ($N_{lo}=2.5\times10^{22} \text{ m}^{-3}$) and a 40 times larger conductivity for the ions ($\mu_q=8\times10^{-13} \text{ m}^2/\text{Vs}$) leading to an unchanged dielectric relaxation rate for the ions. The numeric values of all the parameters describing the solution for the field $E_1(t)$ following Eq. (2.13) are given in Table 2.1.
In the case of Fig. 2.9 one has $E_{qf} = 6E_q$ and the compensation of the grating during the recording process is only partial. The behaviour during the erasure is apparently different than the one of Fig. 2.7 and Fig. 2.8. One recognizes the point where the space-charge field amplitude $E_1$ crosses zero. Such a crossing point is present also in the situation of Fig. 2.7 and 2.8 at the very beginning of the erasure process. It must be mentioned that the dynamics shown in Fig. 2.9 for the erasure process is found also for full compensating crystals having $N_{Io} \gg N_{eff}$ if the recording process is interrupted before saturation is reached.

2.4.2.3 Light intensity dependence

In the discussion of the light intensity dependence of the time rates $\Gamma_2$ and $\Gamma_3$ we limit ourselves to the case where the dielectric relaxation rate for ions is smaller than the corresponding rate for electrons. We can then neglect the first term in (2.20) and $\Gamma_2$ becomes linearly dependent on $\Gamma_{die}$. Using (2.5a) and (2.6) we see that its value increases linearly with illuminating intensity $I_o$ as is expected from the conventional Kukhtarev model [27].

The case of the slow time rate $\Gamma_3$ is more complicated. We recall that this time rate describes the charge compensation process during recording and also the grating dynamics during the hologram handling process under homogeneous illumination. From Eq. (2.21) one deduces that $\Gamma_3$ increases monotonically with light intensity $I_o$ because $\partial(\Gamma_3)/\partial(\Gamma_{die}) > 0$. This increase is very small as long as $\Gamma_{die}$ sufficiently exceeds $\Gamma_{diff}$. However, Eq. (2.21) does not describe all possible conditions. In its derivation it was assumed that the electronic dielectric relaxation rate $\Gamma_{die}$ was small compared to the diffusion rate $\Gamma_{De}$. If this assumption is abandoned, an additional term must be considered in the denominator of Eq. (2.21) and the time rate $\Gamma_3$ can decrease for larger light intensities.$^\dagger$

We give the additional correction term for the special case previously described by expression (2.25), that is, in the limit $N_{Io} \gg N_{eff}$ and $\Gamma_{die} \gg \Gamma_{diff}$. Equation (2.25) transforms to

$$\Gamma_3 \equiv \Gamma_{diff} \frac{K^2}{K_{oe}^2 + K^2 + K^2 \Gamma_{die} / \Gamma_{De}} \quad (2.43)$$

Thus, a large decrease of $\Gamma_3$ with light intensity can be expected when $K^2 \Gamma_{die} / K_{oe}^2 \Gamma_{De} = 1$, which is equivalent to $n_o = N_{eff}$. Thus, the free electron concentration $n_o$ must be comparable to the effective number of photorefractive centers $N_{eff}$. This result is commented in the experimental part.

We illustrate this effect in Fig. 2.10, which shows the intensity dependence of the normalized time rate $\Gamma_3(I_o \neq 0) / \Gamma_3(I_o = 0)$. The smaller intensities required for the drop of $\Gamma_3$

$^\dagger$ This is a very unusual and interesting case. Normally any strong illumination results in a faster erasure of the optical information stored in the crystal while in this case the information is kept for longer time. An experimental demonstration of such a "negative intensity dependence" is given in Chapter 4.1 for KNbO₃.
with decreasing recombination constant $\gamma_e$ are due to the increased electron density $n_0$, whereas the decrease for smaller $N_A$ is mainly due to the decrease of $K_{oe}^2$. The curve for the smaller value of the ionic mobility $\mu_I$ is more flat than the one obtained using the parameters of Appendix A because the condition $\Gamma_{die} >> \Gamma_{diff}$ is fulfilled for lower light intensity in this case.

![Graph](image)

**Fig. 2.10:** Intensity dependence of the time rate $\Gamma_3$ as predicted by equation (2.19b) for $\Lambda = 2\ \mu m$. The values are normalized to the value of $\Gamma_3$ in the dark. The full line is drawn with the parameters of Appendix A. The other curves are obtained modifying only the indicated parameter to the given value.

### 2.4.2.4 Electric field dependence

We concentrate now on the dependencies of the time rates describing the space-charge field dynamics on the applied electric field. Fig. 2.11 shows this dependence for the rates $\text{Re}(\Gamma_2^*)$ and $\text{Im}(\Gamma_2^*)$, that is the rates which describe the evolution during writing and revealing of the hologram. $\text{Re}(\Gamma_2^*)$ approaches $\Gamma_{diff}(K_e^2/K_{oe}^2)$ for high values of $E_0$, this value is the same as the one obtained without a field for small grating spacings ($K --> \infty$ in Eq. (2.20)). Fig. 2.11 shows that, if the ionic mobility is small (conventional Kukhtarev case), the imaginary part (2.33) vanishes both for zero and for large electric fields. At the value $E_0 = (k_BT/e)(K^2 + K_e^2)/K$ the absolute value of $\text{Im}(\Gamma_2^*)$ reaches a maximum. Since the imaginary part of $\Gamma_2^*$ is responsible for oscillations in the dynamics, for this value of $E_0$ one obtains the fastest oscillations during the writing or the revealing time of the hologram.
Although no approximated analytical expressions were given in section 2.3, we discuss also the electric field dependencies of the real and imaginary part of the time rate $\Gamma_3^\ast$. Fig. 2.12 shows $\text{Re}(\Gamma_3^\ast)$ and $\text{Im}(\Gamma_3^\ast)$ for different values of the grating spacing $\Lambda$ obtained from Eq. (2.19b) using the parameters given in Appendix A.
For small $A$ the electric field does not have much influence on the real part of $\Gamma_3^*$. In this case the value of $\text{Re}(\Gamma_3^*)$ is close to $\Gamma_{\text{diff}}$, the dielectric limit predicted from (2.21). In contrary, for large grating spacings where $\text{Re}(\Gamma_3^*)$ in the absence of an applied field is smaller, $E_0$ contributes to increase it to approximately the same value (close to $\Gamma_{\text{diff}}$) found for small fringe spacings.† The region where $\text{Re}(\Gamma_3^*)$ increases faster is found around electric field values fulfilling $K_D(E_0) = K_{oe}(N_{\text{eff}})$. That is, if the crystal contains a larger number of traps, a larger electric field is needed to speed-up the process described by time rate $\text{Re}(\Gamma_3^*)$. For our set of parameters, the condition $K_D = K_{oe}$ is satisfied for $E_0 = 2.2 \text{ kV/cm}$. Physically, the increase of $\text{Re}(\Gamma_3^*)$ is due to the fact that the internal fields driving the charge redistribution process in the crystal increase in magnitude by applying an electric field.

The imaginary part of the time rate $\Gamma_3^*$ describes the oscillations during the compensation, handling or storage of the hologram. Its absolute value first increases linearly with the field (Fig. 2.12, dashed lines). Oscillations are expected if $|\text{Im}(\Gamma_3^*)|$ becomes comparable to $|\text{Re}(\Gamma_3^*)|$, which can be achieved for large grating spacings. It is interesting to note that the maximum of $|\text{Im}(\Gamma_3^*)/\text{Re}(\Gamma_3^*)|$ is obtained when the field again fulfills $K_D(E_0) = K_{oe}(N_{\text{eff}})$. Thus, in our example, moderate electric fields of about 1 kV/cm produce already appreciable oscillations on the part of the dynamics governed by the rate $\Gamma_3^*$.

† This fact is very useful from a practical point of view because it allows the control of the compensation and handling time by the electric field.
Seite Leer / Blank leaf
2.5 Photorefractive effects induced by interband photoexcitation

All models presented so far assumed that the charge carrier photoexcitation takes place from a mid gap defect level to the conduction band or from the valence band to such a defect level. However, if the photon energy of the radiation illuminating the crystal exceeds the band gap energy of the crystal, direct transitions from the valence to the conduction band become the principal photoexcitation process and must be included in the calculations. Beside that, the possibility of a strong direct recombination of charge carriers between the two bands must also be taken into account.

The mathematical analysis of a general situation with an arbitrary distribution of defect levels within the band gap turns out to be very difficult. We consider therefore two simple limiting situations with only one defect level in the band gap. This will give us a qualitative idea of the new physical mechanisms that should occur. The model schematics are shown in Fig. 2.13.

![Model schematics](image)

**Fig. 2.13:** Schematic band scheme of the models for the photorefractive effect with direct photoexcitation and recombination between the bands. Model A: photoexcitation of electrons occurs also from a defect level (ND) to the conduction band. No recombination of holes into the defect level. Model B: Electron and hole recombination into the defect level but no phototransitions from the mid-gap level.

Model A is a simple extension of the conventional Kukhtarev model including the new transitions labelled with $s_{dir}$ and $\gamma_{dir}$. Model B, in contrast, cannot be related directly to

† The generalization of Model A to the symmetrical case where the charge redistribution in the defect level occurs passing through the valence band is trivial.
previous models because of the missing photoionization from the donors. For both models thermal excitation processes are neglected.

We consider the one-dimensional case of light modulation along the x-direction. The set of initial equations describing the situation of Model A and Model B in Fig. 2.13 is

\[
\frac{\partial n}{\partial t} = s_{\text{dir}} I(N_{V} - p) + s_{e} I(N_{D} - N_{D}^{-}) - \gamma_{e} n N_{D}^{-} - \gamma_{\text{dir}} n p + \frac{1}{e} \frac{\partial J_{e}}{\partial x} ,
\]

(2.44a)

\[
\frac{\partial p}{\partial t} = s_{\text{dir}} I(N_{V} - p) - \gamma_{h} p(N_{D} - N_{D}^{+}) - \gamma_{\text{dir}} n p - \frac{1}{e} \frac{\partial J_{h}}{\partial x} ,
\]

(2.44b)

\[
\frac{\partial N_{D}^{+}}{\partial t} = s_{e} I(N_{D} - N_{D}^{+}) + \gamma_{h} p(N_{D} - N_{D}^{+}) - \gamma_{e} n N_{D}^{+} ,
\]

(2.44c)

\[
J_{e} = e \mu_{e} n E + \mu_{e} k_{B} T \frac{\partial n}{\partial x} ,
\]

(2.44d)

\[
J_{h} = e \mu_{h} p E - \mu_{h} k_{B} T \frac{\partial p}{\partial x} ,
\]

(2.44e)

\[
ee_{0} \frac{\partial E}{\partial x} = e(N_{D}^{+} + p - n - N_{A}) .
\]

(2.44f)

For Model A the recombination constant \( \gamma_{h} \) for holes is set zero, for Model B the photoexcitation rate \( s_{e} \) is set to zero. Most of the constants appearing in Eqs. (2.44a)-(2.44f) have been defined previously in section 2.3 while describing the electron-ion model. In addition we have \( p \), the hole concentration in the valence band; \( \gamma_{\text{dir}} \), the direct recombination constant; \( J_{h} \), the hole current density; \( N_{V} \), the number density of electrons close enough to the valence band top to be photoexcited; and \( s_{\text{dir}} \), the photoexcitation constant for direct band to band phototransition. No ions are considered here.

If one considers the case where the valence band is not considerably emptied by the illumination \( (p \ll N_{V}) \) one can rewrite the first terms on the right-hand side of Eqs. (2.44a) and (2.44b) by introducing a phenomenological constant \( g \). This is defined as

\[
g \equiv s_{\text{dir}} N_{V} = \frac{\alpha_{\text{dir}}}{h \nu} .
\]

(2.45)

In the above expression \( \alpha_{\text{dir}} \) is the absorption constant due to direct band to band transitions, \( h \) is the Planck constant, and \( \nu \) is the light frequency. \(^{\dagger}\)

As for the previous models, the solutions of the system of Eqs. (2.44a)-(2.44f) are calculated considering a sinusoidal varying light intensity distribution (Eq. (2.2)) and linearizing the equations using Eq. (2.3) for the case of small modulation \( (I_{1} \ll I_{0}) \). While for the electron-ion model the independent variables were \( n, N_{f} \) and \( N_{D}^{+} \), here they are \( n, p \)

\(^{\dagger}\) As an example, for an absorption constant \( \alpha_{\text{dir}} = 5000 \text{ cm}^{-1} \) and a photon energy \( h \nu = 3.5 \text{ eV} \) (illumination in the ultraviolet spectral region) one gets \( g \approx 10^{24} \text{ (Wms)}^{-1} \).
and \( N_0^+ \). With known external conditions (applied electric field, temperature, etc.) all the other variables in Eqs. (2.44) can be derived from these three quantities. In general, inserting Eqs. (2.2) and (2.3) into (2.44) one gets three zero order and three first order equations. From the three zero order equations, the mean concentrations of electrons and holes may be calculated in the way discussed in the next section.

### 2.5.1 Photoconductivity

#### 2.5.1.1 Stationary photoconductivity and effective trap concentration

For a homogeneously illuminated crystal the photoconductivity \( \sigma_{ph} \) is given by

\[
\sigma_{ph} = e n_0 \mu_e + e p_0 \mu_h
\]

(2.46)

where \( e \) is the unit charge, \( \mu_e \) and \( \mu_h \) are the mobilities, and \( n_0 \) and \( p_0 \) are the electron and hole concentrations respectively. Thus, to determine the dependence of the photoconductivity on the illuminating light intensity \( I_0 \) it is sufficient to know the relations \( n_0(I_0) \) and \( p_0(I_0) \). For all models presented previously in this chapter, one gets a relationship of the type given in Eq. (2.6), implying a linear increase of \( \sigma_{ph} \) with \( I_0 \).

The situation is different in the case where direct photoexcitation and recombination between the two bands can occur. In this case the photoconductivity can be a complicated function of the light intensity. To illustrate the possible dependence, we calculate numerically the concentrations \( n_0 \) and \( p_0 \) for the situations of Fig. 2.13. The zero order rate equations for the electron and hole concentrations derived from (2.44) are

\[
\frac{\partial n_0}{\partial t} = g I_0 + s_e (N_D - N_{D_0}^+) I_0 - \gamma_e n_0 N_{D_0}^+ - \gamma_{dir} n_0 p_0 , \quad \text{and} \quad (2.47a)
\]

\[
\frac{\partial p_0}{\partial t} = g I_0 - \gamma_h p_0 (N_D - N_{D_0}^+) - \gamma_{dir} n_0 p_0 , \quad (2.47b)
\]

where \( \gamma_h \equiv 0 \) for Model A and \( s_e \equiv 0 \) for Model B. There is a third equation which is coupled to (2.47), this is the charge conservation relation

\[
N_{D_0}^+ = N_A + n_0 - p_0 , \quad (2.48)
\]

where \( N_A \) is a constant quantity defined by the requirement that the equation \( N_A = N_{D_0}^+ + p_0 - n_0 \) should be valid in the dark at thermal equilibrium.

Fig. 2.14 (Model A) and Fig. 2.15 (Model B) show numerical solutions of the above set of equations for the steady state \( (\partial n_0/\partial t = \partial p_0/\partial t = 0) \) using a set of model parameters. It should be remarked that for Model A the term \( s_e (N_D - N_{D_0}^+) I_0 \) is much smaller than \( g I_0 \) (Fig. 2.14), indicating that we are treating the case where photoexcitation occurs predominantly by creating electron-hole pairs.
For Model A, the hole concentration is constant at low intensity and is equal to $N_A$ while the concentration of electrons increases linearly in this intensity region. For larger $I_0$, both concentrations approach each other and increase proportionally to the square root of the light intensity. The same behaviour is also predicted for Model B (Fig. 2.15). However, in this case $p_0$ is not constant at low intensity, but increases linearly with $I_0$ as is the case for $n_0$.

Thus, both models predict a square root increase of the photoconductivity $\sigma_{ph}$ for large enough light intensities. The concentrations of free electrons and free holes are then equal and are given by

$$n_0 = p_0 = \sqrt{\frac{g I_o}{\gamma_{\text{dir}}}}.$$  \hspace{1cm} (2.49)

The range of validity of Eq. (2.49) depends mainly on the relative magnitude of the constants $g$, $\gamma_{\text{dir}}$, $\gamma_e$ and $\gamma_h$. In general, large values of $\gamma_e$ and $\gamma_h$ (band to trap recombination

\[ \text{Fig. 2.14: Numerical calculations of the electron (n0) and hole (p0) concentrations for the situation of Model A shown in Fig. 2.13 and for the model parameters given in the box. On the top, the normalized effective number of traps Neff is also shown.} \]

\[ \text{Thus, both models predict a square root increase of the photoconductivity } \sigma_{ph} \text{ for large enough light intensities. The concentrations of free electrons and free holes are then equal and are given by} \]

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\[ \text{The range of validity of Eq. (2.49) depends mainly on the relative magnitude of the constants } g, \gamma_{\text{dir}}, \gamma_e \text{ and } \gamma_h. \text{ In general, large values of } \gamma_e \text{ and } \gamma_h \text{ (band to trap recombination} \]

\footnote{\text{Note that the extrapolation to } I_0=0 \text{ is not possible because we neglected thermal excitation.} }
is dominant) shift this range to larger intensities, while for small values of $\gamma_e$ and $\gamma_h$ (direct recombination is dominant) Eq. (2.49) is valid also for smaller $I_0$. If the intensity is much lower than the ones for which (2.49) is valid, the photoconductivity is either linear in $I_0$ (Fig. 2.15, Fig. 2.14 if $\mu_e \gg \mu_h$) or practically independent of $I_0$ (Fig. 2.14 if $\mu_e = \mu_h$).

$$N_{eff} = \frac{N_{D_0}^+(N_D - N_{D_0}^+)}{N_D}$$

(2.50)

as function of the light intensity. In the conventional theory of the photorefractive effect for cw-illumination these densities are not influenced by $I_0$ because the illumination represents only a small disturbance of thermal equilibrium (see Eq. (2.9)). As shown previously, far from thermal equilibrium [46], or in crystals showing large photoconductivities [47], these densities may however change.

**Fig. 2.15:** Numerical calculations of the electron ($n_0$) and hole ($p_0$) concentrations for Model B and the model parameters given in the box. On the top, the relative concentrations of ionized donors $N_{D_0}^+$ and the effective number of traps $N_{eff}$ are also shown.

Fig. 2.14 and Fig. 2.15 also show the behaviour of the number of ionized donors $N_{D_0}^+$ and of the effective number of traps $N_{eff}$.
Due to the strong interband absorption, large photoconductivities are an intrinsic characteristics of our present models and we may expect that $N_{\text{eff}}$ depends on light intensity too. Fig. 2.14 (Model A) confirms that the effective number of traps is small compared to $N_D$ and increases slightly with intensity. To understand this we have to consider the following particularity of Model A. In the steady state, the electrons recombining in the traps should be balanced by the ones being photoexcited, that is

$$s_e I_o (N_D - N_{D_0}^+) = \gamma_e n_o N_{D_0}^+ .$$

The maximum photoexcitation rate on the left hand side of Eq. (2.51) is $s_e N_D I_o$ electrons per unit time and volume. Thus, if the number of free electrons $n_o$ is big due to a strong direct excitation, Eq. (2.51) can be fulfilled only by a reduction the number of empty donors $N_{D_0}^+$ with respect to their number in the dark. In other words, after the beginning of the illumination the direct photoexcited electrons are filling the trap level till fulfilment of the condition (2.51) is reached. The value of $N_{\text{eff}} = N_{D_0}^+$ in Fig. 2.14 obtained at steady state is thus related to the value of $\gamma_e$ and larger values are predicted if $\gamma_e$ is smaller. The constant value $p_o = N_A$ for low intensity (Fig. 2.14) can also be explained by the small value of $N_{D_0}^+$ and is a consequence of the charge neutrality condition (2.48). In the region where Eq. (2.49) is valid (quadratic recombination), the equilibrium concentrations $N_{D_0}^+$ and $N_{\text{eff}}$ are expressed for Model A by

$$N_{D_0}^+ = N_D \frac{1}{1 + \gamma_e s_e \sqrt{\gamma_{\text{dir}} I_o}} ,$$

$$N_{\text{eff}} = N_D \frac{1}{2 + \gamma_e s_e \sqrt{\gamma_{\text{dir}} I_o} + \frac{s_e \sqrt{\gamma_{\text{dir}} I_o}}{\gamma_e \sqrt{\gamma_{\text{dir}} I_o}}} .$$

For Model B the situation is different. Fig. 2.15 shows that in the region where $n_o$ and $p_o$ increase linearly the densities $N_{D_0}^+$ and $N_{\text{eff}}$ remain more or less constant at the values corresponding to the dark conditions, that is $N_{D_0}^+ = N_A$ and $N_{\text{eff}} = N_A (N_D - N_A)/N_D$. At higher light intensities, the concentrations $N_{D_0}^+$ and $N_{\text{eff}}$ are changing and reach final values which depend on the indirect recombination constants $\gamma_e$ and $\gamma_h$ but not on light intensity. This values are

$$N_{D_0}^+ = N_D \frac{\gamma_h}{\gamma_e + \gamma_h} ,$$

$$N_{\text{eff}} = N_D \frac{\gamma_e \cdot \gamma_h}{(\gamma_e + \gamma_h)^2} .$$

In Fig. 2.15 equal values for the two recombination constants have been chosen. This is the ideal situation which maximizes the effective number of traps to the value $N_{\text{eff}} = N_D/4$. In contrast, if the recombination constants strongly differ from each other, the effective number
of traps goes to zero because the defect centers are either all ionized ($\gamma_e << \gamma_h$) or all filled ($\gamma_e >> \gamma_h$) with electrons.

### 2.5.1.2 Time dependence of photoconductivity

The build-up and decay of photoconductivity can be calculated from the rate Eqs. (2.47) using (2.46). We consider the case where quadratic recombination is dominant (Eq. (2.49) is fulfilled) and neglect photoexcitation from the traps ($s_e = 0$). If one charge carrier species has a mobility $\mu$ much larger than the other species then

$$\sigma_{ph}(t) = e\mu \frac{gL_0}{\gamma_{dir}} \frac{1 - \exp(-2\Gamma_{dir}t)}{1 + \exp(-2\Gamma_{dir}t)}$$

(2.56)

for the build-up of photoconductivity, and

$$\sigma_{ph}(t) = e\mu \frac{gL_0}{\gamma_{dir}} \frac{1}{1 + \Gamma_{dir}t}$$

(2.57)

for the initial decay after switching-off the homogeneous illumination. The time rate $\Gamma_{dir}$ is given by

$$\Gamma_{dir} = \sqrt{gL_0 \gamma_{dir}} = \gamma_{dir} n_0,$$

(2.58)

where $l_0$ is the light intensity.

### 2.5.2 Space-charge fields

#### 2.5.2.1 Basic assumptions and high light intensity solutions

We have shown that for interband photoexcitation the electron and hole densities become complicated functions of the incident light intensity. This fact limits the possibility of predicting in an analytical way the final amplitude and phase of the space-charge fields in an experiment performed under such conditions. It is therefore opportune to consider only some limiting cases. In the following, we calculate the steady-state space charge fields for Model A and for Model B under the main assumption that the charge redistribution in the channels involving the trap level is much slower than the one between the two bands. This means:

For Model A:

- The rate of electrons photoexcited from the valence band is large compared to the rate of charge excitation from the donor level, ($gL_0 >> s_e l_0 (N_D - N_D^0)$).\(^\dagger\)

\(^\dagger\) This assumption is not problematic because we are in the case of strong interband absorption where the absorption constant due to phototransitions from the donor level is much smaller than $\alpha_{dir}$.\(^\dagger\)
• The direct recombination rate is larger than the recombination of electrons into the traps, \( \gamma_{\text{dir}} n_o p_o \gg \gamma_e n_o N_{D_o^+} \).\footnote{This is automatically implied by the previous requirement. The number of ionized donors is adapted to fulfill this condition in the way indicated in section 2.5.1.}

For Model B:

• The number of direct recombining charge carriers is larger than the number of electrons or holes recombining in the traps \( \gamma_{\text{dir}} n_o p_o \gg \gamma_e n_o N_{D_o^+}, \gamma_h p_o (N_D - N_{D_o^+}) \).\footnote{This is valid if Eq. (2.49) can be applied.}

We assume further that the intensity is large enough so that the square root relation (2.49) is valid but the free charge carrier density is still small compared to the density of states \( N_V \) in the valence band. The complex amplitude \( E_1 \) of the space-charge field can then be calculated for the steady state in a similar way as in section 2.3. After some lengthy but straightforward calculations we obtain for Model A

\[
E_1 = -im\left[\left(E_D^2 + E_o^2\right) + \left(E_D - iE_o\right)E_{Rh}\right]E_q + \left[E_D\left(E_{Rh} - E_{Re}\right) - iE_o\left(E_{Rh} + E_{Re}\right)\right]E_{qf}
\]
\[
\left(E_D + 2E_{qf} + E_q + iE_o\right)\left(E_D + E_{Rh} + E_{Re} - iE_o\right) + 2iE_o\left(E_q + E_{qf} - E_{Rh}\right)
\]

(2.59)

where \( E_D = k_B T/e \) is the diffusion field, \( E_o \) is the applied field,

\[
E_q = \frac{e}{\varepsilon\varepsilon_0 K} \frac{N_{D_o^+}(N_D - N_{D_o^+})}{N_D} \equiv \frac{e}{\varepsilon\varepsilon_0 K} N_{\text{eff}}
\]

(2.60)

corresponds to the trap-limited field introduced in (2.9), and

\[
E_{qf} = \frac{e}{\varepsilon\varepsilon_0 K} n_o = \frac{e}{\varepsilon\varepsilon_0 K} \sqrt{\frac{g f_o}{\gamma_{\text{dir}}}}
\]

(2.61)

is a corresponding limiting field giving the maximum space charge field that can be created by the free charge carriers. There are two other important new quantities in Eq. (2.59). These are

\[
E_{Re} \equiv \frac{1}{K\mu_e} \gamma_{\text{dir}} p_o = \frac{1}{K\mu_e} \sqrt{g \gamma_{\text{dir}} f_o}
\]

(2.62)

\[
E_{Rh} \equiv \frac{1}{K\mu_h} \gamma_{\text{dir}} n_o = \frac{1}{K\mu_h} \sqrt{g \gamma_{\text{dir}} f_o}
\]

(2.63)

which have the dimension of an electric field. They can be interpreted as the average electric fields that must be applied in order to drift one electron (or one hole) by a distance \( (K)^{-1} = \lambda/2\pi \) before a direct recombination to the other band takes place. We call these fields the electron and hole recombination fields. The second equalities in Eqs. (2.61), (2.62) and (2.63) are valid only in the range of validity of Eq. (2.49). It is important to notice that these
fields are inversely proportional to the mobilities $\mu_e$ and $\mu_h$. $E_{Re}$ and $E_{Rh}$ are zero in the conventional Kukhtarev model where direct recombination is neglected.

Equation (2.59) shows that in the general case where the number of free charge carriers $n_0$ is comparable to the effective number of traps the space-charge field is composed of two components. The first is given by the first square bracket in the numerator, this term is proportional to the field $E_q$ and describes the field which is produced by trapped charges. The second component (second square bracket) is proportional to $E_{qf}$ and describes the space-charge field created by an inhomogeneous distribution of free charge carriers.

Similar to the previous solution, the expression for the space-charge field obtained for Model B is

$$E_1 = -im \frac{\left[ E_D (E_{Rk} - E_{Re}) - iE_o (E_{Rh} + E_{Re}) \right] (E_q + E_{qf})}{B},$$

(2.64a)

where the denominator $B$ is equal to

$$B = E_D^2 + E_{qf}^2 + (E_q + E_{qf}) \left[ 2E_D + 2E_{Rh} + 2E_{Re} + 2E_{rhe} + E_{rhh} + E_{ree} + E_{rhe} \right] + E_D (E_{Rh} + E_{Re} + E_{rhe} + E_{rhh}) - iE_o (E_{Rh} - E_{Re} + E_{rhe} - E_{rhh}).$$

(2.64b)

The new quantities $E_{ree}$, $E_{reh}$, $E_{rhh}$ and $E_{rhe}$ in (2.64) are fields characterizing the recombination mechanism in the traps. They are defined as

$$E_{ree} = \frac{1}{K\mu_e} \gamma_e N_{eff},$$

(2.65a)

$$E_{reh} = \frac{1}{K\mu_h} \gamma_e N_{eff},$$

(2.65b)

$$E_{rhh} = \frac{1}{K\mu_h} \gamma_h N_{eff},$$

(2.65c)

$$E_{rhe} = \frac{1}{K\mu_e} \gamma_h N_{eff},$$

(2.65d)

with $N_{eff}$ given by Eq. (2.55).

The expressions (2.59) and (2.64) obtained respectively for Model A and B can be simplified if we consider the limiting situation where the crystal does not contain impurities ($N_D = 0$, $E_q = 0$). In this case Eq. (2.49) holds exactly and the following expression can be used to get the correct description of free charge carriers space-charge gratings

$$E_1 = -im \frac{\left[ E_D (E_{Rh} - E_{Re}) - iE_o (E_{Rh} + E_{Re}) \right] E_{qf}}{\left[ (E_D + 2E_{qf}) (E_D + E_{Rh} + E_{Re}) + E_{qf}^2 \right] + iE_o (E_{Re} - E_{Rh})}. $$

(2.66)

Eq. (2.66) shows that in the case of a pure diffusion mechanism ($E_o = 0$), the space-charge field is purely imaginary ($\pi/2$ phase shift) and is proportional to $E_{Re} - E_{Rh}$, that is, to the
difference of the mobilities for electron and holes. In the case where the charge transport is
-dominated by the drift mechanism \(E_o \gg E_D\) the space-charge field \(E_1\) is proportional to the
sum of the fields \(E_{Re}\) and \(E_{Rh}\). Therefore, \(E_1\) depends on the sum of the mobilities \(\mu_e + \mu_h\)
because under the influence of an applied electric field electrons and holes move in different
directions.

2.5.2.2 Fields at intermediate intensities

Finally we want to consider also the case where the average hole and electron concentrations
are not equal. This situation is always encountered at intermediate intensities due to
asymmetrical recombination \(\gamma_e \neq \gamma_h\) or photoexcitation from the traps. An analytical
expression like (2.49) relating the concentrations \(n_o\) and \(p_o\) to the light intensity \(I_o\) cannot be
derived, therefore we consider \(n_o\) and \(p_o\) as parameters of the problem. In addition we
assume that the trap population is not modulated, which can be the result of strongly
asymmetrical recombination as is the situation shown in Fig. 2.14. Experimentally this
regime may be reached also through an intensive homogeneous illumination in the visible
erasing the charge modulation in the traps. The solution for the space-charge field valid for
\(n_o \neq p_o\) has a similar form to (2.66)

\[
E_1 = -i m a \frac{E_D \left( E_{Rh}E_{qf} - E_{Re}E_{qf} \right) - iE_o \left( E_{Rh}E_{qf} + E_{Re}E_{qf} \right)}{(E_D + E_{qf})^2 \left( E_D + E_{Rh} + E_{Re} \right) + E_o^2 + iE_o \left( E_{Re} - E_{Rh} \right)},
\]

what implies that many dependencies of \(E_1\) on material and experimental parameters are the
same as in the trap free case. The field \(E_{qf}\) has been redefined to

\[
E_{qf} = \frac{e}{\varepsilon \varepsilon_o K} n_o \quad \text{and} \quad E_{qf} = \frac{e}{\varepsilon \varepsilon_o K} p_o,
\]

and the fields \(E_{Re}\) and \(E_{Rh}\) are still given by Eqs. (2.62) and (2.63). In Eq. (2.67) the light
modulation index \(m = I/I_o\) is multiplied by the dimensionless factor

\[
a = \frac{gI_o}{\gamma_{dir} n_o p_o} \geq 1.
\]

If one neglects photoexcitation from the traps the term \(a\) correspond to the ratio of the total
number of recombination processes to the number of direct recombinations between the two
bands. Inserting explicitly \(a\) we can rewrite (2.67) in another form, for \(E_o = 0\) this is

\[
E_1 = -i m \frac{e gI_o}{\varepsilon \varepsilon_o K^2} \left( \frac{1}{\mu_h} - \frac{1}{\mu_e} \right) \left( E_D + E_{Rh} + E_{Re} \right).
\]

The term in the square brackets

\[
\pm E_0^2 = \frac{e gI_o}{\varepsilon \varepsilon_o K^2} \left( \frac{1}{\mu_h} - \frac{1}{\mu_e} \right).
\]
has the unity of an electric field squared and is independent on the carrier concentrations \( n_0 \) and \( p_0 \). The insertion of numerical values shows that the values of \((E_b)^2\) can get very large. For \( I_0 = 10 \text{ mW/cm}^2\), \( \alpha_{dir} = 5000 \text{ cm}^{-1} \) and \( \lambda = 1 \mu\text{m} \) one gets \((E_b)^2 > (1 \text{ kV/cm})^2\) if at least one of the mobilities is smaller than \(10^{-7} \text{ m}^2(\text{Vs})^{-1}\).

### 2.5.3 Discussion of the high intensity solutions

We discuss the solution obtained in the high light intensity limits concentrating especially to the trap free case described by Eq. (2.66). We make also additional remarks about the predictions of the solutions (2.59) and (2.64) obtained for Model A and Model B.†

We note first that there are only three quantities in these expressions which are by definition independent on light intensity. These are the light modulation index \( m \), the diffusion field \( E_D \) and the applied field \( E_0 \). The limiting field \( E_{gf} \) for the free charge carriers grating and the recombination fields \( E_{Re} \) and \( E_{Rh} \) depend strongly on \( I_0 \) in the way given by Eq. (2.49), while the fields \( E_1, E_{ree}, E_{reh}, E_{rhh}, \) and \( E_{rhe} \) are proportional to the effective number of traps \( N_{eff} \) which, as discussed in section 2.5.1, also depends on \( I_0 \) (Eqs. (2.53) and (2.55)). It should also be remembered that, strictly speaking, Eqs. (2.59) and (2.64) are satisfied only in the intensity range where the square root law (2.49) is valid,‡ and the extrapolation of these results to low light intensity can be interpreted only qualitatively. In the trap-free case Eq. (2.66) is valid at all intensities.

#### 2.5.3.1 Dependence on free charge carrier density and light intensity

The limiting field \( E_{gf} \), which is linear in the concentration \( n_0 \) of free carriers, is the driving term in the solutions for the steady state space-charge field \( E_1 \). For this reason we discuss first the dependence of \( E_1 \) on \( n_0 \), which is shown in Fig. 2.16. The cases of Models A and B (Fig. 2.13) are considered in addition to the case where the crystal does not contain any traps. In Fig. 2.16 the effective number of traps \( N_{eff} \) is calculated in (b) and (d) using the expressions (2.53) and (2.55). In addition, curves plotted using the final result of Model A (2.59) and a constant value of \( N_{eff} \) are also presented (Fig. 2.16 (c)). In order to get an appreciable value for \( N_{eff} \) we choose for Model A a small value of the recombination constant \( \gamma_e \). The maximum of \( N_{eff} \) in (b) is \( N_D/4 \) and is reached when \( n_0 = 5 \times 10^{20} \text{ m}^{-3} \). For the curves describing Model B \( N_{eff} \) is constant and equal to the dark value \( 4/25 N_D \). We extract the following information from Fig. 2.16:

---

† For the model that assumes \( n_0 \neq p_0 \) (Eq. (2.67-2.70)), the concentrations are not analytically related to the light intensity. Therefore we are not discussing this case further here. However, we recall that the predictions of this model are in many aspects similar to the ones obtained for a crystal without traps (2.66).

‡ The solution for Model A (Eq. (2.59)) transforms to the expression (2.35) of the conventional Kukhtarev model by putting \( E_{gf} = 0 \) (small number of free charge carriers) and \( E_{Re} = E_{Rh} = 0 \) (no direct recombination). In contrast, the solution obtained for Model B (Eq. (2.64)) cannot be reduced to the conventional case because no other photoexcitation mechanisms beside the direct one is included in this model.
For large enough $n_0$, the behaviour is independent on the model used. Thus, for $n_0 \gg N_{\text{eff}}$ there is no charge modulation in the traps. This behaviour is not dependent on whether the traps are empty, partially filled or completely filled. In this regime, the saturation values of $E_1$ are $\text{Re}(E_1) = mE_0/2$ and $\text{Im}(E_1) = mE_D/2$.

As expected, for smaller $n_0$ the grating is the result of spatially modulated trapped charges and spatially modulated free charges. These two charge modulations can influence each other. In general, strong interaction between the two components occurs when the densities $N_{\text{eff}}(t_0)$ and $n_0$ are similar (see (b) and (c)).

The charge redistribution in a real crystal is probably characterised by a combination of the ones depicted in Fig. 2.13 for Models A and B. We suggest that the overall dependence of $E_1$ on light intensity for a real crystal is more similar to the one shown in Fig. 2.16 (c) than to the one shown in (b) and (d). The reason is that the crystal may contain different defect levels. It is reasonable to think that for each value of the light intensity there is one or more defect level being partially filled. If a certain amount of charges can be photoexcited from this level a charge modulation can be stored in it. For different values of light intensity the occupation of a single level changes but other defect levels might become active for storing the charge modulation.
The Photorefractive Effect

2.5.3.2 Grating spacing dependence

We consider now only the case of a purely free carrier grating. Fig. 2.17 shows how in this case the space-charge field depends on the grating spacing for recording with an applied field. This is compared with the predictions of the conventional Kukhtarev model.
The real part of the space-charge field amplitude $E_1$ saturates for large $\Lambda$ at the value $\text{Re}(E_1) = m E_o/2$ instead at $\text{Re}(E_1) = m E_o$ like for conventional photorefractive effects. This is due to the fact that the photoexcited charge modulation in the bands has only half the modulation of the light intensity because of the quadratic recombination (2.49).

- The imaginary part increases faster than linear in $\Lambda$ for small grating spacings. This is due to the influence of the fields $E_{Re}$ and $E_{Rh}$ in Eq. (2.66). These fields are proportional to $\Lambda$ like $E_{ef}$. For large grating spacings, in contrast, a linear decrease of $\text{Im}(E_1)$ with $\Lambda$ is found in both cases.

![Graph](image)

Fig. 2.17: Grating spacing dependence of the real and imaginary part of the space-charge field amplitude $E_1$. Applied electric field $E_o = 10 \text{ kV/cm}$. Solid lines: Free charge carrier grating (Eq. (2.66)) with a charge density $n_0 = 5 \times 10^{21} \text{ m}^{-3}$. Dashed lines: conventional Kukhtarev case (Eq. (2.35)) with an effective trap density $N_{eff} = 5 \times 10^{21} \text{ m}^{-3}$. The other parameters used in the computation of the free charge carrier grating are $\mu_e = 3 \times 10^{-6} \text{ m}^2(\text{Vs})^{-1}$, $\mu_h = 10^{-6} \text{ m}^2(\text{Vs})^{-1}$ and $\gamma_{dir} = 10^{-15} \text{ m}^3 \text{s}^{-1}$ giving $E_{Re}/\Lambda = 2.65 \text{ kV (cm$\mu$m) }^{-1}$ and $E_{Rh}/\Lambda = 7.96 \text{ kV (cm$\mu$m) }^{-1}$.

It is also interesting to note that in the absence of an applied field one gets $\text{Re}(E_1) = 0$, while the curves for $\text{Im}(E_1)$ look similar to the one shown in Fig. 2.17 but with a maximum that is lower in value and that occurs at smaller $\Lambda$. In addition, it should be mentioned that for the free grating the position of this maximum is strongly influenced by the values of $E_{Re}$ and
$E_{Rh}$ and shifts towards smaller $\Lambda$ for larger values of these fields.\(^\dagger\) The influence of the field $E_{Re}$ and $E_{Rh}$ is discussed in more detail in section 2.5.3.3.

2.5.3.3 Dependence on mobilities and recombination constant

In Fig. 2.18 we show which influence the values of the recombination fields $E_{Re}$ and $E_{Rh}$ have on the space-charge field amplitude $E_1$. The model values for the mobilities are the same used in Fig. 2.17 so that the ratio $E_{Rh}/E_{Re} = \mu_e/\mu_h = 3$ is constant. The curves are drawn by varying the value of the recombination constant $\gamma_{\text{dir}}$ in the range between $10^{-18}$ and $10^{-13}$ m$^3$s$^{-1}$ and the number of free electrons $n_0$ is kept constant by ideally adapting the light intensity. The same curves would be obtained by changing together the values of the mobilities $\mu_e$ and $\mu_h$ in a proportional way.

![Diagram](image)

Fig. 2.18: Dependence of the real and imaginary part of the space-charge field amplitude $E_1$ on the fields $E_{Rh}$ and $E_{Re}$ for a free charge carrier grating (Eq. (2.66)). Charge density $n_0 = 5 \times 10^{21}$ m$^{-3}$. The curves are obtained by varying the value of the recombination constant $\gamma_{\text{dir}}$ with the other parameters being the same as in Fig. 2.17.

Fig. 2.18 shows that large values ($\approx 100$ kV/cm) of the fields $E_{Re}$ and $E_{Rh}$ are needed for reaching the saturation region of the field $E_1$. For such values of the recombination fields the distance travelled by the carriers by diffusion or under the influence of the applied electric

\(^\dagger\) The fitting of the grating spacing dependence of Im($E_1$) is used in the conventional case for the experimental determination of the effective number of traps $N_{\text{ef}}$ through the determination of the limiting field $E_q$ in relation (2.35). The analogous determination of $n_0$ by fitting $E_{\text{ef}}$ for a free carrier grating is complicated by the influence of $E_{Re}$ and $E_{Rh}$ on Im($E_1$). It turns out that this influence is negligible only if the values of $E_{Re}$ and $E_{Rh}$ are much larger than $E_1$ (small mobilities or fast direct recombination).
field before recombining is short compared to the grating spacing. This means that small mobilities for electrons and holes or strong direct recombination are advantageous for getting large final space-charge fields.† Of course, if the light intensity has to be kept low, crystals possessing a too large recombination constant γdir which affects the value of the limiting field $E_{eq}$ (Eq. (2.61)) are not ideal. In Fig. 2.18 this effect was compensated by assuming an increase in intensity which gives a constant value of $E_{eq}$. In contrast, small mobilities are always advantageous, what may appear astonishing because one could expect that large mobilities favorize the charge separation. However, if the mobility is so big that $E_{Re}$ and $E_{Rh}$ are smaller than the internal fields driving the charge redistribution process (diffusion field $E_D$, applied field $E_o$, space-charge field $E_1$) the carriers are travelling too far (eventually many grating spacings) and they recombine then preferentially on the wrong place (that is where there are more charge carriers of the other kind). For small mobilities, in contrast, the place of recombination is forced and after some photoexcitation-recombination steps the maximum possible space-charge field can build-up. For large grating spacings, this maximum value is given by $E_1 = mE_o/2$ (Fig. 2.17).

![Graph](image)

Fig. 2.19: Dependence of the real, imaginary part and of the absolute value of the space-charge field amplitude $E_1$ on the ratio $E_{Rh}/E_{Re}$ for a free charge carrier grating (Eq. (2.66)). Charge density $n_0 = 5 \cdot 10^{21}$ m$^{-3}$. The curves are obtained by varying the value of the electron mobility $\mu_e$ with the other parameters being the same as in Fig. 2.17.

It should be noted that large $E_{Re}$ and $E_{Rh}$ give the optimum space-charge field only in the ideal situation of a trap-free crystal. The above considerations can be applied also to the cases of Model A and Model B (Fig. 2.13) if the free carriers grating dominates ($n_0 >> N_{eff}$, $E_{eq} >> E_q$ in Eqs. (2.59) and (2.64)). In contrast, if the grating builds-up predominantly in

† Note that Eqs. (2.59), (2.64) and (2.66) are not valid in the limits $\mu_e = 0 (E_{Re} = \infty)$ and $\mu_h = 0 (E_{Rh} = \infty)$ for which no electric field can be created.
the traps \((n_0 \ll N_{\text{eff}}, E_{\text{df}} \ll E_0)\), small values of \(E_{\text{Re}}\) and \(E_{\text{Rh}}\) are advantageous because direct recombination is then less probable and more charges can be trapped.

In Fig. 2.18 the ratio \(E_{\text{Re}}/E_{\text{Rh}}\) has been kept constant. To study the influence of the relative values of the mobilities for electrons and holes we plot \(E_1\) on Fig. 2.19 as function of \(\mu_e/\mu_h\). Only \(\mu_e\) is varied while \(\mu_h\) is kept fixed. We can extract the following information:

- The imaginary part of \(E_1\) changes sign depending on whether \(\mu_e\) or \(\mu_h\) is larger. For equal values of the mobilities \(\text{Im}(E_1)\) is always zero for any value of the applied field \(E_0\). \(\text{Im}(E_1)\) is larger for \(\mu_e \ll \mu_h\) because for \(\mu_e \gg \mu_h\) the value of \(E_{\text{Re}}\) gets too small (see above discussion).

- The real part of \(E_1\) shows a maximum for a certain value of \(\mu_e/\mu_h\). It can be shown that for \(E_{\text{Rh}} \gg E_0, E_D, E_{\text{df}}\) this maximum is obtained for equal mobilities \(\mu_e = \mu_h\) and becomes much larger and narrower.

### 2.5.3.4 Dependence on applied field

In Fig. 2.20 the electric field dependence of a free charge carriers grating is compared to the one predicted for conventional photorefractive effects.

![Electric field dependence of the real and imaginary parts of the space-charge field amplitude \(E_1\). Full lines: Free charge carrier grating (Eq. (2.66)). Dashed lines: conventional Kukhtarev case (Eq. (2.35)). The same parameters as in Fig. 2.17 are used.](image)
The following can be observed:

- For the real part of $E_1$ the behaviour in the two cases is similar. There is a linear increase for small values of $E_0$, a maximum and an inverse proportionality for large $E_0$.
- In the conventional case the imaginary part of $E_1$ reaches for large $E_0$ a constant saturation value. In contrast, in the free carrier case $\text{Im}(E_1)$ decreases quadratically with the applied field if this is large compared with $E_{R\text{e}}$ and $E_{R\text{h}}$. This behaviour can be explained with the same arguments used in the discussion of the dependence of $E_1$ on the recombination constant and mobilities.

2.5.3.5 *Estimation of the required light intensities*

We make some final remarks about the conditions that should be fulfilled to be able to observe a free charge carrier grating in an interband photorefractive experiment. We consider an hypothetical crystal with following properties: effective dielectric constant $\varepsilon = 50$, absorption constant $\alpha_{\text{dir}} = 5000 \text{ cm}^{-1}$ ($g = 10^{24} \text{ (Wms)}^{-1}$), effective number of traps $N_{\text{eff}} = 10^{15} \text{ cm}^{-3}$, mobility of the slower carriers (for instance holes) $\mu = 10^{-7} \text{ m}^2(\text{Vs})^{-1}$, direct recombination constant $\gamma_{\text{dir}} = 10^{-16} \text{ m}^3\text{s}^{-1}$. In addition we consider the experimental situation where $\Lambda = 5 \mu\text{m}$.

A space-charge field strength $E_1 = 0.1 \text{ kV/cm}$ can be easily experimentally detected. Such a field can build-up if the limiting field $E_{q\text{f}}$ and the recombination field $E_{R\text{h}}$ are about 0.2 kV/cm. In addition, free carrier gratings can be distinguished from the one building-up in the traps only if the number of free carriers $n_o$ is at least equal to $N_{\text{eff}}$. The conditions for the required light intensity are then:

1) $n_o > 10^{15} \text{ cm}^{-3}$, that is $I_o [\text{W/cm}^2] > 10^{14} \gamma_{\text{dir}}$

2) $E_{R\text{h}} > 0.2 \text{ kV/cm}$ , that is $I_o [\text{W/cm}^2] > 1.6 \cdot 10^{-18} \frac{\mu^2}{\gamma_{\text{dir}} \Lambda^2}$

3) $E_{q\text{f}} > 0.2 \text{ kV/cm}$ , that is $I_o [\text{W/cm}^2] > 0.05 \frac{\gamma_{\text{dir}} e^2}{\Lambda^2}$

where the values of $\mu$, $\gamma_{\text{dir}}$ and $\Lambda$ are in SI units. All three conditions must be fulfilled simultaneously. Inserting the above numerical values one gets

1) $I_o > 10 \text{ mW/cm}^2$

2) $I_o > 6 \mu\text{W/cm}^2$

3) $I_o > 50 \mu\text{W/cm}^2$ .

This indicates that the observation of free charge carriers gratings with a cw-experiment should be possible already for low light intensities. The experiments presented in chapter 4.3 indicate that the situation is even more favorable (smaller $\gamma_{\text{dir}}$). Note that, due to the strong absorption, the strength of the free carrier grating decreases from the surface toward the depth of the crystal.
2.5.4 Space-charge field dynamics

For a space-charge field generated by trapped and free carriers, the time evolution is strongly influenced by the recombination mechanism in the trap level. The expressions for the involved time rates are complicated and depend on grating spacing, applied field and other parameters. Therefore, we limit our discussion of the dynamic response to the case of free carrier gratings in ideal impurity-free crystals helping us with numerical simulations of the charge transport.

\[ \gamma_{dir} = 10^{-15} \text{ m}^3/\text{s} \]
\[ \Gamma_{dir} = 3.2 \times 10^6 \text{ s}^{-1} \]
\[ \gamma_{dir} = 10^{-16} \text{ m}^3/\text{s} \]
\[ \Gamma_{dir} = 10^6 \text{ s}^{-1} \]

\[ \text{Fig. 2.21: Numerical simulations of the build-up of free carrier gratings for an intensity of 1 W/cm}^2. \text{ Solid and dashed curves -- > simulations; dotted curves -- > single exponentials } E_1(t) = E_{1\text{sat}} (1 - \exp(-\Gamma_{dir}t)) \text{ with values of } E_{1\text{sat}} \text{ obtained from Eq. (2.66). Parameters: } g = 10^{24} \text{ (Wms)}^{-1}, \mu_e = 10^{-6} \text{ m}^2/(\text{Vs})^{-1}, \mu_h = 10^{-7} \text{ m}^2/(\text{Vs})^{-1}. \]

Fig. 2.21 shows the simulated response for 1 W/cm² light intensity and for a crystal with absorption constant in the order of 5000 cm⁻¹ (photoconstant \( g = 10^{24} \) (Wms)⁻¹). To show the influence of the relative values of different characteristic time rates we have drawn curves using two values of the recombination constant, \( \gamma_{dir} = 10^{-15} \text{ m}^3/\text{s}^{-1} \) (solid lines) and \( \gamma_{dir} = 10^{-16} \text{ m}^3/\text{s}^{-1} \) (dashed line). As a consequence of Eq. (2.49) smaller values of \( \gamma_{dir} \) have the effects of decreasing the direct recombination rate \( \Gamma_{dir} \) defined in (2.58) and increasing the dielectric rates for electrons and holes, \( \Gamma_{die} = e\mu_e n_0/(\varepsilon\varepsilon_0) \) and \( \Gamma_{dih} = e\mu_h n_0/(\varepsilon\varepsilon_0) \). We discuss first the two lower curves in Fig. 2.21. The parameters have been chosen in such a way that for the solid curve the recombination rate \( \Gamma_{dir} \) is the
The largest of all characteristic time rates (see box). In this case the space-charge field increases monotonously until it reaches a saturation value. For the dashed curve, in contrast, the dielectric rate $\Gamma_{\text{die}}$ is larger than $\Gamma_{\text{dir}}$ and the space-charge field amplitude undergoes a maximum before reaching steady-state. A similar behaviour is seen also for the upper curves that are simulated for the case where an external field is applied. A transient maximum is seen here for the solid curve too, which is the result of the damped oscillations produced by the applied field (see section 2.3.3). Damped oscillations are also the reason for the fact that the upper dashed curve does not appear completely smooth. They become much more evident if one simulates the dynamics for smaller grating spacings, larger applied fields or using larger carrier mobilities.

In Fig. 2.21 single exponential functions of the type $E_1(t) = E_{1\text{sat}} (1 - \exp(-\Gamma_{\text{dir}} t))$ are also shown as dotted lines, the full dynamics is definitely not described well enough by this function. Nevertheless one sees that the simulated curves (solid and dashed lines) reach saturation approximately in the same time as the above single exponential, which can be explained by the fact that the space-charge field cannot reach a steady-state before the average charge concentration $n_o$ has also reached a constant value. Therefore, even when other time rates ($\Gamma_{\text{die}}, \Gamma_{\text{dir}}, \Gamma_{\text{Dh}}$) are larger in magnitude, the space-charge field reaches saturation in a time comparable to the recombination rate $\Gamma_{\text{dir}}$. When one or more of the other rates are larger than $\Gamma_{\text{dir}}$, one may observe transient maxima of $E_1(t)$ but the steady-state is not reached before the charge generation process is completed.

We want finally to derive some consequences for the realistic build-up time that can be expected in an experiment. We have seen above that the build-up time of the space-charge field correspond roughly to the inverse recombination rate $(\Gamma_{\text{dir}})^{-1} = (g I_o \gamma_{\text{dir}})^{-1/2}$. We consider values of $g$ in the range $10^{23}..10^{24} \text{ (Wms)}^{-1}$ that correspond to an absorption constant $\alpha_{\text{dir}} = 500..5000 \text{ cm}^{-1}$ at $h\nu = 3.5 \text{ eV}$. For the arbitrary range $10^{-14} \text{ m}^3\text{s}^{-1} \geq \gamma_{\text{dir}} \geq 10^{-20} \text{ m}^3\text{s}^{-1}$, the response time $\tau$ is then expected to be in the range $3 \mu\text{s} \leq \tau \leq 10 \text{ ms}$ for $I_o = 1 \text{ mW/cm}^2$ and $0.1 \mu\text{s} \leq \tau \leq 300 \mu\text{s}$ for $I_o = 1 \text{ W/cm}^2$. 

3. Interaction of light waves with the space-charge field

The space-charge field modulates the optical properties of the crystal through the linear electro-optic effect. The proportionality between the change of the inverse of the dielectric constant at optical frequencies (symmetric second rank tensor $\varepsilon^{-1}$, optical indicatrix) and the electric field is given by the third-rank tensor $\mathbf{r}$

$$
\Delta \left( \frac{1}{\varepsilon} \right)_{ij} = \sum_{k=1}^{3} r_{ijk} E_k ,
$$

where $E_k$ are the components of the static internal electric field. The electro-optic tensor $\mathbf{r}$ is symmetric in the first two indices and is non zero only in non-centrosymmetric materials. Using the identity $\varepsilon \varepsilon^{-1} = 1$ the change of the dielectric tensor $\mathbf{\varepsilon}$ can be related to the change of the inverse dielectric tensor $\mathbf{\varepsilon}^{-1}$

$$
\Delta \varepsilon = -\varepsilon'' \mathbf{r} E_1 \varepsilon'' ,
$$

where $\varepsilon''$ is the undisturbed dielectric tensor and $E_1$ is the space-charge field vector.

3.1 Two-wave mixing in photorefractive media

Fig. 3.1 shows the typical configuration for two-wave mixing in a photorefractive experiment.

![Fig. 3.1: Two-beam coupling configuration. $\theta$ is the angle inside the crystal.](image)

The reference (R) and signal (S) waves enter the crystal symmetrically to the surface normal. Their interaction produces through the photorefractive effect a space-charge grating along the x-direction. This space-charge field is responsible for the spatial modulation of the dielectric
60 Interaction of light waves with the space-charge field
tensor (Eq. (3.2)) which produces a coupling term between the wave equations for the two waves. As a result of this coupling one of the waves is damped while passing the crystal and the other is amplified, i.e. there is an energy transfer between the two waves. If one of the waves has a much larger intensity than the other (\(|R|^2 >> |S|^2\), non-depleted pump approximation) the spatial evolution of the intensity of the signal wave \(I_s\) is exponential

\[
I_s(z) = I_s(z = 0) \exp((\Gamma - \alpha)z) ,
\]

where \(\alpha\) is the average (intensity) absorption constant. The exponential gain \(\Gamma\) depends only on the imaginary part of the space-charge field \(E_1\) and is expressed by [28, 42]

\[
\Gamma = \left(\frac{2\pi}{\lambda}\right)^2 \frac{1}{k_z} \cdot \mathbf{p}_R \cdot \mathbf{e}_1 \cdot \mathbf{p}_S \cdot \mathbf{e}_1 \cdot \frac{\text{Im}(E_j)}{m} ,
\]

where \(k_z = \frac{2\pi n(\theta)}{\lambda} \cos \theta\) is the projection of the signal and reference wave wavevector on the z-axis. \(\mathbf{p}_R\) and \(\mathbf{p}_S\) are unit vectors describing the polarization of the two waves and \(\mathbf{e}_1\) is the unit vector along the direction of the grating wavevector.

### 3.2 Light diffraction by photorefractive media

If a probe beam is testing a previously recorded grating or a grating which is being recorded by two other recording waves we speak of light diffraction. Beside phase gratings (diffraction due to a spatial modulation of \(\text{Re}(\varepsilon)\)) also absorption gratings (modulation of \(\text{Im}(\varepsilon)\)) are able to diffract light. We consider first the case of phase gratings, which is proper to photorefractive materials. One can distinguish the two regimes of thin and thick holographic gratings by the parameter

\[
Q = \frac{2\pi \lambda d}{n \Lambda^2} ,
\]

with \(d\) being the thickness of the medium (interaction length), \(n\), the refractive index, and \(\Lambda\) the grating spacing [48]. The hologram is thick if \(Q >> 1\) (typical \(Q \approx 10\) [49]) and thin for \(Q<1\).

For thin gratings the incident light is diffracted into many diffraction orders (Raman-Nath diffraction regime). The diffraction efficiency \(\eta\) is defined as the ratio of the diffracted intensity to the incident intensity inside the crystal. The diffraction efficiency of the \(m^{th}\) order produced by a phase grating is given by [50]

\[
\eta = J_m^2 \left(2\pi d \Delta n / \lambda \cos \theta \right) \exp\left(-\alpha d / \cos \theta \right) ,
\]

where \(J_m\) is the \(m^{th}\)-order Bessel function and \(\theta\) is the internal angle of incidence of the incoming wave. \(\Delta n\) is the (scalar) effective amplitude of the refractive index modulation seen by the incident and diffracted waves and is given by

\[
\Delta n = \frac{1}{2n(\theta)} | \mathbf{p}_d \cdot \mathbf{e}_1 \cdot \mathbf{e}_d \cdot \mathbf{p}_i \cdot \mathbf{E}_1 | ,
\]

with
where \( \mathbf{p}_i \) and \( \mathbf{p}_d \) are the unit polarization vectors for the incoming and diffracted waves respectively and \( n(\theta) \) is the average refractive index. Note that here, in contrast to beam coupling, the absolute value of the space-charge field \( E_1 \) and not only the imaginary part is relevant. For first order diffraction and small refractive index changes \( (d\Delta n/\lambda \ll 1) \) Eq. (3.6) simplifies to

\[
\eta \equiv \left( \frac{\pi d\Delta n/\lambda \cos \theta}{\cos \theta} \right)^2 \exp \left(-\frac{\alpha d}{\cos \theta} \right).
\] (3.8)

For thick gratings only one diffraction order is observed (Bragg diffraction regime). There is a well defined angle of incidence for which the Bragg-diffraction condition is exactly fulfilled. This angle is derived from the phase matching condition \( k_d - k_i = K \), \( K \) being the grating wavevector. Its value \( \theta_0 \) inside the crystal is

\[
\theta_0 = \arcsin (\lambda / 2n\lambda).
\] (3.9)

A general form for the diffraction efficiency of fixed transmission holograms has been derived by Kogelnik [49], and is given by

\[
\eta = \frac{\sin^2 \left( \sqrt{\nu^2 + \xi^2} \right) / 2}{1 + \xi^2 / \nu^2} \exp \left(-\alpha d / \cos \theta \right),
\] (3.10)

where \( \nu = (\pi n d / \lambda \cos \theta) \) and \( \xi = \Delta K d (\cos \theta d / 2 \cos \theta) \) is a parameter proportional to \( \Delta \theta = \theta_0 - \theta_0 \) and describes the deviation from the Bragg-condition (3.10). For \( d\Delta n/\lambda \ll 1 \) (small index modulation or small thickness) and exact fulfilment of the Bragg-condition \( (\xi = 0) \), Eq. (3.10) coincides with expression (3.8) for the first Raman-Nath diffraction order.

The expressions (3.6)-(3.10) are valid for a phase grating in the arrangement shown in Fig. 3.1 (K || x), with recording beams being symmetric to a principal crystal axis. They describe the case of isotropic diffraction \( (\mathbf{p}_i, \mathbf{p}_d \neq \mathbf{0}) \) in all crystals, when the incident and diffracted probe waves are not influencing the strength of the refractive index modulation. Otherwise the longer expressions given by Kukhtarev et al. [27] should be used. Eq. (3.6)-(3.10) can be applied also for anisotropic diffraction \( (\mathbf{p}_i, \mathbf{p}_d = \mathbf{0}) \) in cubic crystals, while for optical anisotropic crystals some corrections terms should be considered because the function \( n(\theta) \) is then a complicated function which depends on the directions of the incident and diffracted waves. Such cases have been discussed in [51] and [52]. General expressions that include also the case where the recording beams are not symmetric have been given recently by Zgonik et al. [53].

A simple substitution transforms the expressions (3.6), (3.8) and (3.10) for the diffraction efficiency of phase gratings to the corresponding ones applying to absorption gratings. For completeness we give this transformation

\[
\frac{\pi \Delta n}{\lambda} \rightarrow \frac{i \Delta \alpha}{4},
\] (3.11)

where \( \Delta \alpha (\leq \alpha) \) is the scalar modulation amplitude of the absorption coefficient corresponding to the polarization of the incident and diffracted waves. With (3.11),
expressions (3.6), (3.8) and (3.10) maintain their validity in absolute value. Tab. 3.1 compares the maximum possible diffraction efficiencies for phase and absorption gratings.

Table 3.1: Maximum diffraction efficiency for phase and absorption gratings.

<table>
<thead>
<tr>
<th></th>
<th>Phase grating ($\Delta \alpha = 0$)</th>
<th>Absorption grating ($\Delta n = 0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thick grating: Bragg-diffraction</td>
<td>100 %</td>
<td>3.7 %</td>
</tr>
<tr>
<td>Thin grating: 1st order diffraction</td>
<td>34 %</td>
<td>4.8 %</td>
</tr>
</tbody>
</table>
4. Hologram recording in photorefractive materials

4.1 Hologram fixing in KNbO₃

4.1.1 Material properties of KNbO₃

Due to its strong polarizability, KNbO₃ is one of the oxygen octahedra ferroelectrics exhibiting the larger nonlinear optical effects. The combination of the large electro-optic coefficients [54] with the high photoconductivity [55] and photosensitivity [56] makes this material one of the best for use in photorefractive dynamic holography in the visible spectral range. KNbO₃ has a perovskite crystal structure with the oxygen octahedron centred at the Nb-atom. As temperature changes, KNbO₃ undergoes different first order structural phase transitions [57].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>426</td>
<td>cubic</td>
</tr>
<tr>
<td>436</td>
<td>tetragonal</td>
</tr>
<tr>
<td>203</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>218</td>
<td>trigonal</td>
</tr>
<tr>
<td>-50</td>
<td>paraelectric</td>
</tr>
<tr>
<td>-29</td>
<td>ferroelectric</td>
</tr>
</tbody>
</table>

Due to the first order nature of the phase transitions, KNbO₃ can be used for photorefractive experiments only in the room temperature orthorhombic phase precluding the heating of the crystal above 200 °C or the cooling below -30 °C. In this phase the spontaneous polarization $P_s$, which defines the crystallographic c-axis, is given by the displacement of the Nb atom in the direction of a two-fold symmetry axis of the oxygen octahedron. The a-axis is parallel to another two-fold symmetry axis and the b-axis is perpendicular to a and b and is parallel to a four-fold axis.

KNbO₃ is transparent from the infrared to the blue region of the spectrum with a room temperature band-gap energy of 3.3 eV [58] corresponding to the wavelength $\lambda = 375$ nm.† The dispersion and temperature dependence of the refractive indices has been given by Zysset et al. [59], the values at some selected wavelengths are given below.

† The band gap energy is defined at the value $\alpha = 100$ cm⁻¹ and is slightly anisotropic being larger by $\approx 0.03$ eV for light polarized parallel to the a or c axis than for b-polarized light [58].
Table 4.1: Room temperature refractive indices of KNbO₃.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>nₐ</th>
<th>nᵦ</th>
<th>nᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>2.4145</td>
<td>2.4974</td>
<td>2.2771</td>
</tr>
<tr>
<td>488</td>
<td>2.3527</td>
<td>2.4187</td>
<td>2.2274</td>
</tr>
<tr>
<td>514</td>
<td>2.3337</td>
<td>2.3951</td>
<td>2.2121</td>
</tr>
<tr>
<td>633</td>
<td>2.2801</td>
<td>2.3296</td>
<td>2.1687</td>
</tr>
</tbody>
</table>

Due to crystal symmetry, in the orthorhombic phase only the following elements of the linear electro-optic tensor $r$ and of the dielectric tensor $\varepsilon$ are non zero:

$$r_{mk} = \begin{pmatrix}
34 \pm 2 \\
6 \pm 1 \\
63.4 \pm 1 \\
450 \pm 30 \\
120 \pm 10 \\
. 
\end{pmatrix} \text{ pm/V } ; \quad \varepsilon_{ij} = \begin{pmatrix}
150 \pm 5 \\
. \\
985 \pm 20 \\
. \\
44 \pm 2 \\
. 
\end{pmatrix} \text{ pm/V}$$

The above values for the electro-optic coefficient and the dielectric constant are taken from Ref. [53] and are appropriate for an unclamped crystal. As shown recently by Günter and Zgonik [60], in photorefractive experiments the values to be used are neither the ones describing a clamped sample nor the ones for unclamped ones, but a combination of them. The reason is that the geometry constraints given by the periodic space-charge electric field limit the number of elastic deformations that can develop. The values to be used in KNbO₃ for a general photorefractive configuration have been recently given by Zgonik et al. [53]. Their values $r_{33}^{\text{eff}} = 54 \pm 2$ pm/V and $\varepsilon_{33}^{\text{eff}} = 35 \pm 2$ valid for the usual configuration with the grating wavevector parallel to the crystal c-axis and light polarized in the plane of incidence are used throughout this text to fit the experimental data.

4.1.2 Experimental set-up and general characterization of crystals

Fig. 4.1 shows schematically the set-up used for the holographic experiments in KNbO₃. The shutters are used to start or stop the recording, dark erasure or light erasure processes. The diffraction efficiency of the recorded grating is measured by a He-Ne beam which is polarized in the plane of incidence (electro-optic coefficient $r_{33}^{\text{eff}}$ is accessed). The intensity of the He-Ne light is low enough (< 100 µW/cm²), thus minimizing the influence on the grating formation. The same set-up is also used with small modifications for two-beam coupling measurements. In this case the intensity $I_A$ of one of the recording beams is attenuated by inserting a neutral density filter (typical 1/1000) in one of the beams. The transmitted intensity of this beam ($I_A(L)$, L: crystal thickness) is detected by an additional photomultiplier behind the crystal and the exponential gain $Γ$ is calculated from Eq. (3.3).

*: The reduced form of the electro-optic tensor is used with $r_{ijk} = r_{mk}$ with the transformation $ij \rightarrow m$: 11→1; 22→2; 33→3; 23, 32→4; 13, 31→5; 12, 21→6.
Hologram fixing in K\textsubscript{2}NiO\textsubscript{3}  

Temperature controlled furnace with crystal sample

Fig. 4.1: Schematics of the experimental set-up used for the holographic experiments. BS: Beamsplitter, M: Mirrors, S\textsubscript{1}, S\textsubscript{2}: Shutters, PMT: Photomultiplier.

The furnace permits a temperature stability of 0.05 °C and is used to characterize the dynamics at temperatures between 20° and 180 °C. Electrical connections allow to apply electric fields in the positive c direction of the crystal.

We investigated the charge compensation dynamics in different K\textsubscript{2}NiO\textsubscript{3} crystals samples grown by the top-seeded high temperature-solution growth method [61]. Beside nominally pure crystals and crystals doped with iron, rubidium or tantalum, we studied this behaviour also in multiple doped crystals with Li, Na and Fe. Two crystals of this kind were grown using melt compositions K\textsubscript{0.95}Li\textsubscript{0.025}Na\textsubscript{0.025}Nb\textsubscript{0.025}O\textsubscript{3} + 1000 ppm Fe (K\textsubscript{2}NiO\textsubscript{3}:LiNaFe\textsubscript{1}) and K\textsubscript{0.85}Li\textsubscript{0.1}Na\textsubscript{0.05}Nb\textsubscript{0.05}O\textsubscript{3} + 1000 ppm Fe (K\textsubscript{2}NiO\textsubscript{3}:LiNaFe\textsubscript{2}). A list of the crystals used which also includes some of their properties is given in Appendix C.

We tested the orthorhombic-tetragonal phase transition temperature of the multiple doped crystals by differential thermal analysis tests (DTA). The results showed that the phase transition temperature \( T_c \) is lowered by a maximum of \( \approx 23 \) °C in the highest doped crystal (K\textsubscript{2}NiO\textsubscript{3}:LiNaFe\textsubscript{2}).

Table 4.2: Orthorhombic-tetragonal phase transition temperature measured for increasing temperature

<table>
<thead>
<tr>
<th>Crystal</th>
<th>( T_c ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\textsubscript{2}NiO\textsubscript{3} (undoped)</td>
<td>218</td>
</tr>
<tr>
<td>K\textsubscript{0.95}Li\textsubscript{0.025}Na\textsubscript{0.025}Nb\textsubscript{0.025}O\textsubscript{3} + 1000 ppm Fe</td>
<td>216</td>
</tr>
<tr>
<td>K\textsubscript{0.9}Li\textsubscript{0.05}Na\textsubscript{0.05}Nb\textsubscript{0.05}O\textsubscript{3} + 1000 ppm Fe</td>
<td>210</td>
</tr>
<tr>
<td>K\textsubscript{0.85}Li\textsubscript{0.1}Na\textsubscript{0.05}Nb\textsubscript{0.05}O\textsubscript{3} + 1000 ppm Fe</td>
<td>195</td>
</tr>
</tbody>
</table>

The absorption spectrum of the crystals K\textsubscript{2}NiO\textsubscript{3}:LiNaFe\textsubscript{1} and K\textsubscript{2}NiO\textsubscript{3}:LiNaFe\textsubscript{2} is similar to the one usually observed in unreduced K\textsubscript{2}NiO\textsubscript{3} crystals doped with Fe [52], while the

\[ \text{\textsuperscript{1}} \] The rubidium and tantalum doped crystals were kindly provided us by Sandoz AG, Basel.
undoped crystals and the crystals doped with Rb and Ta do not show evidence for any absorption band in the visible.

4.1.3 Dynamics of charge compensation in KNbO$_3$

In KNbO$_3$ at temperatures above 70 °C the build-up, the dark decay and the optical erasure of the space-charge field do not follow the normal single exponential time behaviour predicted by the Kukhtarev model.† If the recording is prolonged for long times (typical > 100 s), the diffraction efficiency ($\eta \propto |E_1|^2$) begins to decrease and reaches finally a steady state value close to zero. An example is shown in Fig. 4.2. The recording ($t<550$ s) and the subsequent development of the diffraction efficiency in the dark ($t>550$ s) are shown for the KNbO$_3$:LiNaFe1 crystal.

![Graph](image)

**Fig. 4.2:** Time dependence of the diffraction efficiency during recording ($t<550$ s) and decay in the dark ($t>550$ s) in KNbO$_3$:LiNaFe1 at $T=95$ °C and for a grating spacing $A=1.75$ μm. At the beginning of part C the two recording beams are switched off. Parts A, B, C and D correspond to the ones given schematically in Fig. 2.2. The insets show that the time evolution at the end of parts B and D is well approximated by single exponential functions.

The behaviour shown in Fig. 4.2 is the one predicted by the electron-ion model of section 2.3 for a crystal having a large density of compensating ions (cf. Fig. 2.6). One can show that the phase between the grating and the light fringes is reversed in parts C and D with respect to the one in parts A and B (space-charge field $E_1$ has opposite sign). We demonstrate this by simultaneously measuring Bragg-diffraction and two-beam coupling.

† In most of the crystal samples, the conventional behaviour is still observed if the hologram recording is interrupted immediately after $E_1$ has reached its maximum value.
Such a measurement is shown in Fig. 4.3 for a slightly reduced undoped crystal. The value of the amplification factor $\gamma_0 = \exp(Fd)$ during the dark erasure is measured by periodically switching on the recording beams for a short time. At the first and second peaks of $\eta$ we have $\gamma_0 < 1$ and $\gamma_0 > 1$ respectively, showing that the primary and the secondary grating are mutually phase shifted by an angle $\pi$.

![Graph](image)

**Fig. 4.3:** Simultaneous measurement of diffraction efficiency $\eta$ (circles, left-hand scale) and effective gain $\gamma_0$ (dots, right-hand scale) during recording ($t < 150$ s) and subsequent dark erasure ($t > 200$ s) in pure KNbO$_3$ (Sample P1S-1). Modulation index: $m = 0.06$.

### 4.1.3.1 Grating spacing dependence

All observations mentioned above are consistent with the electron-ion model. Therefore, we expect to observe the slowing down of the compensation dynamics for large grating spacings which is predicted by the theoretical relation (2.21). To verify this we proceeded as follows. We switched-off one of the recording beams after the compensation of the two gratings had reached saturation. The diffracted intensity of the remaining beam was then recorded by a photomultiplier tube and transferred to a computer. The handling time in part D (Fig. 4.2) was then fitted by a single exponential function to obtain a value for the decay time constant $\tau_3 \equiv (F_3)^{-1}$. This procedure was repeated at the same temperature for different values of the grating spacing $\Lambda$. Care was taken to insure that the dielectric relaxation rate $F_{die}$ for the primary charge carriers was much larger that the one corresponding to the ions ($F_{dil}$), which was achieved by choosing the working temperature and the erasing intensity. This insures that no remaining effect of the time rate $F_2$ is left in part D.
Fig. 4.4: Grating spacing dependence of the handling time $\tau_3=(\Gamma_3)^{-1}$ in a pure KNbO$_3$ sample (P1S-1) measured at $T=107 \degree$C with an erasing intensity $I=40$ mW/cm$^2$. The solid line indicates the best fit to Eq. (2.21). From the fitted parameters we determine $\tau_{dif}=(6.5\pm0.7)$ s and $N_{eff}=(1.15\pm0.2)\times10^{15}$ cm$^{-3}$. The inset shows a two-beam coupling measurement in the same crystal giving $N_{eff}=(1.65\pm0.4)\times10^{15}$ cm$^{-3}$.

Fig. 4.4 shows the values of $\tau_3$ for the case $E_0=0$, where the solid line shows the best fit according to Eq. (2.21). The expected quadratic increase for longer grating spacings as well as the saturation at shorter grating spacings are well reproduced. This kind of measurement proves to be a new easy way to characterize material properties. For example, from the fitted curve in Fig. 4.4 we get $(\Gamma_{dif})^{-1} = \tau_{dif} = (6.5\pm0.7)$ s and $K_{oe} = (2.65\pm0.25)\times10^6$ m$^{-1}$. With Eq. (2.22) we determine an effective number of traps $N_{eff}=(1.15\pm0.2)\times10^{15}$ cm$^{-3}$ for our crystal. This value is in good agreement with $N_{eff}=(1.65\pm0.4)\times10^{15}$ cm$^{-3}$ obtained from independent room temperature two-beam coupling measurements in the same crystal (inset in Fig. 4.4). The quadratic divergence of $\tau_3$ with $\Lambda$ is observed in all the samples investigated, and the value of the effective number of traps derived in this novel way is always in good agreement with the one obtained with two-beam coupling.

4.1.3.2 Electric field dependence

As was shown in Fig. 2.12, the theory predicts that the time rate $\Gamma_3$ is strongly influenced by an applied field, thus permitting an electric control of the time needed for compensation. This influence is expected to be stronger for large grating spacings $\Lambda$. Fig. 4.5 shows an experimental confirmation of this prediction. The grating dynamics in part D for the grating spacing $\Lambda=3$ $\mu$m is shown for three values of the externally applied field $E_0$. 
Hologram fixing in KNbO₃

Normalized diffraction efficiencies observed during the erasure process in pure KNbO₃ for different values of the applied field $E_0$. The values for the decay time constants $\tau_3=(T_3)^{-1}$ decrease for larger fields allowing an electrical control of the time needed for compensation and of the handling time. ($\tau_3(E_0=0)=18$ s, $\tau_3(E_0=1$ kV/cm$)=13$ s, $\tau_3(E_0=2$ kV/cm$)=8.2$ s). (Sample P1S-1).

It is seen that the decay is well described by a single exponential.† As expected, the decay time constant decreases with $E_0$ and approaches the value $\tau_{di}=6.5$ s for large fields. This decrease is more pronounced if larger grating spacings are chosen. For $\Lambda=18$ μm we measured in the same crystal $\tau_3(E_0=0)=380$ s, $\tau_3(E_0=1$ kV/cm$)=60$ s and $\tau_3(E_0=2$ kV/cm$)=25$ s.

Because it produces an additional phase shift between the electronic and the ionic contributions to the space-charge field, the applied electric field can also be used to modulate the diffraction efficiency during the handling time of the hologram, that is while reading out with the wavelength used for recording. We demonstrate this in Fig. 4.6, where the time evolution of a grating with $\Lambda=18$ μm illuminated by a 40 mW/cm² homogeneous Ar⁺-laser beam ($\lambda=514$ nm) is shown. The space-charge gratings were previously recorded with $I_0=66$ mW/cm² and an applied field $E_0=2$ kV/cm. At the beginning of the erasure process the applied field is kept on (solid line). After a while, the field is switched periodically off (dashed lines) and on again (solid lines). When the field is removed, the diffraction efficiency $\eta$ drops to a much lower value with a ratio $\eta(E_0\text{ off})/\eta(E_0\text{ on})$ of about 0.0015. When the field is switched on again, the diffraction efficiency recovers in large

† There are no oscillations in the dynamics because the described Bragg-diffraction experiments (with a single complex time rate) are not sensitive to the relative phase between light fringes and refractive index grating. This is valid until the diffraction efficiency does not become so big that the space-charge grating is modified as a result of beam coupling effects between incident and diffracted beam.
extent. The inset in Fig. 4.6 shows the same measurement but for a grating spacing \( \Lambda = 0.7 \) \( \mu \)m and an initially applied field \( E_0 = 1 \) kV/cm. Again, at a certain point the field is switched off (dashed line) with only a small change in diffraction efficiency and in the time constant \( \tau_3 \). Note also the big difference in the value of the diffraction efficiency which is about 100 times bigger for \( \Lambda = 18 \) \( \mu \)m than for \( \Lambda = 0.7 \) \( \mu \)m.

![Graph showing electric field dependence of the diffraction efficiency](image)

Fig. 4.6: Electric field dependence of the diffraction efficiency \( \eta \) measured during the handling process at the grating spacing \( \Lambda = 18 \) \( \mu \)m. The inset shows the same kind of measurement but for the grating spacing \( \Lambda = 0.7 \) \( \mu \)m. During the recording and the beginning of the erasure process the electric field \( E_0 = 2 \) kV/cm is on. After the grating compensation has reached saturation, one of the recording beams is switched-off at time \( t = 5 \) s. Later, the field is switched-off (dashed lines) and on again (solid lines) several times in order to show the jumps in diffraction efficiency. (Sample P1S-1)

In the experiment presented in Fig. 4.6, the electronic and the ionic contributions to the space charge field resume their relative phase shift of \( \pi \) predicted by equations (2.12b) and (2.12c) every time the field is switched off. This phase shift gives the optimum compensation, therefore the total space-charge field \( E_1 \) decreases in magnitude. This explains the observed drop of the diffraction efficiency \( \eta \). If the field is switched on again the two components shift again in phase giving rise to the new increase of \( \eta \). Since only one beam illuminates the crystal during this measurement, the described effects cannot be understood without assuming the simultaneous presence of two complementary gratings having similar amplitudes. If the amplitudes of the compensating components are strongly different, one expects a weaker influence of the applied field. This situation is found during the handling of the hologram at very small grating spacings where the ionic contribution \( E_{i1} \) is much larger than the electronic contribution \( E_{e1} \). This explains the small influence of the field in the measurement shown in the inset of Fig. 4.6. The smaller values of \( E_{e1} \) and \( E_{i1} \).
at small $A$ (see Fig. 2.4) explain also the smaller diffraction efficiency observed for $A = 0.7 \mu m$ than for $A = 18 \mu m$.

### 4.1.3.3 Light intensity dependence

The speed of grating writing (A) and revealing (C) (cf. Fig. 2.2) increases with light intensity. This is expected because a larger number of primary charge carriers are photoexcited. In contrast, because the secondary grating is not directly influenced by light, the speed of the processes occurring during grating compensation (B) and the handling of the grating (D) are only very weakly dependent on the intensity of illumination. This dependence is such that in most of the crystals the time constant $\tau_3$ gets slightly shorter (typically up to 15%) by increasing the light intensity from 0 to 1 W/cm$^2$. This is consistent with the theoretical predictions presented in Fig. 2.10 for low light intensities.

![Image of graph showing light intensity dependence](image)

Fig. 4.7: Erasure process after compensation. Note that the erasure in the dark (dots) is faster than the erasure under homogeneous illumination (full squares). The time constants are resp. $\tau_3 = 80\pm 4$ s (dark) and $\tau_3 = 103\pm 4$ s (hom. illum). Inset: Writing-dark erasure cycles in the same crystal at room temperature. +: Crystal in the dark during 5 min before the beginning of recording; o: Crystal homogeneously illuminated before beginning of recording (Light intensity during writing = 0.45 W/cm$^2$, $\Lambda = 1.7 \mu m$).

In one crystal (KNbO$_3$:LiNaFe$_{1.2}$Fe$_{0.6}$), however, we observed an increase of the time rate $\tau_3$ [41, 62] (Fig. 4.7). In the measurement shown in Fig. 4.7 the time constant $\tau_3$ is smaller by about 30% in the dark than with an homogeneous illumination of 0.25 W/cm$^2$. In chapter 2 we predicted that such a behaviour is possible if the density of free charge carriers $n_o$ (or $p_o$) becomes comparable to the effective number of traps $N_{eff}$ (Eq. (2.43), Fig. 2.10), which is about $10^{16}$ cm$^{-3}$ in this crystal. However, a very small hole mobility $\mu$ (the majority carriers...
in the mentioned crystal are holes) on the order of $10^{-8}$ cm$^2$(Vs)$^{-1}$ has to be assumed to explain by Eq. (2.60) the photoconductivities ($\approx 10^{-10}$ (Ωm)$^{-1}$) measured at the same intensity levels. We believe that such a small mobility is not realistic if the charge transport takes place only in the band. In contrast, such small values of $\mu$ can be understood if the mobility is trap limited [44], i.e., it is limited by many trapping and reexcitation processes in shallow traps placed close to the conduction or valence band [39]. There is some experimental evidence for the presence of such shallow traps in our crystal KNbO$_3$:LiNaFe$_1$. The first is illustrated by the inset of Fig. 4.7 which shows the unusual recording dynamics observed at room temperature in the same crystal, where the ions do not play any role. Nevertheless, if the crystal is kept for a sufficiently long time in the dark before starting the writing process the diffraction efficiency shows a transient peak. In contrast, if the crystal was previously illuminated, the same steady state level as in the previous case is reached, but without a transient peak. Our interpretation is based on the presence of shallow trap levels being close to the valence band. In thermal equilibrium (dark) these traps are normally empty. Due to the inhomogeneous illumination during hologram writing, they are subsequently filled with holes. Initially this happens predominantly in the bright regions of the crystal. The resulting inhomogeneous charge distribution in these traps contribute first to the space-charge field detected during the transient peak in Fig. 4.7 (inset). Later, this shallow-trap charge modulation disappears again because the traps get filled with holes also in the dark regions of the crystal. If the traps are already completely filled before starting the recording process (previous illumination of the sample), there is no transient charge modulation in the shallow-traps and thus no transient peak. We note that the charge modulation amplitudes in the deep and shallow traps during the transient peak are similar, because the height at maximum is about two times the final steady state value of $\eta$. Therefore, one can conclude that the density of shallow traps $N_{ST}$ and the effective (deep) trap density $N_{eff}$ have the same order of magnitude. The second evidence for the shallow-traps in this crystal is given by our observation that the dark-decays of the primary space charge grating at room temperature are strongly non-exponential and depend also on the writing intensity and on the recent illumination history of the sample. Stroh kendl [63] has shown that such effects are expected for crystals containing a large number of shallow traps.

The effect of such shallow trap levels is not explicitly included in our electron-ion model of chapter 2. However, without modifying it we may consider that the electrons trapped in shallow traps also contribute to the free charge concentration $n_0$ but only the electrons in the conduction band are free to move.† This leads to a decreased effective mobility $\mu_{eff} = \mu_{free}(n_{free}/n_0)$, where $n_{free}$ is the true electron concentration in the conduction band and $\mu_{free}$ is the true conduction band mobility. As stated in section 2.4.2.3, a large $n_0$ represents the necessary condition for the observation of the decrease of the slow time rate $\Gamma_3$ with light intensity. Thus, our observations can be explained if $n_{free} << n_0$, which is confirmed by our above considerations.

† For consistency with the electron-ion model we consider electrons as primary charge carriers although in crystal KNbO$_3$:LiNaFe$_1$ they are holes.
All the above discussions clearly demonstrate the problems connected with the determination of the true mobility in crystals containing a number of different defect levels which can act as traps for the charge carriers. Such problems have been discussed by Partanen et al. [64]. A method to overcome them may be represented by the investigation of the grating dynamics after excitation with short pulses in the ps range [39, 65]. The determination of $\mu_{\text{free}}$ would be possible also by the investigation of the described charge compensation dynamics. Measurements of the intensity dependence of the time rate $\Gamma_3$ (Eq. 2.43) give the ratio $n_0/N_{\text{eff}}$. Correlation with measurements of the grating spacing dependence of the same rate (giving $N_{\text{eff}}$, see section 4.1.3.1) and measurements of the conductivity or of the time rate $\Gamma_2$ (giving $\Gamma_{\text{die}}=\mu_{\text{eff}}n_0$) allow then the determination of $\mu_{\text{eff}}$. The true conductivity can then be determined if $n_{\text{free}}=n_0$, that is, if the density of shallow traps $N_{ST}$ is small compared to $n_{\text{free}}$. However, with cw-experiments we were not able to reach this regime in our crystals.

### 4.1.3.4 Thermal activation energy of compensating charge carriers

The driving term in the expression (2.21) for the time rate $\Gamma_3$ is the dielectric relaxation rate $\Gamma_{\text{dif}}$ for the ions. We expect a strong dependence of this term on temperature because the ion mobility $\mu_I$ changes. Fig. 4.8 shows the temperature dependence measured in different crystals using a grating spacing $\Lambda=1.75\ \mu$m. In two crystals, the temperature dependence of the time rate $\Gamma_2$ during the dark decay was investigated as well (Fig. 4.9). In contrast to the case of the rate $\Gamma_3$, for $\Gamma_2$ the ions play a negligible role. In order to identify better the functional dependence on temperature we have plotted the inverse time rates in logarithmic scale as function of the inverse temperature. The full lines correspond to the best fits to an Arrhenius law

$$\tau(T) = \tau_0 \exp(\Delta E/k_B T),$$  

where $\tau_0$ is a preexponential term and $\Delta E$ is an activation energy. In the case of the time constant $\tau_3=(\Gamma_3)^{-1}$, $\Delta E$ is the activation energy for the ionic mobility $\mu_I$, while for $\tau_2=(\Gamma_2)^{-1}$ the activation energy describes the process of thermal excitation of electronic charge carriers.

We discuss first the left side of Fig. 4.8 which shows the time constant $\tau_3$, measured with wavevector parallel to the crystal $c$-axis (isotropic Bragg-diffraction). Since the curves are nearly parallel the activation energy for the ionic mobility is approximately the same in all the crystals. Within the experimental error the value $\Delta E = 1.02\pm0.06\ \text{eV}$ is consistent with all measurements. The preexponential term varies between $\tau_0=0.03\ \text{ps}$ (KNbO$_3$:LiNaFe2) and $\tau_0=10\ \text{ps}$ (KNbO$_3$:LiNaFe1). In the past, similar values of $\Delta E$ were obtained from the slope of the dark conductivity plot versus inverse temperature at temperatures above 100 $^\circ$C. The reported activation energies are $\Delta E = 1.0\ \text{eV}$ for Fe doped KNbO$_3$ [52] and $\Delta E = 1.2\ \text{eV}$ in pure reduced KNbO$_3$ [66].
It should be noted that the crystals used for the measurements shown in Fig. 4.8 behave in the same way although they are very different from each other. As summarized in Appendix C, under light illumination some crystals (LiNaFe1, LiNaFe2, Rb) are predominantly hole-conducting, other (P1S-1, Ta) are electron conducting, while the sample P1S-2, that is cut from the same boule as P1S-1, shows a mixed conduction. In the crystal KNbO3:LiNaFe1 we were able to change the primary charge carriers from holes to electrons after applying an electric field of about 100 V/cm at 180 °C for 14 hours. After this reduction treatment the crystal still showed the same unusual dynamics without any relevant change in the activation energy. The time constant $\tau_3$ decreased by about 15%. Thus, we conclude that the secondary carriers remained the same also after the reduction treatment and are the same for all the KNbO3 crystals. This excludes an electron-hole mechanism, like the one described in Appendix B.2, as the origin of the charge compensation and suggests an intrinsic mechanism common to all crystals.

In the right part of Fig. 4.8 we show the time constant measured in anisotropic Bragg diffraction geometry. The squares show the results in one of the crystals (KNbO3:LiNaFe2) in the geometry where the charge compensation takes place by motion of the ions in the direction of the crystal $b$-axis. The circles belong to the case where the ions move along the crystal $a$-axis (KNbO3:LiNaFe1). We see that the ionic motion is easier in the $b$-direction.
Hologram fixing in KNbO$_3$

where the activation energy for the ionic mobility is only $\Delta E = 0.8\pm0.05$ eV ($\tau_\phi = 90$ ps), that is 0.2-0.3 eV smaller than for motion along the c or a-axis.† The nearly equal activation energies measured for $K\parallel c$ ($\Delta E = 1.02$ eV) and $K\parallel a$ ($\Delta E = 1.07$ eV) are consistent with the fact that these two axes are identical from a crystallographic point of view. They are both two-fold axis passing by the central Nb-atom and between two neighbouring oxygen atoms in the oxygen octahedron. In contrast, the b-axis is a four-fold symmetry axis connecting the Nb-atom with a corner oxygen atom.

For the geometry with $K\parallel b$ charge compensation can be obtained in less than one hour already at room temperature. We observed room temperature charge compensation in the b-direction (but not in c-direction) in a time scale shorter than one hour in two other samples, which shows that the ionic mobility in KNbO$_3$ is anisotropic and systematically larger in direction of the b axis. There are some indications that BaTiO$_3$, another oxygen octahedra ferroelectric, also has a larger ionic mobility in the b than in the c direction [67].

It is interesting to estimate the ionic mobility by means of the curves shown in Fig. 4.8. For the grating spacing used, the time rate $\Gamma_3$ is close to the value of dielectric relaxation rate $\Gamma_{\text{di}} = \mu_j N_{\text{i0}} / e \varepsilon_0$ for the ions. For the crystal KNbO$_3$:LiNaFe1 we obtain $\mu_j N_{\text{i0}} = 7.6\times10^8$ (Vms)$^{-1}$ at $T= 150$ °C and $\mu_j N_{\text{i0}} = 1700$ (Vms)$^{-1}$ at room temperature. Assuming a defect concentration $N_{\text{i0}} = 10^{23}$ m$^{-3}$ the mobility of the secondary charge in KNbO$_3$:LiNaFe1 can be estimated to vary between $\mu_j = 10^{-14}$ m$^2$(Vs)$^{-1}$ at $T = 150$ °C and $\mu_j = 10^{-20}$ m$^2$(Vs)$^{-1}$ at room temperature. With this values the time needed by a single ion to pass a 1 cm long crystal under the influence of an electric field of 1 kVcm$^{-1}$ is about 4 months at $T = 150$ °C and $3\times10^5$ years at room temperature. However, due to the large density of ions, the compensation of the electronic space-charge grating over distances of few micrometers can anyway proceed very fast. The above values hold for ionic movement in the c direction, for movement in the b direction the room temperature mobility is about two orders of magnitude larger. The mobilities approach each other for temperatures close to 200 °C.

Fig. 4.9 show the temperature dependence of the time rate $\Gamma_2$ measured in the dark. The interpretation has to be related to the defect distribution in the band gap and not to the ions because the time rate $\Gamma_2$ is only weakly influenced by the ionic mobility. The activation energy obtained is related to the energetic separation from some trap level to the valence or the conduction band. Surprisingly, we obtain for both crystals an activation energy $\Delta E = 0.6\pm0.1$ eV, although one of the crystals (P1S-1) is electron (photo)-conducting and the other is hole (photo)-conducting. This may be interpreted in two ways. First, the dark relaxation of the primary grating occurs by transport of charge carriers thermally excited from the same kind of defect level both for reduced and unreduced crystals. Second, thermal excitation occurs for the two kinds of crystals from defect levels being placed symmetrically across the band gap and having both an energetic distance of about 0.6 eV from the

† One does not expect a large anisotropy for the thermal activation energy or mobility of electrons or holes, what again excludes electron-hole charge compensation (Appendix B) for explaining the observations.
corresponding band. There are some experimental indications [65, 68] and theoretical calculations in other oxygen octahedra materials [69] that may support both the possibilities.

\[ \Delta E = 0.6 \pm 0.1 \text{ eV} \]

\[ \tau_2 = (\tau_2)^{-1} \text{[s]} \]

Fig. 4.9: Temperature dependence of the inverse time rate $\tau_2$ measured in the dark for two crystals. The activation energy is $\Delta E = 0.6 \pm 0.1 \text{ eV}$ (Kilc, $\Lambda = 1.75 \text{ mm}$).

### 4.1.3.5 Origin of compensating charge carriers

In the previous sections we implicitly assumed that ions are the compensating charge carriers in KNbO$_3$. This is justified because all the experiments described in section 4.1.3 are in very good agreement with the predictions of our electron-ion model of chapter 2. Other physical mechanisms which could potentially lead to similar effects can be ruled out by our measurements. The case of an electron-hole mechanism (Appendix B) has already been discussed. The formation of ferroelectric domains has been suggested to be responsible for the electrical fixing of holograms observed in some ferroelectric crystals [70]. In this case the field resulting from the sum of an external applied field and the internal space-charge field is believed to be responsible for the flipping of ferroelectric domains in the direction of the crystal spontaneous polarization. This mechanism is not compatible with our observations because we observed that the fixation occurs also for space-charge fields directed along the $b$ or $c$-crystal axis and without the need of applied fields.

The identification of the kind of ionic defects being responsible for charge compensation is more difficult. In LiNbO$_3$ the motion of protons seems to contribute to the fixing mechanism [71]. Their thermal activation energy is 1.1 eV and lies very close to the values that were measured in this work for KNbO$_3$. The protons form OH$^-$-groups in the crystal and their vibrational absorption band in the infrared can be measured. In this way the presence of protons in an amount normally exceeding $10^{18}$ cm$^{-3}$ has also been demonstrated in the case of KNbO$_3$ crystals [72]. Protons may therefore be responsible for the fixing in our samples.

A second possible origin for the moving ions is represented by oxygen vacancies. Matull and Rupp [73] proposed a connection between the thermal fixing of holograms and the
thermoelectret properties † [74] in the case of LiNbO₃. Since the two phenomena are very similar, the assumption of a common microscopic origin seems reasonable and could probably be applied to most of the materials allowing high temperature thermal fixing. The existence of an electret state in a number of ABO₃ oxides with the perovskite structure has been demonstrated recently [75]. It was shown that a high concentration of A and O vacancies favours the formation of thermoelectrets. The role played by the diffusion of oxygen vacancies in the formation and discharge of the electrets was emphasized also in a previous paper by Bondarenko et al. [76]. Further arguments suggest a possible relation between hologram fixing and diffusion of oxygen vacancies. The electrocoloration of SrTiO₃ single crystals at temperatures over 100 °C has been attributed to the drift of oxygen vacancies creating reduced and oxidized regions in the crystal [77]. The authors estimated an oxygen vacancy concentration \( N_V \) of \( 10^{18} \) cm\(^{-3} \) and a mobility \( \mu_V \) of \( 10^{-12} \) m\(^2\)(Vs\(^{-1} \) at 200 °C. The related activation energy varies in SrTiO₃ between \( \approx 0.7 \) and \( \approx 1.0 \) eV, which is close to the values obtained for our crystals using holographic methods.

Reduced and oxidized regions are formed also in KNbO₃ during electro-chemical reduction treatment at temperatures around 190 °C [52, 68, 78]. In the reduced region of the crystal there is an increased number of oxygen vacancies compensating for the change in valence of some impurity ions (e.g. Fe\(^{3+} \rightarrow \) Fe\(^{2+} \)). The typical time needed for the redistribution of oxygen vacancies during the reduction process is some hours to few days at \( T = 200 \) °C and \( E_o = 1 \) kVcm\(^{-1} \), what implies a mobility of the order of \( 10^{-13} \) to \( 10^{-10} \) m\(^2\)(Vs\(^{-1} \). These values are consistent with the ones estimated in section 4.1.3.4 from holographic measurements and with the above data for the mobility of oxygen vacancies in SrTiO₃.

We discuss further the role of the crystal reduction state by comparing the behaviour in the different crystals of Fig. 4.8. We believe that for the same conditions the ionic mobility is the same in all the crystals. However, for a fixed temperature, different crystals show different values of the time rate \( \tau_3 \). Thus, the measured differences are mainly due to a different concentration of ions, although a different effective number of traps \( N_{eff} \) can also slightly influence the value of \( \tau_3 \) at the used grating spacing (Eq. 2.21). In general, we notice that the time constant \( \tau_3 \) is smaller in reduced crystals than in as grown or oxidized ones. For instance, in sample P1S-1, which is slightly reduced, \( \tau_3 \) is about a factor of 3 smaller than in the as grown sample P1S-2 cut from the same crystal boule. The oxidized sample KNbO₃:Fe (224) that shows the largest values of \( \tau_3 \) was cut near the anode of a sample inhomogeneously reduced by the electro-chemical method. In this area the sample is hole conducting and contains a smaller number of oxygen vacancies [68, 79]. We compared the handling time \( \tau_3 \) measured in the oxidized region with the one measured in a piece cut

† An electret is a piece of dielectric material exhibiting a quasi-permanent electrical charge. The conventional classification include photoelectrets and thermoelectrets among other kind of electrets. In the former case the charge is formed by illumination under an applied field. In the latter case the electret is formed by application of an electric field at elevated temperature and subsequent cooling while the field is still applied. The photorefractive effect could be seen as a special case of photoelectret formation with charge separation by a distance corresponding to the grating spacing, while thermally fixed photorefractive gratings are related to thermoelectrets.
from the same original sample but close to the cathode, where the result of the electro-
chemical treatment was a strong reduction of the crystal. Under the same external conditions
at \( T = 85 \, ^\circ C \) we measured \( \tau_3 = 8500 \, s \) in the center of the oxidized region and \( \tau_3 = 170 \, s \)
in the center of the reduced region. This difference cannot be understood only by the \( \approx 10 \)
times larger effective number of traps that has been measured in the oxidized region [79]
(Appendix C). By assuming an equal ionic mobility in the two parts of the crystal, this result
suggest that in the reduced (electron conducting) part of the crystal the concentration of ions
is larger by at least a factor of 5 with respect to the oxidized region.

Oxygen vacancies are needed for local charge compensation in the reduced region. Since in
this region, the concentration of ionic defects responsible for photorefractive charge
compensation is much larger than in the oxidized region, we believe that these ionic defects
are oxygen vacancies rather than protons. Oxygen vacancies are in general doubly positively
charged, the experimental results can therefore be explained assuming a concentration being
only half the one required for single charged ions. To explain the complete compensation
observed in the KNbO\(_3\) samples, the number of oxygen vacancies should be at least about
\( 5 \times 10^{16} \, \text{cm}^{-3} \) or larger, which means that at least 1 oxygen atom for every \( 10^6 \) is missing.
The oxygen vacancies are either the result of a doping (for instance with iron) or of slightly
nonstoichiometric growth conditions which can lead to the formation of potassium vacancies
(whose charge is compensated by half an oxygen vacancy).

We remark that the investigation of the high temperature dynamics after photorefractive
charge compensation could also be used as a novel sensitive method for calibrating the
reduction state and its homogeneity in a crystal sample. While handling the hologram, the
diffraction efficiency decreases faster in the highly reduced regions of the crystal and images
taken at different times give the needed information. As the initial concentration of oxygen
vacancies in as grown samples cannot be easily predicted, this method is useful to quantify
the changes induced by the reduction treatment in a particular sample rather than to compare
different samples grown under different conditions.

### 4.1.4 Fixing procedure for photorefractive gratings in KNbO\(_3\)

The strong temperature dependence of the ionic mobility (see Fig. 4.8) can be used for the
fixing of holograms by a thermal cycling method. The fixing procedure is:

(a) A photorefractive hologram is recorded at a given fixing temperature. A
temperature of about 80 \(^\circ C\) is optimal. The compensation of the primary space-
charge grating by the ions reaches saturation in about 50-500 \( s \).

(b) After steady state is reached, the crystal is cooled down to room temperature.
During the cooling process the recording can either be continued or interrupted.
In the second case the cooling process should be fast in order to avoid
redistribution of ions before reaching room temperature.
(c) At room temperature the hologram can be read-out non destructively at the appropriate Bragg angle with the same wavelength that was used for recording. An initial transient due to redistribution of primary charge carriers to an equilibrium position (revealing) is followed by an exponential decay. From this point on the primary and secondary carriers redistribute with the same time rate $\Gamma_3$ which is much smaller than the one at the fixing temperature (Fig. 4.10).

The best conditions are obtained for recording at large grating spacings and with an applied field. The time rate $\Gamma_3$ at the fixing temperature is increased by the applied field; however, longer storage and handling times are obtained at room temperature due to the larger grating spacing (see section 4.1.3.1). Fig. 4.11 shows an example of an image stored in a KNbO$_3$ crystal using the above fixing procedure.

The diffraction efficiencies obtained for the fixed grating are typically between one tenth and one half of the values measured for the primary grating alone and reach about 0.5-1% in samples of $\approx$ 2 mm thickness.

The storage and handling times of the fixed grating measured at room temperature vary from sample to sample because the ion concentration is not the same. We measured a storage time of 20 days for KNbO$_3$:LiNaFe1 and of 1 day for KNbO$_3$:pure (P1S-1) for a grating spacing $\Lambda$= 1.5 μm. These values agree well with the extrapolation of the fitted straight lines in Fig. 4.8 to room temperature. Oxidized samples can store holograms for longer times because of a smaller number of compensating ions. For instance, the room temperature storage and handling time in the sample KNbO$_3$:Fe(224) (Fig. 4.8) is about 6-7 months even for small grating spacings. A further increase of the time constants is achieved by cooling further to 0 oC (one order of magnitude more) or by recording at larger grating spacings. For instance the storage time is 10-100 times longer at $\Lambda$= 10 μm than at $\Lambda$= 1.5 μm. In general, the handling time of a fixed hologram in KNbO$_3$ is about seven to eight orders of magnitude larger than that of a non-fixed grating.
In KNbO₃ the dielectric relaxation rate \( \Gamma_{\text{die}} \) is relatively large also in the dark and lies in the region 0.1-100 s\(^{-1}\) depending on crystal sample and temperature. The consequence of this fact is that the handling and the storage time are nearly equal in this crystal. This is valid at all temperatures and can be regarded as an advantage because the illuminating light does not contribute to a faster erasure of the hologram. The drawback is that the recording of multiple holograms in the same crystal volume is made difficult by the fact that during the recording of a new grating the previous recorded ones are slowly being erased. This is a direct consequence of the fact that the time needed for compensation is comparable to the time needed for the combined electron-ion grating to disappear again. In practice, a maximum of 3-4 holograms can be recorded by lowering the temperature at each step. If multiple hologram recording is needed, LiNbO₃ is still the best material because the asymmetric recording-erasure process which is mainly governed by the bulk photovoltaic effect guarantees the conservation of the old information while recording a new hologram.
4.1.5 Summary

We have demonstrated the possibility of using KNbO$_3$ as a long term storage medium. All the experimental results are consistent with the predictions of the electron-ion model of chapter 2 and a purely electronic mechanism cannot explain all the observation. By the comparison of the behaviour in different crystal samples we suggest that oxygen vacancies are the ions being responsible for charge compensation. The activation energy for their mobility is 1.0 eV for motion in direction of the $a$ or $c$-crystal axis and 0.8 eV for motion along the $b$-axis. The mobility ($\mu$) of such vacancies at $T=200$ °C is on the order of $10^{-12}$ m$^2$(Vs)$^{-1}$. This charge compensation mechanisms has been used for a thermal fixing method leading to fixed holograms with diffraction efficiency on the order of 1% and storage times on the order of some months.

It was shown that a number of relevant photorefractive parameters such as the effective number of electron traps $N_{eff}$, the inverse diffusion length $K_e$, the dielectric rates $\Gamma_{die}$ and $\Gamma_{diff}$ for electrons and ions, or the trap limited electronic mobility $\mu_{eff}$ can be determined by measuring the charge compensation dynamics as a function of certain external conditions (grating spacing, electric field, light intensities, temperature, ...). Besides fundamental material research and hologram fixing, we proposed the use of the charge compensation mechanism for the calibration of the reduction state of KNbO$_3$ samples. Another potential practical application of these phenomena is their use in a “novelty filter” [80], that is a device that displays only the changes (motion) of a given image. After the primary hologram is compensated (at point 2 in Fig. 2.2), each small variation in the position of the recording light fringes gives rise to a large increase in diffraction efficiency $\eta$. The reason is that the newly recorded information (which modifies first the primary grating) does not correspond to the one stored in the compensated hologram. The old information remains stored for a while in the secondary grating and the diffraction efficiency is then a mass for the difference between old and new information. The resulting peak of $\eta$ can be detected and the “death time”, i.e. the time the device needs to be ready to display a new event, can be adjusted by varying the crystal temperature.
4.2 Ultraviolet grating recording in Bi$_4$Ge$_3$O$_{12}$

4.2.1 Material properties of Bi$_4$Ge$_3$O$_{12}$

4.2.1.1 General properties

Bi$_4$Ge$_3$O$_{12}$, the first material used for investigating photorefractive effects in the ultraviolet belongs to the cubic point group $43m$. It is a well known scintillator crystal for X-ray and positron detectors [81] and can be grown in good quality and very large size. The material has a wide transparency range extending from about 300 nm to about 6 μm. Data on crystal structure [82, 83], calculations of the electronic structure [84] and a list of different electromechanical properties of Bi$_4$Ge$_3$O$_{12}$ [85] can be found in the original literature and are not repeated here. Table 4.3 shows a list of some of the physical properties which are relevant for optical applications.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point group symmetry</td>
<td>43m</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>$\rho = 7.1$ kg/m$^3$</td>
<td>Ref. [85]</td>
</tr>
<tr>
<td>Transmission range</td>
<td>0.3 - 6 μm</td>
<td></td>
</tr>
<tr>
<td>Low frequency dielectric constant</td>
<td>$\varepsilon = 16$</td>
<td></td>
</tr>
<tr>
<td>Refractive index</td>
<td>$n = 2.0975$</td>
<td></td>
</tr>
<tr>
<td>Electro-optic coefficient</td>
<td>$r_{41} = +0.96$ pm/V</td>
<td></td>
</tr>
<tr>
<td>Polarization-optic coefficient</td>
<td>$f_{41} = +7.2 \times 10^{-3}$ m$^2$/C</td>
<td></td>
</tr>
<tr>
<td>Nonlinear optical susceptibility</td>
<td>$\alpha = 2$ pm/V</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>$\alpha = 5 \times 10^{-6}$ (°C)$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

Note that, unlike the related sillenite crystals Bi$_{12}$GeO$_{20}$ and Bi$_{12}$SiO$_{20}$, Bi$_4$Ge$_3$O$_{12}$ is not optically active. The dispersion of the refractive index $n$ has been determined by Bortfeld and Meier [86]. Throughout this work their single term Sellmeier relation

$$\left(\frac{n^2 - 1}{\lambda_o^2}\right) = \frac{S_o \lambda_o^2}{1 - (\lambda_o / \lambda)^2},$$

with $S_o = 9.508 \times 10^{13}$ m$^{-2}$ and $\lambda_o = 181.1$ nm is used to fit our data.

4.2.1.2 Electro-optic properties

Since no detailed investigations of the dispersion and magnitude of the electro-optical coefficients in the ultraviolet spectral range has been reported yet we first investigated this parameters. Due to its point group symmetry, Bi$_4$Ge$_3$O$_{12}$ possesses only three nonvanishing (and equal) electro-optic coefficients, $r_{41} = r_{52} = r_{63} \neq 0$. In a coordinate system with $x_1 \parallel [100]$, $x_2 \parallel [010]$, $x_3 \parallel [001]$ and a field direction parallel to $x_3$ we have simply

$$\Delta \left(\frac{1}{n^2}\right)_{12} = r_{63} T E_3 = r_{41} T E_3 = f_{41} T P_3.$$

(4.4)
The latter case applies if the field induced crystal polarization $P$ is chosen as driving term instead of the electric field. $f_{41}$ is an element of the polarization-optical tensor $f$ which has the same symmetry constraints as the $\varepsilon$-tensor. In particular, for the point group 43m the only nonvanishing elements of $f$ and $\varepsilon$ are simply related by $f_{41} = \frac{1}{\varepsilon_0 (\varepsilon-1)} (\varepsilon_0 (\varepsilon-1))^{-1}$ (Table 4.3).

The measurement of the unclamped coefficient $r_{41}$ was performed using a crystal cut along the [001], [110] and [110] crystallographic axis. The precise orientation and direction of crystallographic axes was determined by preliminary piezoelectric tests in accordance with the IEEE Standards on Piezoelectricity [88] (piezoelectric coefficient $d_{36} > 0$). For the electro-optic measurements we used the modulated field method [89] with a 10 kHz ac electric field applied along the [001] direction. The polarizer and the analyzer, placed in front and behind the crystal, were oriented at ±45° with respect to the crystal [110] axis and the resulting modulated intensity of the light travelling parallel to [110] was detected by a RCA 1P28 photomultiplier tube. For this configuration the electric-field induced phase-shift between a wave polarized along [001] and a wave polarized along the [110] axis is

$$\Delta \phi = \frac{2 \pi}{\lambda} n^3 r_{41} E_0 d$$

where $d$ is the crystal thickness. The reduced half-wave voltage $v_\pi$ and the electro-optic coefficient $r_{41}$ are then related by $v_\pi = \frac{\lambda}{n^3 r_{41}}$. The measured values of $v_\pi$ and $r_{41}$ in the wavelength range 300-700 nm are shown in Fig. 4.12a [90]. While $v_\pi$ shows a minimum at about $\lambda = 360$ nm, $r_{41}$ monotonically decreases towards shorter wavelengths. An extrapolation of the measured dispersion of the electro-optic coefficients shows that $r_{41} = 0$ at $\lambda = 260$ nm, which is in the region of maximum absorption. The straight lines in Fig. 4.12(b) are best fits to the data following the polarization-potential model of Wemple and DiDomenico [91]. This model considers the crystal-polarization-induced shift of the optical absorption edge and the related change of the Sellmeier oscillator frequencies and strengths. Taking the refractive index dispersion of equation (4.3) and differentiating with respect to the field-induced crystal polarization $P$, the following dispersion relation for the electro-optic coefficient $r(\lambda)$ is obtained [91]

$$r(\lambda) = \varepsilon_0 (\varepsilon-1) \left( \frac{1}{n^2(\lambda)} - 1 \right)^2 \frac{-\partial \lambda_o / \partial P}{\lambda_o S_o} \left[ (1 - K) + (1 + K) \left( \frac{\lambda_o}{\lambda} \right)^2 \right]$$

In (4.5) $\lambda_o$, $S_o$ are the oscillator wavelength and the oscillator strength in the Sellmeier equation (4.3). $\varepsilon$ is the static dielectric constant, $\partial \lambda_o / \partial P$ represents the polarization-induced shift of the resonance wavelength $\lambda_o$, and $K$ is the dispersion constant defined by
Ultraviolet grating recording in Bi$_4$Ge$_3$O$_{12}$

\[
K = \frac{\partial (S_o \lambda_o)/\partial P}{S_o (\partial \lambda_o/\partial P)}.
\]  

(4.6)

Fig. 4.12: a) Dispersion of the unclamped electro-optic coefficient $r_{41T}$ (right hand scale) and of the reduced half-wave voltage $v_e$ (left hand scale) of Bi$_4$Ge$_3$O$_{12}$. The curves are fits according to Eq. (4.5) using $S_o = 9.508 \times 10^{13}$ m$^{-2}$, $\lambda_o = 181.1$ nm, $\varepsilon = 16$, $\partial \lambda_o/\partial P = 4.7 \times 10^{-9}$ m$^3$/C, and $K = 2.8$. b) Linear relationship between $r_{41}/(1-1/n^2)^2$ and $(\lambda_0/\lambda)^2$.

Formula (4.5) predicts a linear relationship between $r(x(1-1/n^2)^2$ and $(\lambda_0/\lambda)^2$, which is well fulfilled in the case of Bi$_4$Ge$_3$O$_{12}$ (Fig. 4.12 (b)). From a least squares fit of $r(\lambda)$ one obtains for the dispersion constant $K = +2.8 \pm 0.2$ and for the polarization induced shift of the resonance wavelength $\partial \lambda_0/\partial P = + (4.7 \pm 0.4) \times 10^{-9}$ m$^3$/C. This corresponds to $\partial E_0/\partial P = -(0.18 \pm 0.02) \text{ eVm}^2$/C where $E_0 = h c / \lambda_0$ is the oscillator energy. In literature, no information could be found about the absolute sign of the electro-optic coefficient in Bi$_4$Ge$_3$O$_{12}$. Considering the precise orientation and direction of crystallographic axes and the experimentally observed relative phase between the applied electric field and the transmitted and modulated light intensity, we conclude that the sign of the electro-optic coefficient $r_{41}$ is positive.

In Fig. 4.12 the unclamped values of the electro-optic coefficient are shown. However, in the geometries used for the photorefractive experiments reported in the next section the elastic contribution are not active. Therefore, the clamped electro-optic coefficient $r_{41S}$ should be used [60, 92]. Interferometric measurements of the electro-optic response under pulsed electrical excitation allowed the determination of the ratio of the clamped to the unclamped electro-optic coefficient. At the wavelength $\lambda = 633$ nm we obtained [93]

\[\text{In the same way one has to use the relative static dielectric constant } \varepsilon^S \text{ for a totally clamped (strain free) crystal and not the one for an unclamped stress free crystal (} \varepsilon^T). \text{ However, the piezoelectric coefficient given in Ref. [85] indicates that } \varepsilon^T - \varepsilon^S = 0.007 \text{ is negligible with respect to } \varepsilon^T = 16.\]
indicating that the elastic contribution to the electro-optic effect is small in any case. With

$$r_{41}^T - r_{41}^S = p_{44}d_{14},$$

and using the piezoelectric coefficient $d_{14} = 0.87 \text{ pm/V}$ given in Ref. [85] and $r_{41} = 0.96 \text{ pm/V}$ we deduce that the elasto-optical coefficient $p_{44} = p_{2323}$ is smaller than 0.22 for $\lambda = 633 \text{ nm}$.

### 4.2.2 Photorefractive effects in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$

The characterization of the UV photorefractive properties of our crystals were performed using different methods, including measurement of optical absorption, dark- and photoconductivity, space-charge field dynamics and steady-state two beam coupling.

**Fig. 4.13:** Photorefractive geometries for 45°-cut $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals. a) Grating wavevector $K \parallel [001]$, isotropic Bragg-diffraction and two-beam coupling energy transfer are obtained for $s$-polarization. b) $K \parallel [110]$, no two-beam coupling, anisotropic Bragg-diffraction from a $p$-polarized incident beam into a $s$-polarized diffracted beam (or vice versa).

The investigations were performed on pieces cut from two nominally undoped crystal boules of different origin.† Cubes in different shapes were cut with two or more faces polished to optical quality (planity $\lambda/4$). For the photorefractive experiments samples with faces perpendicular to the crystallographic [110], [110] and [001] axis were used. This orientation is specially adapted for cubic crystals with point group $43m$ because isotropic Bragg-diffraction and two-beam coupling can occur in the same sample geometry (grating wavevector pointing in [001] direction). In addition, for a grating wavevector in [110] (or

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† The first (BG1) was kindly provided us by Prof. P. Grosse, University of Aachen (Germany). The second (BG2) was a commercially available crystal purchased from Harshaw Chemistry BV, De Meern (Holland).
Ultraviolet grating recording in Bi$_4$Ge$_3$O$_{12}$ 87

([110]) direction, *anisotropic* (self-) diffraction can be observed as well. These two geometrical arrangements are depicted schematically in Fig. 4.13.

4.2.2.1 **Optical Absorption**

Absorption measurements were performed at room temperature using a Perkin-Elmer λ9 spectrometer in the wavelength region from 200 to 1000 nm. The absorption constant $\alpha$ is calculated from the measured transmission taking into account multiple reflections at the crystal surfaces. Fig. 4.14 shows the absorption constant $\alpha$ of our samples in the vicinity of the electronic absorption edge. The dispersion of light transmission in our undoped Bi$_4$Ge$_3$O$_{12}$ crystal is similar to the one reported in reference [86]. There is no evidence for any absorption band between the lattice absorption located at $\lambda = 6 \mu$m and the electronic absorption edge which is near $\lambda = 300$ nm. However, the smaller absorption of crystal BG2 in the visible seems to indicate a reduced number of absorbing centers in this crystal.

![Absorption Constant](image)

**Fig. 4.14:** Dispersion of the absorption constant $\alpha$ for the Bi$_4$Ge$_3$O$_{12}$ crystals BG1 and BG2. Some of the principal laser lines in the considered spectral region are indicated.

4.2.2.2 **Dark conductivity and Photoconductivity**

Detailed studies on dark- and photoconductivity have been made by measuring the current-voltage characteristics of the crystal at different wavelengths and intensities of illumination. Static electric fields of up to 6 kV/cm were applied to the sample along the [001] direction. The electrical contacts were provided by painted silver electrodes. The current was determined from the value of the voltage over a series reference resistor, which was
measured with a multimeter having a large input impedance. For measurements of the dark conductivity at high temperatures, the samples were mounted in a temperature stabilized furnace. The measured dark conductivities are
\[
\sigma_d = (5.2 \pm 0.4) \times 10^{-14} \text{ (}\Omega \text{ cm)}^{-1} \quad \text{for BG1, and}
\]
\[
\sigma_d = (4 \pm 0.5) \times 10^{-15} \text{ (}\Omega \text{ cm)}^{-1} \quad \text{for BG2.}
\]
For crystal BG1 we measured the increase of the dark-conductivity with temperature. In the temperature range between 90 and 200 °C the dark conductivity follows an Arrhenius exponential law of the type \( \sigma_d = \sigma_0 \cdot \exp(-\Delta E/k_B T) \) with an activation energy \( \Delta E = (0.90 \pm 0.06) \text{ eV} \).
For the case where the charge transport occurs dominantly in one of the two bands the photoconductivity \( \sigma_{ph} \) can be expressed by
\[
\sigma_{ph} = e \frac{\alpha I}{h \nu} (\phi \mu \tau),
\]
where \( e \) is the elementary charge, \( \alpha \) is the optical absorption constant, \( I \) is the light intensity, \( h \nu \) is the photon energy, \( \phi \) is the quantum efficiency for generating a free charge carrier per absorbed photon, \( \mu \) is the average carrier mobility and \( \tau \) is the lifetime of a free charge carrier before recombination in a deep trap. The linear dependence of the photoconductivity on light intensity predicted by Eq. (4.9) is confirmed (Fig. 4.15).

![Fig. 4.15: Intensity dependence of the conductivity \( \sigma \) for illumination at different wavelengths. Inset: Current-field characteristics at \( \lambda = 351 \text{ nm} \) for an illumination intensity \( I_0 = 0.41 \text{ W/cm}^2 \) (Crystal BG1)](image)
The values for the photoconductivity and the related parameter \( \phi \mu \tau \) are summarized in Table 4.4. Evidently, the photoconductivity increases strongly for decreasing wavelength. This increase is much stronger than the increase in the absorption constant \( \alpha \) and is due to the change in the factor \( \phi \mu \tau \). Since the product \( \mu \tau \) is expected to be independent on wavelength (\( \tau \) is essentially inversely proportional to the number of trapping centers), the increased photoconductivity must be due to a more efficient generation of free charge carriers (larger \( \phi \)). This aspect will be discussed again later (section 4.2.2.4).

Table 4.4: Photoconductive properties of Bi\(_4\)Ge\(_3\)O\(_{12}\).

<table>
<thead>
<tr>
<th>( \lambda ) [nm]</th>
<th>( \sigma_{\text{ph}} / \text{[cm}(\Omega \text{W})^{-1}] )</th>
<th>( \phi \mu \tau [10^{-10} \text{cm}^2/\text{V}] )</th>
<th>( \sigma_{\text{ph}} / \text{[cm}(\Omega \text{W})^{-1}] )</th>
<th>( \phi \mu \tau [10^{-10} \text{cm}^2/\text{V}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>514.5</td>
<td>( 6 \times 10^{-14} )</td>
<td>0.09±0.04</td>
<td>( 2 \times 10^{-13} )</td>
<td>1.7±0.8</td>
</tr>
<tr>
<td>457.9</td>
<td>( 1.5 \times 10^{-13} )</td>
<td>0.2±0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>351.1</td>
<td>( 1.1 \times 10^{-11} )</td>
<td>5±0.7</td>
<td>( 1 \times 10^{-11} )</td>
<td>20±7</td>
</tr>
<tr>
<td>334.5</td>
<td>( 0.8 \times 10^{-10} )</td>
<td>20±2</td>
<td>( 3 \times 10^{-11} )</td>
<td>38±10</td>
</tr>
</tbody>
</table>

The probable reason for the difference in the quantum efficiency-mobility-lifetime product \( \langle \phi \mu \tau \rangle \) between the two crystals is that a reduced number of trapping centers increases the values of the lifetime \( \tau \) for crystal BG2. Our \( \langle \phi \mu \tau \rangle \)-values are comparable to the ones measured previously in undoped crystals using spectral lamps [94, 95] and are similar to the ones obtained for the fastest photorefractive materials like Bi\(_{12}\)SiO\(_{20}\), Bi\(_{12}\)GeO\(_{20}\) or KNbO\(_{3}\) [96] showing that Bi\(_4\)Ge\(_3\)O\(_{12}\) is a good candidate for applications in dynamic holography.

4.2.2.3 Steady-state two-beam coupling

The measurement of the energy transfer between the pump and the signal wave in a two-wave mixing configuration give information about both the sign of the majority charge carriers and on the effective density of traps \( N_{\text{eff}} \) in the crystal [97]. We performed the experiments in the geometry of Fig. 4.13(a). Electric fields were applied in the positive [001] direction and the intensity of the signal wave \( S \) at the input surface was about 1/300 of the reference wave \( R \). The intensity of the signal beam \( I_s(\Lambda) = I_s(0) \exp((\Gamma - \alpha)\Lambda) \) at the crystal output was measured as a function of the grating spacing \( \Lambda \). In the configuration used the gain factor \( \Gamma \) (Eq. (3.4)) takes the form

\[
\Gamma = \frac{2 \pi r_{41}^2 E_q E_D^2 + E_q E_o^2 + E_o^2 E_D^2}{\lambda \cos \theta (E_q + E_D)^2 + E_o^2},
\]

where \( r_{41} > 0 \) and the fields \( E_q \) and \( E_D \) are positive for electron conduction (section 2.3.4). In all our crystals we observed that the gain coefficient \( \Gamma \) is positive, indicating that holes are the majority charge carriers responsible for the build-up of the space-charge field in our Bi\(_4\)Ge\(_3\)O\(_{12}\) crystals. This situation is found for recording in the UV as well as for recording in the visible at the green \( \lambda \)-laser line (\( \lambda = 514 \) nm). The grating spacing dependence of \( \Gamma \) at the wavelength \( \lambda = 351 \) nm is shown in Fig. 4.16.
Fig. 4.16: Exponential gain coefficient \( \Gamma \) measured in two-wave mixing experiments as a function of the grating spacing \( \Lambda \) for \( \lambda = 351 \) nm (BG1, externally applied field \( E_0 = 0 \) and \( E_0 = 10 \) kV/cm). Inset: Crystal BG2, \( E_0 = 0 \). The full lines are fits using the values of the effective number of traps given in the text.

The gain is larger for BG1, this is due to the larger effective number of traps \( N_{\text{eff}} \) in this crystal. From the value of \( E_q \) (2.9) which best fits the measurements to Eq. (4.10) we obtain

\[
N_{\text{eff}} = (2.1 \pm 0.3) \times 10^{15} \text{ cm}^{-3} \quad \text{for BG1, and}
\]

\[
N_{\text{eff}} = (2.5 \pm 1) \times 10^{14} \text{ cm}^{-3} \quad \text{for BG2.}
\]

It should be noted that \( \Gamma \) may exceed by up to a factor of 4 the absorption coefficient \( (\alpha = 0.06 \) cm\(^{-1}\) for BG1 at \( \lambda = 351 \) nm). The effective amplification factors \( \exp((\Gamma - \alpha)\Delta) \) are therefore larger than unity and one can therefore propose to use Bi\(_4\)Ge\(_3\)O\(_{12}\) crystals for laser beam amplification in the ultraviolet spectral range.

### 4.2.2.4 Space-charge field dynamics

The time dependence of the photorefractive grating build-up and decay has been investigated by means of Bragg diffraction experiments. If the recording time is not too long,\(^\dagger\) the time dependence of the refractive index changes can be satisfactorily described by the simple exponential laws of equations (2.38) and (2.39) (Fig. 4.17). For crystal BG2, however, we

\[^\dagger\text{In this section only the case of short (typically 5-20 s) recording is discussed. In the case where the recording beams are kept for longer times one may observe a partial charge compensation, what is discussed in section 4.2.2.7.}\]
observed some deviations from this behaviour. For this reason, less conclusions can be drawn from the dynamic behaviour measured in this crystal (see section 4.2.2.7).

Fig. 4.17: Photorefractive recording-erasure cycle. Experimental conditions: Grating spacing $\Lambda = 1.94 \mu m$; Recording intensity = 17 mW/cm$^2$; Erasure intensity = 11 mW/cm$^2$; No externally applied electric field. The full lines represent simple exponential fits to the data (Eqs. (2.38) and (2.39)). Sample thickness = 0.49 cm, Crystal BG1.

Since we found a linear dependence of the photoconductivity on the light intensity we expect that the time constant for recording and erasure is inversely proportional to the illuminating power density ($\tau = (I_2)^{-1} \propto (\sigma_{ph})^{-1}$). This is well fulfilled experimentally as can be seen considering the unity slopes of the straight lines shown in Fig. 4.18 that shows the intensity dependence of the recording and erasure time. By extrapolating the straight lines of Fig. 4.18, a recording time constant of $\tau_2 = 60$ ms is found for $I = 1$ W/cm$^2$ at $\lambda = 351.1$ nm. For recording with shorter wavelengths this time constant is further decreased. As an example, for $\lambda = 305.4$ nm and $I = 1$ W/cm$^2$ we obtain $\tau_2 \approx 1.3$ ms, a value comparable to the ones obtained for the fastest materials Bi$_2$SiO$_2$, Bi$_2$GeO$_2$ and KNbO$_3$, and slightly larger than the ones typical for semiconducting photorefractive crystals [98].

For recording in the visible ($\lambda = 514$ nm) the time constants are typically two orders of magnitude larger than the one observed in the UV ($\lambda = 351$ nm) at the same power levels. Note that a minimum power level ($\approx 100$ mW/cm$^2$ for crystal BG1, $\approx 50$ mW/cm$^2$ for BG2) is required to get an appreciable efficiency of recording in the visible. Below this level the thermal exited charge carriers prevent the formation of strong space-charge fields of the order of kV/cm.

For the crystal BG1 the dark decay times are in the order of 30-40 s and depend slightly on the history of the crystal [90]. These values agree satisfactorily with the dielectric relaxation time $\tau_{die} = (\Gamma_{die})^{-1} = 27$ s calculated from dark conductivity. In contrast, the dark decay for BG2 ($\tau_{dark} = 17 \pm 3$ s) is faster than $\tau_{die} = 350$ s, indicating that a larger dark conductivity is induced after illumination with the recording beams due to nonequilibrium effects.
In the conventional single charge carrier model of Kukhtarev the time rate $\Gamma_2$ for grating recording or erasure depends on grating spacing by Eq. (2.40). If the value of the Debye wavevector $K_{oh}$ is known, a measurement of the response time as function of grating spacing allows the determination of the inverse diffusion length

$$K_h = \frac{e}{\sqrt{k_BT\mu\tau}},$$

with $\tau$ being the recombination time. The measured grating spacing dependence of $(\Gamma_2)^{-1}$ is shown in Fig. 4.19(a) for crystal BG1. The full line in the figure is the best fit to (2.40) with a fixed value of $K_{oh}$ obtained inserting into Eq. (2.22) the value of $N_{eff}$ derived with two-beam coupling measurements. In this way we find $K_h^2 = (2.56\pm0.7)\times10^{13}$ m$^{-2}$ which implies $\mu\tau = (1.5\pm0.4)\times10^{-8}$ cm$^2$V$^{-1}$. This result indicate that in Bi$_4$Ge$_3$O$_{12}$ the drift length $L_E = \mu\tau E_0$ of the free charges can reach values comparable to the fringe spacing, similarly to fast responding photorefractive materials like KNbO$_3$ and Bi$_{12}$SiO$_{20}$. For example, for an applied field of 10 kV/cm the drift length is 1.5 $\mu$m.

The above result can be related to the direct measurements of photoconductivity to get an estimate of the value of the quantum efficiency $\phi$ (Eq. (4.9)). Fig. 4.19(b) shows the calculated value of $\phi$ at various wavelengths, the eye-guiding line shows the saturation of $\phi$ in the band edge region. It is evident that a good quantum efficiency is obtained only for UV wavelengths smaller than 350 nm.

\[\text{† For our Bi}_4\text{Ge}_3\text{O}_{12} \text{crystals the symmetrical situation of hole conduction holds (} \Gamma_{die} \rightarrow \Gamma_{dih}, \ K_{oe} \rightarrow K_{oh}, \ K_e \rightarrow K_h)\]
Ultraviolet grating recording in Bi$_4$Ge$_3$O$_{12}$

Fig. 4.19: a) Grating spacing dependence of erasure time constant. Wavelength: $\lambda = 334.5$ nm, Light intensity $I = 34$ mW/cm$^2$, no externally applied field. The curve is a fit using Eq. (2.40) with $K_0h^2 = 9.32 \times 10^{13}$ m$^{-2}$, $K_h^2 = 2.56 \times 10^{13}$ m$^{-2}$ and $\tau_{die} = 186$ ms. b) Dispersion of the quantum efficiency $\phi$. The curve is only for visualization.

4.2.2.5 Diffraction efficiency, sensitivity

In our experiments the refractive index change $\Delta n$ ranges between $2 \times 10^{-8}$ and $2 \times 10^{-6}$ giving (normalized) diffraction efficiencies $\eta$ between $10^{-4}$ %/cm to 1%/cm. For crystal BG2 the values of $\eta$ are smaller than for crystal BG1 at small grating spacing ($\Lambda \leq 3$ $\mu$m) because the smaller trap concentration prevents the formation of larger space-charge fields. The mentioned values for $\eta$ are smaller than the one normally obtained in most of the ferroelectric photorefractive crystals like e.g. BaTiO$_3$, KNbO$_3$, LiNbO$_3$. However, since large and low cost crystals of Bi$_4$Ge$_3$O$_{12}$ can be grown, the small refractive index changes are not a fundamental obstacle for the use of this crystal for dynamic holography.

Since the wavelengths of operation of our Bi$_4$Ge$_3$O$_{12}$ crystal are relatively close to the absorption edge, we investigated also if band-edge effects, such as the Franz-Keldysh effect [99, 100], contribute to the generation of the refractive index gratings. However, the results of investigations made for different crystal orientations and for different values of the applied electric field indicate that such effects are negligible in Bi$_4$Ge$_3$O$_{12}$ crystals at all wavelengths longer than 330 nm. At these wavelengths a contribution of the Franz-Keldysh effect to the refractive index gratings would not exceed $\Delta n = 10^{-8}$ for recording with an applied field of 10 kV/cm.

A useful parameter for describing the photorefractive characteristics of a material is the photorefractive sensitivity at the initial stage of the recording process. We define alternatively this photosensitivity as $S_{n1} = \partial(\Delta n)/\partial(I_{abs})$ the refractive index change per absorbed energy density, or $S_{n2} = \partial(\Delta n)/\partial(I_{int})$ the refractive index change per incident energy density [35]. Typical values of $0.05-0.1 \times 10^{-3}$ cm$^3$J$^{-1}$ for $S_{n1}$ and of $2.5 - 5 \times 10^{-6}$ cm$^2$J$^{-1}$ for $S_{n2}$ were measured at $\lambda = 351$ nm without an applied field. Values larger by up to a factor of five can
be obtained by using shorter wavelengths or by applying an external electric field. The photorefractive sensitivity $S_{n1}$ determined for Bi$_4$Ge$_3$O$_{12}$ is in the same range as the one reported in LiNbO$_3$ and is about two orders of magnitude smaller than in KNbO$_3$ crystals [96]. This is due to the fact, that the electro-optic coefficients ($r_{41} = 0.57$ pm/V at $\lambda=351$ nm) are about two orders of magnitude smaller than in KNbO$_3$.

4.2.2.6 Two-beam coupling by moving gratings

The two-beam coupling gain $\Gamma$ of section 4.2.2.3 can be made larger by using the so called moving-fringes technique [101]. At the beginning of the recording of a stationary photorefractive grating with an applied electric field the space-charge field is running with the velocity $\text{Im}(F_2^*/K)$, where $\text{Im}(F_2^*)$ is given by Eq. (2.42). The effect of this drifting of the grating on the final space-charge field in the steady-state is that the phase-shift between the light fringes and the grating differs from the optimum value ($\pi/2$) for beam amplification. The idea underlying the moving fringes technique is to let the light intensity fringes run at approximately the velocity given above. In this way no steady-state is reached in a reference frame fixed to the crystal. However, in a reference frame fixed to the moving light fringes the space-charge field reaches a steady value with the optimum $\pi/2$ phase difference, thus maximizing the imaginary part of the space-charge field $\text{Im}(E_1)$ and $\Gamma$.

![Diagram](image)

Fig. 4.20: Experimental set-up for grating recording using the moving fringes technique.

For our experiments we modified the conventional set-up used for the investigation of two-beam coupling inserting a mirror mounted on a piezoelectric rod in one arm of the holographic set-up as shown in Fig. 4.20. The fringe velocity was measured by directly...
detecting the fringes with a photomultiplier. Fig. 4.21 shows that the gain coefficient of our Bi$_4$Ge$_3$O$_{12}$ crystals are enhanced by nonstationary recording by more than a factor of two. The measurements were performed in crystal BG1 with an applied field $E_0 = 10$ kV/cm.

The theoretical analysis of the moving fringes technique has been performed by many researchers [102-104]. For the ratio $G$ of the gain for optimal fringe velocity $v_{opt}$ to the one obtained with stationary recording one expects [102]

$$G = \frac{\Gamma_{v=v_{opt}}}{\Gamma_{v=0}} = \frac{1}{2} \left( \frac{\sqrt{1 + a^2 + a(1 + b^2)}}{b(1 + ab)} \right),$$

where

$$a = \frac{E_0}{E_M},$$

$$b = \frac{E_0}{E_q},$$

and $E_M$ is defined as

$$E_M = \frac{1}{K(\mu \tau)}.$$

Using the experimental value $E_0 = 10$ kV/cm and the values $\mu \tau = 1.5 \times 10^{-8}$ cm$^2$V$^{-1}$ and $N_{eff} = 2.1 \times 10^{15}$ cm$^{-3}$ derived in the precedent sections we have $a = 1.89; b = 0.53$ for $\Lambda = 2\pi/K = 5$ \(\mu\)m, and $a = 0.94; b = 0.27$ for $\Lambda = 10$ \(\mu\)m. With (4.12) we expect theoretically $G_{th}(5 \mu m) = 2.4$ and $G_{th}(10 \mu m) = 3.7$. These values compare well with the ones measured experimentally (Fig. 4.21), $G_{exp}(5 \mu m) = 2.3 \pm 0.3$ and $G_{exp}(10 \mu m) = 3.2 \pm 0.6$.

Fig. 4.21: Gain coefficient $\Gamma$ as function of the fringe velocity. Applied electric field $E_0 = 10$ kV/cm; Light intensity $I_0 = 0.185$ W/cm$^2$, Wavelength $\lambda = 351$ nm. a) $\Lambda = 5$ \(\mu\)m, b) $\Lambda = 10$ \(\mu\)m. The curves are for visualization. Crystal BG1.
4.2.2.7 Quasi permanent photorefractive gratings in the UV

We investigated the possibility of recording quasi permanent gratings in our Bi$_4$Ge$_3$O$_{12}$ crystals. In analogy with our measurements in KNbO$_3$, we studied the dynamic evolution observed for different durations of the recording process. As mentioned in section 4.2.2.4, for crystal BG1 the time evolution is given by a simple exponential function (Fig. 4.17). At room temperature this is also true if the duration of the recording process is long. In contrast, for crystal BG2 the recording and erasure do not obey a single exponential law and a partial compensation of the space-charge field is obtained by prolonging the recording for some minutes. An example is shown in Fig. 4.22, where during the recording at the wavelength $\lambda = 351$ nm the sample was additionally illuminated homogeneously with green light ($\lambda = 514$ nm). During the erasure process ($t > 29$ min), only this green light and a weak read-out beam ($\lambda = 633$ nm) were still illuminating the crystal.

The behaviour shown in Fig. 4.22 is very similar to the one observed during charge compensation in KNbO$_3$ (Fig. 4.2) and to the theoretical expectations for crystals exhibiting a partial charge compensation (Fig. 2.9). In the particular case shown here the dynamics in the last part of the erasure process ($t > 35$ min) is simple exponential with a time constant $\tau_3 = (\Gamma_3)^{-1} = 30$ min, which is about 100 times more than the dark decay time usually measured in the same crystal. If the conditions during the erasure process are the same, the time $\tau_3$ remains constant by variation of the recording conditions (light intensities, durations). In contrast, the height of the peak occurring during the erasure is changed. We
investigated the influence of different experimental parameters on the recording of quasi-
permanent gratings.

The observations are:

(a) The behaviour of Fig. 4.22 is also observed for crystal BG2 without the
homogeneous illumination with green light. However, the green radiation accelerates
the generation of the secondary grating during the recording at room temperature.

(b) In crystal BG1 no compensation takes place at room temperature but a behaviour like
the one shown above is observed at temperatures exceeding $T = 100$ °C.

(c) The time needed for compensation and the handling time decrease for increasing value
of the applied electric field $E_0$ and for decreasing grating spacing $A$.

(d) If the other experimental parameters are constant, the diffraction efficiency measured
during the handling time increases for increasing recording time. However, no
complete compensation ($\eta = 0$ during recording) could be obtained at any temperature
and for any duration of recording.

(e) The diffraction efficiency during the handling (erasure) of the hologram can be
modulated by the applied field in exactly the same way as shown in Fig. 4.6 for
KNbO$_3$.

(f) The handling time of the hologram depends on the intensity of the read-out beam at the
recording wavelength. For larger intensities the grating disappears faster (Fig. 4.23).

(g) By recording in the configuration shown in Fig. 4.13b with the grating wavevector
parallel to the crystallographic [110] axis, anisotropic (but not isotropic) Bragg
diffraction is observed during the handling time.

From point (g) we conclude that the diffraction from the quasi permanent hologram is due to
a phase grating that follows the symmetry of the electro-optic tensor. Since no rotation of the
light polarization can be induced by absorption gratings, this possibility can be excluded.
This is also consistent with the fact that we did not measure detectable changes of the
absorption constant in the visible produced by UV illumination.†

† In strongly doped Bi$_4$Ge$_3$O$_{12}$ crystals ($\alpha = 10$ cm$^{-1}$ at $\lambda = 350$ nm) large photochromic
changes of the absorption constant in the visible are induced by illumination in the UV
($\lambda = 310$ nm) [105]. In our undoped crystals such effects were not observed.
Fig. 4.23: Time dependence of erasure dynamics for different erasure intensities at room temperature. One recording beam is switched-off at time \( t = 0 \) and the diffracted power from the other beam is detected. The recording time was 1 min for \( I = 41 \text{ mW/cm}^2 \) and 3 min for the other two intensities. The exponential time constants during the handling time (after the maximum) are \( \tau_3 = 7 \text{ s}, \tau_3 = 14 \text{ s} \) and \( \tau_3 = 48 \text{ s} \) for the three intensities in decreasing order.

The observations listed above indicate that the recording of quasi permanent gratings in \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) behaves in a similar way as the charge compensation mechanism in \( \text{KNaO}_3 \) that was discussed in chapter 4.1. This is particularly apparent considering the influence of electric fields and the dependence on grating constant (points (c) and (e)). Therefore, we conclude that charge compensation of two carrier species is responsible for the observed effects. However, there are two major differences with respect to \( \text{KNaO}_3 \). These are the ones given at points (d) and (f), that is the incomplete charge compensation and the strong dependence of the handling time on intensity. This implies, first, that the number density of the compensating secondary carriers is small, and second, that this species can be excited optically. Since ions are not directly influenced by light, they cannot be the secondary charge carriers in \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \). It will be shown in Appendix B that if there is only one impurity level in the band gap, even when both kind of carriers (electrons and holes) are photoexcited, no charge compensation can occur. In contrast, one may explain the observations using a model which considers two independent mid gap levels from which electrons and holes can be photoexcited. Charge redistribution occurs within each single level through transport in one of the bands. This model was first presented by Kukhtarev et al. [106] and Valley [107]. The main predictions are summarized shortly in Appendix B (Model 2) where we calculate also the time rates finding that they have the same form as the ones obtained for the electron-ion model of chapter 2. Therefore, the observations of point (c) for \( \text{Bi}_4\text{Ge}_3\text{O}_{12} \) are compatible with the situation proposed by Kukhtarev et al. and Valley.
Different authors propose the use of this model for explaining charge compensation mechanisms similar to ours occurring in $\text{Bi}_{12}\text{SiO}_{20}$ [108-110] or $\text{Bi}_{12}\text{TiO}_{20}$ [111] crystals at room temperature. However, our opinion is that the mentioned model is not very realistic. It assumes the presence of two partially filled defects levels at thermal equilibrium in the band gap. This is possible at room temperature only if their energetic separation is not larger than a few hundreds of eV. We propose therefore an alternative charge redistribution process like the one shown in Fig. 4.24. The redistribution of charges occurs principally within level 2 by hole transport in the valence band (thick line). In addition some holes can be moved from level 2 to level 1 at a somewhat slower rate. Recently, Jariego and Agullo-Lopez [112] analyzed theoretically a situation like the one of Fig. 4.24, they showed that partial compensation and a modification of the dynamics is obtained in this case. It should be noted that a large space-charge modulation in level 1 can occur only if this trap level can be emptied by some mechanisms, for instance optical hole excitation or hole thermal transitions to the valence band. This emptying mechanism which is indicated in Fig. 4.24 by the dashed arrow should ensure that the number of filled and empty centers of type 1 are not too different. In our particular case we propose that green light empties level 1 in crystal BG2 more efficiently than in the dark (point (a)), while in crystal BG1 the same process is obtained by increasing the dark thermal excitation of holes at high temperature.

From the practical point of view, the described quasi-permanent gratings are useful if stable phase holograms are needed for a time scale between some minutes and a few hours. The diffraction efficiencies of the compensated gratings are smaller than in $\text{KNbO}_3$ and typically reach about 1/5 of the value obtained for an unfixed grating recorded under the same conditions in the same crystal. We obtained experimentally a maximum of $\eta = 0.03 \%/\text{cm}$ in BG1 at the temperature $T = 120 \, ^\circ\text{C}$. We mentioned that the handling times for the hologram under illumination in the UV depend on the electric field and on the light intensity. For $I = 50 \, \text{mW/cm}^2$ a maximum handling time of $\approx 2\text{h}$ is obtained at $T = 100 \, ^\circ\text{C}$ in BG1 corresponding to an increase by a factor of $\approx 5000$. In crystal BG2 at room temperature the

\[\text{CB}\]

\[\text{trap level for primary charge carriers}\]

\[\text{level emptying}\]

\[\text{VB}\]

![Fig. 4.24: Model for charge compensation in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$. In thermal equilibrium level 2 is partially filled with holes and level 1 is empty. The principal charge redistribution occurs within level 2 (thick lines). The hole transitions are shown.}^\dagger\]

\[^\dagger\] The symmetrical case of redistribution from level 1 to level 2 by transport of electrons in the conduction band is also possible. We have chosen this diagram because in all samples we observed that holes were the majority carriers at all wavelengths (section 4.2.2.3).
increase is only a factor of 100 ($\tau = 1$ min, $I = 50$ mW/cm$^2$) because the influence of the UV light is stronger in this case. It is evident that the great disadvantage with respect to K$_{2}$Nb$_{2}$O$_{7}$ is the fact that the compensating charge carriers can be photoexcited. For this reason a procedure for fixing the holograms by a thermal cycling method like the one described in chapter 4.1 is not meaningful for Bi$_4$Ge$_3$O$_{12}$.

4.2.3 Summary

Our investigations of the electro-optic properties of Bi$_4$Ge$_3$O$_{12}$ show that the spectral dependence of the unclamped electro-optic coefficient $r_{41}$ follow well the predictions of the polarization-potential model of Wemple-DiDomenico. The value of the electro-optic coefficient decreases as the wavelength approaches the absorption edge. The simultaneous increase of the refractive index $n$ and the decrease in wavelength produce a minimum of the reduced half-wave voltage $\nu$ in the UV ($\lambda = 360$ nm, $\nu = 50$ kV). Because the coupling coefficient in photorefractive wave mixing experiments is proportional to $(\nu)^{-1}$, the UV wavelength $\lambda = 360$ nm is ideal for such applications in Bi$_4$Ge$_3$O$_{12}$.

Different experiments were made to investigate the characteristics of Bi$_4$Ge$_3$O$_{12}$ as a photorefractive material. For our experiments, visible and UV laser beams were employed ($\lambda > 305$ nm). The photorefractive properties of our crystals in the ultraviolet are superior compared to the ones in the visible, as demonstrated by the strong increase of photoconductivity and the much shorter hologram writing times at smaller wavelength ($\tau_2 = 4$ ms at $\lambda = 305$ nm and $I = 0.25$ W/cm$^2$). The diffraction efficiencies ($\eta \leq 1$ %/cm) are smaller than in ferroelectric photorefractive crystals due to the smaller electro-optic coefficient. Different properties of the crystals were determined by correlating the photoconductivity data with stationary and dynamic photorefractive measurements. We found a strong increase of the quantum efficiency $\phi$ towards the absorption edge with $\phi = 0.13$ at $\lambda = 334$ nm, while the value of the mobility-lifetime product $\mu\tau = 1.5 \times 10^{-8}$ cm$^2$/V suggests an efficient charge transport in our undoped crystals. Two wave mixing experiments indicate that holes are the majority carriers in all our crystals and allowed the determination of the effective trap concentrations. The two beam coupling gain coefficients ($G = 0.25$ (cm)$^{-1}$) exceed the absorption losses by a factor of 4 allowing effective coherent amplification of laser beam in the UV. The gain can be enhanced by about a factor of 3 by using a moving fringes technique.

Our attempts to generate fixed holograms in the UV were only partially successful. On one hand we were able to prolong the handling time under UV illumination by more than a factor of 1000 using a method similar to the one employed for K$_{2}$Nb$_{2}$O$_{7}$. On the other hand we found that a stronger light intensity in the UV-green spectral range erases in part the compensating grating because the secondary species is not formed by ions but by charges trapped in additional defects levels within the band-gap. The number densities of the secondary and primary charge carriers are similar and the secondary carriers cannot compensate completely the primary hologram. This affects in part the diffraction efficiency of the quasi-permanent hologram, because the value corresponding to the one obtained for the primary space-charge grating cannot be reached. This situation is common with the one
of the photorefractive crystals Bi$_{12}$SiO$_{20}$ and Bi$_{12}$TiO$_{20}$ for which similar effects have been reported in literature.

At present, Bi$_4$Ge$_3$O$_{12}$ is the only material where the photorefractive effect works well at wavelengths close to 300 nm. We found that its main drawback with respect to materials being sensitive in the visible is the relatively small electro-optic coefficient which affects the diffraction efficiency and the gain coefficient for beam amplification. Since large and low cost crystals of Bi$_4$Ge$_3$O$_{12}$ are commercially available, this disadvantage can be partly compensated by using longer crystals. The other properties like the ones characterizing the dynamic response are comparable or better than those of most “visible” materials. Therefore, the material is attractive for use for coherent image amplification, dynamic holography or medium time memory (hours) in the ultraviolet region where the optical resolution is enhanced. We think that the use of this crystal in the visible spectral range is not meaningful because the sensitivity is low and other materials like KNbO$_3$, BaTiO$_3$ or Bi$_{12}$SiO$_{20}$ show better properties.
Seite Leer / Blank leaf
4.3 Interband photorefractive effects in KNbO₃

In this chapter we describe the experiments on interband photorefractive effects in KNbO₃ crystals. Simple theoretical models for this case were presented in section 2.5.

4.3.1 Absorption constants and refractive indices

The absorption constant $\alpha$ is a key parameter for interband photorefractive effects because it determines the rate of electron-hole pair formation. The dispersion of $\alpha$ at the band edge of KNbO₃ has been previously measured by Wiesendanger [58]. He found that for photon energies smaller than 3.3 eV $\alpha$ increases exponentially with photon energy, which is consistent with an Urbach-rule behaviour [113]. For larger energies (e.g. for the ones corresponding to the wavelength range $\lambda = 330$-365 nm used in our photorefractive experiments) one expects a saturation of the absorption so that the increase of $\alpha$ with energy is smaller than exponential.

![Dispersion of the absorption constant at the band edge of KNbO₃ for light polarization parallel to the b and c crystal axis. The values for polarization parallel to the a crystal axis are expected to be equal to the ones for c-polarization. The dashed lines show the exponential Urbach behaviour of Ref. [58]. The vertical lines show the position of two UV Ar-ion laser lines.](image)

Fig. 4.25: Dispersion of the absorption constant at the band edge of KNbO₃ for light polarization parallel to the b and c crystal axis. The values for polarization parallel to the a crystal axis are expected to be equal to the ones for c-polarization. The dashed lines show the exponential Urbach behaviour of Ref. [58]. The vertical lines show the position of two UV Ar-ion laser lines.

We measured the transmission in the band edge region of undoped thin samples of KNbO₃ using a Perkin-Elmer λ9 spectrophotometer. The samples were two KNbO₃ a-plates. They were glued on a fused silica substrate by polymethyl-metacrylate (PMMA) and subsequently polished to a final thickness of 25 μm (sample Nr. 137) or 70 μm (Nr. 144).
Fig. 4.25 shows the absorption curves that are calculated from the measured transmission curves. The reflection losses at the crystal-PMMA interface are not perfectly known and were determined by the requirement that the absorption constant calculated for our thin sample at wavelengths larger than 375 nm agree with the ones measured by Wiesendanger in thicker samples. This procedure introduces an error of about 10% in the values of $\alpha$ determined for $\lambda<375$ nm. The results shown in Fig. 4.25 indicate that the absorption constant begins to saturate for values larger than about 100-200 cm$^{-1}$, the increase of $\alpha$ as a function of the photon energy is therefore smaller than the one obtained extrapolating the data of Ref. [58].

Table 4.5 shows the values for the absorption constant at the two major Ar-ion laser lines ($\lambda = 351.1$ nm and $\lambda = 363.8$ nm). The values determined from the measurements shown in Fig. 4.25 are listed together with values determined from photorefractive investigations (section 4.3.3.2). The result of the direct and of the indirect method are in good agreement.

Table 4.5: Absorption constants of KNbO$_3$ at two ultraviolet Ar-ion laser wavelengths.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>$\alpha_c$ [cm$^{-1}$]</th>
<th>$\alpha_b$ [cm$^{-1}$]</th>
<th>$\alpha_c$ [cm$^{-1}$]</th>
<th>$\alpha_b$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>363.8</td>
<td>510±50</td>
<td>1050±150</td>
<td>560±40</td>
<td>940±100</td>
</tr>
<tr>
<td>351.1</td>
<td>1950±250</td>
<td>5000±2000†</td>
<td>1860±100</td>
<td>6000±1800</td>
</tr>
</tbody>
</table>

† extrapolated

The refractive indices of KNbO$_3$ in the ultraviolet have been determined by Rogin [114] through the measurement of the Brewster angle in different crystal plates. His values at three different wavelengths are listed in Table 4.6. Within the experimental error the values are in relative good agreement with extrapolations of the Sellmeier functions given in Ref. [59].

Table 4.6: Refractive indices of KNbO$_3$ in the ultraviolet.

<table>
<thead>
<tr>
<th>Wavelength [nm]</th>
<th>$n_a$ (±0.06)</th>
<th>$n_b$ (±0.06)</th>
<th>$n_c$ (±0.06)</th>
</tr>
</thead>
<tbody>
<tr>
<td>364</td>
<td>2.63</td>
<td>2.73</td>
<td>2.43</td>
</tr>
<tr>
<td>351</td>
<td>2.73</td>
<td>2.76</td>
<td>2.48</td>
</tr>
<tr>
<td>334</td>
<td>2.83</td>
<td>2.87</td>
<td>2.55</td>
</tr>
</tbody>
</table>

4.3.2 Photoconductivity by band-to-band excitation

As we discussed in section 2.5.1, we expect that at high incident light intensities $I_o$ the photoconductivity should be proportional to the square root of $I_o$. At lower intensities, in contrast, the photoconductivity should be linear in $I_o$. Fig. 4.26 shows an experimental curve giving the total current flowing in the positive c-direction through a 1.4 mm thick crystal. The experiment was performed by chopping the incident light in order to avoid the influence of thermal effects and of slow charge diffusion into the bulk of the crystal. The photocurrent response (response time in the order of 10 $\mu$s to 100 $\mu$s) was recorded on a storage oscilloscope. Tests in absence of an electric field showed that the pyroelectric effect was not influencing the measurements.
Interband photorefractive effects in KNbO₃

λ = 364 nm
Polarization || c-axis
E₀ = 0.56 kV/cm

Fig. 4.26: Dependence of photocurrent on incident light intensity in pure KNbO₃ (sample 216:P152, thickness = 1.4 mm). The wavelength used is λ = 364 nm with the polarization parallel to the crystal c-axis. The approximated photoconductivity σph given on the right-hand axis is calculated assuming that all the current is flowing in a layer of thickness d₀ = 40 μm = 2εᵣ⁻¹. The dark conductivity of the same crystal is about σd = 10⁻¹²(Ω cm)⁻¹. The solid line is the best fit to a simple model assuming two distinct regions in the crystal with the border shifting following the light intensity (see scheme on the right side).

The results of experiments performed in other crystals and/or other ultraviolet wavelengths and polarization directions were all similar to the one shown in Fig. 4.26. In all cases a linear increase at low intensity was followed by a less than linear increase at higher intensities I₀. For very large I₀ the photocurrent increases as I₀ᵦ, with an exponent β approaching 0.5.

The observed deviation from the linearity is due to the deviation from the linear recombination regime (section 2.5.1) and two different reasons can be responsible for it:

(a) The light intensity is so large that quadratic recombination by direct transitions from the conduction to the valence band dominates. In this case the number of electrons and the one of holes are both large and are given by Eq. (2.49). This situation is more likely to occur if the direct recombination constant γdir is large (γdir > 10⁻¹⁴ m³s⁻¹).

(b) The recombination to the traps is highly asymmetric so that the concentration of filled traps changes rapidly as a function of light intensity. In this case either the electron or the hole density can be comparable to the initial concentration N₀ of empty traps in the dark. Due to the charge conservation relation (2.48) a quadratic recombination term (γₚ₀² or γₚ₀²) appears in the rate equations (2.47). This term is responsible for the deviation from linearity. This situation is more likely to occur if the direct recombination constant γdir is small (γdir < 10⁻¹⁴ m³s⁻¹).
Both the cases mentioned above have the common implication that at least one of the carrier species should have a very large density, i.e. a concentration in the order of $N_A$.

From the photoconductivity data one can estimate the product of the number of carriers $c_0$ (equal to $n_0$ or $p_0$) times the mobility $\mu$ (equal to $\mu_e$ or $\mu_h$) for the dominant charge carrier species. We get a rough estimation of this product by assuming that the current is flowing homogeneously in a layer of width $h$ and depth $d_0 = 2\alpha^{-1}$, where 87% of the ultraviolet light is absorbed. The total current $I$ flowing through the crystal is then approximated by

$$I = h \int_0^d J(z) dz = hE_0 \int_0^d \sigma_{ph}(z) dz = e\hbar E_0 \mu \int_0^d c(z) dz = e\hbar E_0 (\mu c_0)$$

where $d$ is the crystal thickness, $J(z)$ is the current density, $E_0$ is the applied electric field and $c(z)$ is the carrier density ($n(z)$ or $p(z)$) with the average number $c_0$ defined in (4.17). The approximated values of $\mu c_0$ for different crystals and different wavelengths and polarizations of the illuminating ultraviolet light are given in Table 4.7. The values are given for an intensity $I_0 = 10$ mW/cm$^2$, at which the photocurrent was in all cases in the sublinear regime (Fig. 4.26).

Table 4.7: Approximated mobility-carrier density product $\mu c_0$ for pure KNbO$_3$ crystals illuminated with an ultraviolet intensity $I_0 = 10$ mWcm$^{-2}$.

<table>
<thead>
<tr>
<th>Crystal sample</th>
<th>$\lambda$ [nm]</th>
<th>Polarization</th>
<th>$d_0$ [\mu m]</th>
<th>$\mu c_0$ [(Vms)$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNbO$_3$:216(P1S2)</td>
<td>351</td>
<td>$\parallel$ b</td>
<td>3.3</td>
<td>$2.2 \times 10^{14}$</td>
</tr>
<tr>
<td>KNbO$_3$:216(P1S2)</td>
<td>364</td>
<td>$\parallel$ c</td>
<td>38</td>
<td>$2.5 \times 10^{13}$</td>
</tr>
<tr>
<td>KNbO$_3$:4A5(137)</td>
<td>351</td>
<td>$\parallel$ c</td>
<td>10.5</td>
<td>$4.6 \times 10^{14}$</td>
</tr>
<tr>
<td>KNbO$_3$:4A5(137)</td>
<td>364</td>
<td>$\parallel$ c</td>
<td>25 $^\dagger$</td>
<td>$2.7 \times 10^{14}$</td>
</tr>
<tr>
<td>KNbO$_3$:4A5(144)</td>
<td>364</td>
<td>$\parallel$ c</td>
<td>38</td>
<td>$1.0 \times 10^{14}$</td>
</tr>
</tbody>
</table>

$^\dagger$ $d_0 = d$

The accuracy of the values of $\mu c_0$ given above is in the range from -50% to +100%. The value of the concentration $c_0$ can be obtained if the mobility $\mu$ is known. From ps-pulsed experiments [65] an electron mobility of $\mu_e = 0.5 \pm 0.2$ cm$^2$(Vs)$^{-1}$ was deduced. However, this value for the mobility is valid only for a high conducting state having a lifetime shorter than 5 ns before thermalization. For the intensity $I_0 = 10$ mWcm$^{-2}$, a carrier lifetime of 5 ns implies a carrier density smaller than $5 \times 10^{11}$ cm$^{-3}$ for the entire investigated wavelength range. This density is too small to be comparable to $N_A$ which is expected to be around $10^{15}$ cm$^{-3}$ in pure crystals (KNbO$_3$:216, $N_{eff} = 9 \times 10^{15}$ cm$^{-3}$). Therefore, longer lifetimes and smaller mobilities should be used to describe our experiments in a time scale longer than $\mu$s. In this time scale, a 50 times smaller mobility of $\mu_e = 0.008$ cm$^2$(Vs)$^{-1}$ was estimated from numerical simulations of the photorefractive response after a 200 ns pulse excitation [43]. Using this trap-limited mobility we get from Table 4.7 averaged carrier concentrations $c_0$ smaller than $5.8 \times 10^{14}$ cm$^{-3}$ (KNbO$_3$:137, $\lambda = 351$ nm) for power densities of 10 mW/cm$^2$. This is still smaller than $10^{15}$ cm$^{-3}$. Therefore we deduce that the mobility
valid for our experimental situation is even smaller than $\mu = 0.008 \text{ cm}^2\text{(Vs)}^{-1}$. Such a small value of $\mu$ can be due to two possible reasons. Either the electronic mobility is trap limited [44] and thus sample dependent, or the photoconductivity is given by hole conduction ($\mu c_o = \mu_h p_o > \mu_e n_o$ with $\mu_h < \mu_e$ and $p_o \gg n_o$).

Strongly different densities for electrons and holes are obtained only if the sublinear increase of the photocurrent is due to the quadratic trap recombination described in (b). At moderate intensities of few mW/cm$^2$ we think that this mechanism describes better our measurements than the quadratic band-to-band recombination described in (a). If the latter process would occur at low light intensity the direct recombination constant would have to be large ($\gamma_{\text{dir}} = 10^{-13} \text{ m}^3\text{s}^{-1}$), what is little likely for KNbO$_3$. In contrast, the interpretation (b) implies that $\gamma_{\text{dir}}$ cannot be larger than a few $10^{-17} \text{ m}^3\text{s}^{-1}$ because a stronger direct recombination would prevent large carrier concentrations to build-up.

Fig. 4.27: Photocurrent response by interband ultraviolet excitation in pure KNbO$_3$ (sample 139). The value of $\mu c_o$ is estimated in the same way as in Table 4.7. The data are fitted to Eq. (2.56) and (2.57) giving $(\Gamma_{\text{dir}})^{-1} = 14.3 \mu\text{s}$ for the on state and $(\Gamma_{\text{dir}})^{-1} = 5.3 \mu\text{s}$ for the photocurrent decay.

Values of the direct recombination constant on the order of $10^{-17} \text{ m}^3\text{s}^{-1}$ are consistent also with the speed of the photocurrent response shown in Fig. 4.27. The illumination is switched on and off by an acousto-optical modulator (response time $\approx 100$ ns). The wavelength, light polarization and intensity are such that we can assume the direct recombination to be the principal mechanism limiting the photocurrent.$^\dagger$ The data are fitted with the theoretical relations (2.56) and (2.57). The agreement between the theory and the

$^\dagger$ If this is not the case, the value of the direct recombination constant $\gamma_{\text{dir}}$ estimated below has to be corrected towards lower values.
data is not especially good, particularly for the photocurrent increase. This may be due either to a residual influence of recombination to the traps or to the fact that Eq. (2.56) and (2.57) are strictly valid only for a layer of infinitesimal thickness. From the fitting parameters we get the recombination rate \( \Gamma_{\text{dir}} = (g l_0 \gamma_{\text{dir}})^{1/2} \). As the fits are not perfect, the values obtained for the increase \((\Gamma_{\text{dir}})^{-1} = 14.3 \, \mu s\) and the decrease of the photocurrent \((\Gamma_{\text{dir}})^{-1} = 5.3 \, \mu s\) are not equal. If we use a mean value of \((\Gamma_{\text{dir}})^{-1} = 10 \, \mu s\), \( g = 3.3 \times 10^{23} \, (\text{Wms})^{-1} \), which corresponds to the absorption constant measured for the wavelength and light polarization used, and \( I_0 = 160 \, \text{mW/cm}^2 \), we obtain for the recombination constant \( \gamma_{\text{dir}} = 2 \times 10^{-17} \, \text{m}^3\text{s}^{-1} \). The related charge density is \( n_0 = g l_0 / \Gamma_{\text{dir}} = 5.3 \times 10^{15} \, \text{cm}^{-3} \). We think that the exact value of \( \Gamma_{\text{dir}} \) should be rather smaller than larger than the above estimate because otherwise one would expect a faster response and smaller charge concentrations as in Fig. 4.27. This was never observed.

In conclusion, the photoconductivity investigations show that quadratic recombination (deviation of the linear increase of the current with light intensity) occurs in all crystals and at all investigated UV wavelengths even at moderate intensities \( (1-10 \, \text{mW/cm}^2) \). The measurements suggest that at moderate intensities this is due to an asymmetrical recombination to traps producing their filling or emptying. An electron or hole mobility \( \mu \) smaller than 0.008 \, \text{cm}^2(\text{Vs})^{-1} and a direct recombination constant \( \gamma_{\text{dir}} \) not larger than a few \( 10^{-17} \, \text{m}^3\text{s}^{-1} \) are suggested by the experiments.

### 4.3.3 Photorefractive diffraction experiments

Diffraction experiments on interband photorefractive effects in KNbO\(_3\) were performed in two different geometries by using Ar-ion laser wavelengths in the 334-364 nm region. The longitudinal geometry (Fig. 4.28a) corresponds to the conventional one used to test the photorefractive grating strength (cf. sections 4.1 and 4.2). In this geometry the wavevectors of the incident ultraviolet recording beams and of the visible testing beam are all in the same plane. This geometry is appropriate for the investigation of the dependence of the effects on the writing and reading angles and for potential applications for correlators and spatial light modulators.

In the transversal geometry, in contrast, the wavevector of the read-out beam is aligned parallel to the surface of the sample while the recording beams are aligned as before (Fig. 4.28b). Here the interaction length of the read-out beam is not limited by the finite thickness of the grating but can be increased by using longer crystals. This geometry allows the investigation of the depth dependence of the effects as well as their time response in a given depth and may find applications in photorefractive beam steering in bulk crystals or in planar or channel waveguides.

In transversal geometry the read-out beam is focused in the vertical direction by a cylindrical lens \((f = 60 \, \text{mm})\), which limits its vertical extension and allows to get a good depth resolution. The vertical beam waist \( w_o \) of this beam in the center of the crystal is

\[
 w_o = \frac{2f}{\pi w} = \frac{0.633 \times 10^{-3} \, \text{mm} \cdot 60 \, \text{mm}}{\pi \cdot 0.6 \, \text{mm}} \equiv 20 \, \mu \text{m} \quad , \quad (4.18)
\]
and the divergence is such that at the two end surfaces of a \( L = 2 \) mm long crystal we have

\[
w(\pm L/2) = w_o \sqrt{1 + \left( \frac{\lambda L/2}{n\pi w_o^2} \right)^2} = 1.03 w_o.
\]

(4.19)
4.3.3.1 Diffraction efficiencies

Interband photorefractive effects give rise to efficient light diffraction. Especially suited is the transversal configuration, where the optical interaction length is longer. At grating spacings $\Lambda$ larger than $\approx 1 \mu m$, applied electric fields induce an increase in the grating strength and thus even larger diffraction efficiencies are obtained. In our experiments we measured diffraction efficiencies $\eta$ up to 60-70% in 7.5 mm long KNbO$_3$ crystals by applying electric fields of about 2 kV/cm. Fig. 4.29 shows such measurements done by variation of the electric field.

![Figure 4.29](image)

**Fig. 4.29:** Electric field dependence of the diffraction efficiency. The curve for $\lambda = 334$ nm is multiplied by a factor of 10, while the ones for $\lambda = 351$ nm and $\lambda = 364$ nm are translated upward by 10 resp. 20% for better visualization. The full lines are fits to Eq. (3.10) with an additional multiplying factor. For maximum diffraction efficiency the space-charge field is about $E_1 = 1.5$ kV/cm. The polarization of the writing beams is approximately parallel to c and the one of the reading beam ($\lambda = 633$ nm) is in its plane of incidence. The recording intensities are $I_0 = 57$ mW/cm$^2$, $I_0 = 18$ mW/cm$^2$ and $I_0 = 2.0$ mW/cm$^2$ for decreasing wavelength. (Crystal KNbO$_3$:4A5(138), $\Lambda = 2.8 \mu m$, Interaction length = 7.5 mm, Read-out depth $d = 15 \mu m$).

The curves in Fig. 4.29 are fits to Eq. (3.10) under the assumption that the refractive index change $\Delta n$ and the space-charge field $E_1$ increase linearly with the applied field ($\Delta n(E_0) = \Delta n(E_0=0) + kE_0$). This assumption is justified because the applied fields are moderate ($E_0 < 3.5$ kV/cm). The expression (3.10) has been multiplied with a factor $s$ to account for the fact that the maximum diffraction efficiency does not reach 100%. This factor is $s = 0.6$ for 364 and 351 nm and $s = 0.065$ for 334 nm. The reason for not reaching 100% diffraction efficiency is probably connected with the finite thickness of the read-out beam. The lower part of the wave sees a different refractive index change and reaches maximum diffraction for another value of $E_0$ than the centre of the beam. For maximum
Interband photorefractive effects in KNbO₃

Diffraction efficiency the average space-charge field $E_1$ in the volume probed by the read out beam is $E_1 = 1.5 \text{ kV/cm}$ corresponding to an average refractive index change $\Delta n = 4.2 \times 10^{-5}$. For the two longer wavelengths the mentioned value of $E_1$ is slightly larger than $E_{0/2} = 1.1 \text{ kV/cm}$, which is expected for a grating formed uniquely by free carriers (Fig. 2.17).

In the longitudinal configuration the diffraction efficiency is smaller. In the diffusion regime ($E_o = 0$) we measured a maximum of $\eta = 0.05\text{-}0.1 \%$. Also here $\eta$ is increased with the help of an external field and a nice quadratic dependence of the diffraction efficiency on the field ($\eta - \eta (E_o = 0) \propto E_o^2$) is observed at large enough grating spacings. The maximum diffraction efficiency of $\eta = 1.4 \%$ has been measured in crystal KNbO₃:216(P1S-2) with $E_o = 5 \text{ kV/cm}$ ($\lambda = 364 \text{ nm}$, writing polarization $\parallel c$, $A = 2.1 \mu \text{m}$, $I_o = 12 \text{ mW/cm}^2$). In this case the diffraction efficiency did not reach saturation, but larger fields were not applied.

In one case, we also tested the field dependence of the diffracted signal in the UV, what gives information on a possible influence of the Franz-Keldysh effect (section 4.2.2.5) on the physical mechanisms leading to the diffraction in the UV [15, 99, 100]. We used the thin sample KNbO₃:137 (effective crystal thickness = 25 $\mu \text{m}$) where the transmission of the ultraviolet light ($\lambda = 364 \text{ nm}$, Pol. $\parallel c$) is about 25%. The intensity of the first order self-diffracted beam by a grating recorded at $A = 6 \mu \text{m}$ was detected. Up to the maximum applied field of 2.7 kV/cm we observed a slightly less than quadratic increase of the diffracted signal with $E_o$.

The Franz-Keldysh effect can change the real part of the refractive index. The dependence is quadratic in the electric field [15]

$$\Delta n = -\frac{1}{2} n^3 s E^2 , \quad (4.20)$$

where $s$ is a quadratic electro-optic coefficient and $E = E_0 + |E_1| \cos(Kx-\phi)$ is the total electric field in the crystal. At large grating spacings, where the space-charge field $|E_1|$ is proportional to the applied field $E_o$ ($|E_1| = kE_o$), and for first order diffraction one expects then

$$\eta \propto E_o^4 \quad (4.21)$$

for diffraction due to the Franz-Keldysh effect. This result is different from the prediction $\eta \propto E_o^2$ valid in the case where the linear electro-optic effect produces the largest refractive index changes. Since the increase of the diffraction efficiency with the fourth power of the applied field was not observed experimentally, we conclude that the Franz-Keldysh effect does not play any role for the experimental conditions used ($\lambda = 364 \text{ nm}$, Pol. $\parallel c$, and

\[\text{Since } K_{1lc}, \text{ the polarization of the writing beams cannot be exactly parallel to } c. \text{ In this case there is a small component of the polarization that is parallel to the } a \text{ direction. However, we indicate always only the direction of the largest component to be able to identify the absorption constant by Table 4.5.}\]

\[\text{In the experiment this was verified by simultaneous diffraction of a red beam by the same grating.}\]
$E_0 < 3 \text{kV/cm})$. Measurements at larger fields were not possible due to instability of the sample.†

4.3.3.2 Grating thickness and shape

For interband photorefractive effects the thickness of the grating does not correspond to the one of the sample. The light is absorbed predominantly near the surface and does not reach the deepest regions. Therefore, no grating is generated there.

In the longitudinal geometry, an estimate of the grating thickness can be obtained by measuring the angular selectivity of the Bragg condition. For a grating with a constant amplitude $\Delta n$ over the whole depth the predicted angular selectivity is described by the 's formula (3.10) [49]. If the function $\Delta n(z)$ is not constant over the depth $z$ of the crystal, the amplitude of the diffracted wave $S$ can be integrated in the undepleted limit. For $p$-polarized read-out beams the general expression is then [114]

$$S(d) = \frac{-i\pi R \cos 2\theta}{\lambda \cos \theta} \exp \left( \frac{i\phi d}{\cos \theta} \right) \int_0^d \exp \left( \frac{i\phi z}{\cos \theta} \right) \Delta n(z) \, dz,$$

where $d$ is the crystal thickness and $R$ is the pump wave amplitude. The parameter $\psi$ is defined by

$$\psi = \Delta \theta K \cos \theta_0,$$

and contains the angle mismatch $\Delta \theta$. The other quantities have been all defined in chapter 3. Considering a function $\Delta n(z)$ of the type $\Delta n(z) = \Delta n_0 \exp(-\alpha_0 z)$ one finds for $d\gg\alpha_0^{-1}$ that the diffraction efficiency is given by

$$\eta = \frac{\pi^2 \Delta n_0^2 \cos^2(2\theta)}{\lambda^2 (\alpha_0^2 \cos^2 \theta + \psi^2)}.$$  

Fig. 4.30 shows the experimental dependence of the diffraction efficiency on the internal angle of incidence of a He-Ne read-out beam. The curves are fits following a step profile (Eq. (3.10)) or an exponential profile (Eq. (4.24)). The parameters for the best exponential profile are $\Delta n_0 = 5.3 \times 10^{-5}$ and $\alpha_0 = 109.5$ cm$^{-1}$. This value of $\alpha_0$ is about 5 times smaller than the absorption constant $\alpha$ of the crystal. Assuming a step profile we obtain for the amplitude of the refractive index change $\Delta n_0 = 2.4 \times 10^{-5}$ and for the effective thickness $d^* = 192 \pm 7$ µm. The fit with a step profile follows the experimental points better.

† Besides an instability of the sample domain structure, another effect complicates the measurements at large electric fields. This is the local heating caused by the large current density flowing through the crystal. The related change in temperature induces a shift of the absorption edge toward the red, and thus an increase of the absorption constant.
Interband photorefractive effects in KNbO$_3$

![Graph]

**Fig. 4.30**: Angular selectivity of the Bragg diffraction for grating read-out by a $p$-polarized He-Ne laser beam. The data are fitted assuming a step or an exponential grating profile. The fit parameters are given in the text. (Crystal KNbO$_3$:216(P1S-2)).

The absorption of beams of shorter wavelengths or polarized parallel to the crystal b-axis is larger than the case considered above (Table 4.5). Therefore the effective grating thickness $d^*$ becomes smaller, as confirmed by Table 4.8, where measurements similar to the one above are summarized.

We notice that in the crystal KNbO$_3$:216(P1S-1) the space-charge field $|E|_1$ is much larger than the trap limiting field $E_{q(vis)}$ which is obtained inserting in Eq. (2.9) the effective trap density $N_{eff}$ measured at the visible wavelength $\lambda = 514$ nm.

**Table 4.8**: Results of measurements of the kind shown in Fig. 4.30. The grating thickness $d^*$ is obtained assuming a step profile. The field $E_{q(vis)}$ is the trap limiting field obtained using the effective trap density measured in the visible for the same crystals (see Appendix C).

| Crystal sample | $\lambda$ [nm] | Pol | $\Lambda$ [\mu m] | $E_0$ [kV/cm] | $I_0$ [mW/cm$^2$] | $d^*$ [\mu m] | $\Delta n$ [$10^{-5}$] | $|E|_1$ [kV/cm] | $E_{q(vis)}$ [kV/cm] |
|----------------|----------------|-----|------------------|----------------|-----------------|---------------|-----------------|----------------|----------------|
| P1S-2          | 364            | c    | 0.93             | 0              | 16              | 192±7         | 2.4±0.2        | 1.0            | 3.2            |
| P1S-1          | 364            | b    | 1.50             | 4.6            | 51              | 50±7          | 7.5±0.8        | 3.0            | 0.7            |
| P1S-1          | 351            | b    | 1.42             | 4.6            | 28              | 14±2          | 5.3±0.7        | 2.1            | 0.7            |

Unlike conventional photorefractive effects, for interband excitation the thickness of the grating depends on the incident intensity. For this reason the diffraction efficiency measured in the longitudinal geometry depends on the ultraviolet intensity. We assume that a photorefractive grating can be created at a certain depth only if the ultraviolet intensity is so large that the photoconductivity $\sigma_{ph}$ is larger than the crystal dark conductivity $\sigma_d$. We define
therefore the thickness $d^*$ of the photorefractive grating by the requirement $\sigma_{ph}(d^*) = \sigma_d$. In the neighbourhood of the point $d^*$ the intensity is so low that a linear increase of $\sigma_{ph}$ with intensity is expected. As the incident intensity $I_0$ increases the point where photo- and dark conductivity are balanced moves deeper in the crystal, thus contributing to the increase in diffraction efficiency. We analyze this case under the assumption that the grating strength is constant between the crystal surface and the depth $d^*$.\footnote{Experiments in transversal geometry (below) show that the actual shape is more complicated. The step profile is the best approximation when the read-out intensity is low, what is fulfilled in the present case.} We use the Kogelnik relation (3.10) to calculate the diffraction efficiency for the undepleted case. After some simple algebra we get

$$\sqrt{\eta} \propto \frac{\Delta n}{\alpha} \ln\left(\frac{I_0}{I_{\text{ref}}}\right),$$  

(4.25)

where $\Delta n$ is the amplitude of the refractive index change, $\alpha$ is the absorption constant for the ultraviolet light, $I_0$ is the incident intensity corrected for Fresnel reflections at the input surface, and $I_{\text{ref}}$ is a reference intensity.

![Graph showing the intensity dependence of the square root of the diffraction efficiency. The straight lines are curve fits to the simple model illustrated by the scheme. The wavelength and polarizations of the recording light are given above. The grating was tested with a He-Ne beam and no electric fields were applied.](image)

Fig. 4.31: Intensity dependence of the square root of the diffraction efficiency. The straight lines are curve fits to the simple model illustrated by the scheme. The wavelength and polarizations of the recording light are given above. The grating was tested with a He-Ne beam and no electric fields were applied.

Fig. 4.31 shows experimental curves plotted in the appropriate coordinates. The expression (4.25) is satisfactorily fulfilled at all wavelengths. We attribute the deviations from a perfect straight line to the fact that the assumption of a constant refractive index change $\Delta n$ is not exactly fulfilled in our experiments. For a constant intensity, the largest diffraction...
Interband photorefractive effects in KNO$_3$

Efficiencies are obtained in the longitudinal geometry for $\lambda = 364$ nm and polarization parallel to the c-crystal axis (Fig. 4.31). This wavelength is less absorbed and gives the largest effective grating thickness $d^*$. The shape (depth dependence) of the grating amplitude can be determined easier in the transversal geometry (Fig. 4.28). We moved the crystal with respect to the He-Ne read-out beam propagating parallel to the input surface of the writing beams, examples are shown in Fig. 4.32. The parameter $d$ is the read-out depth below the crystal surface and the point $d = 0$ is defined at the position where one observes the maximum scattering from the crystal edge. At $d = 20$ $\mu$m, the full read-out beam is inside the crystal and $E_1$ reaches its maximum.

![Graph](image)

Fig. 4.32: Dependence of the space-charge field amplitude $E_1$ on the read-out depth $d$. The corresponding diffraction efficiencies are shown on the right-hand axis. The valid points are only for $d > 20$ $\mu$m where the full read-out beam is propagating in the crystal. The ultraviolet recording intensities are a) $I_o = 41$ mW/cm$^2$, $I_o = 5.0$ mW/cm$^2$ and $I_o = 0.41$ mW/cm$^2$ from top to bottom, and b) $I_o = 2.1$ mW/cm$^2$. Due to the focusing in the vertical direction the intensity of the read-out He-Ne beam is large. The curves in a) and b) differ by a factor of 100 in the read-out intensity. The solid curves in a) are tentative fits to the free carrier model (Eq. (2.66)) while the dashed line shows the exponential decay of the square root of the light intensity. ($\lambda = 364$ nm, Pol. $\parallel$ c, $\Delta = 0.82$ $\mu$m, $E_o = 0$, crystal KNO$_3$:pure 4A5(139), interaction length = 2 mm).
Fig. 4.32 shows two slightly different situations. In a) the focused read-out beam (\( \lambda = 633 \) nm) has an intensity of about 10 W/cm\(^2\). In this case, the space-charge field \( E_1 \) decreases monotonically with increasing \( d \). In contrast, by attenuating the read-out beam (Fig. 4.32 b)), a more or less constant component appears in the depth of the crystal. The discontinuity seen at \( d = 90 \mu m \) seems to indicate that the two components have opposite sign and that a zero crossing point occurs at that point.† Due to its flatness and its time response (up to several seconds), the deeper component has to be attributed to charges trapped at mid-gap centers.

The component seen close to the crystal surface is not erased by the read-out light and its space-charge field amplitude has a nearly exponential tail.‡ The only models predicting such a tail are the free carrier models presented in chapter 2.5.2. For \( E_1 < 100 \) V/cm the space charge field decreases approximately with an exponential decay constant of \( \alpha/2 \) (dashed straight line), that follows the square root of the UV light intensity \( I(z) \). Such a behaviour is consistent with the free carrier model (Eq. (2.66)) because the limiting field \( E_{gf}(z) \) and the recombination fields \( E_{Re}(z) \) and \( E_{Rh}(z) \) are all proportional to \( I(z)^{1/2} \). The most appropriate model is probably the one that considers also different free concentrations for electrons and holes (Eq. (2.67)) because this situation is more easily realized at low UV intensities.

The full lines in Fig. 4.32 are fits to

\[
E_1 = R \frac{E_D E_R E_{gf}}{(E_D + 2E_{gf})(E_D + E_R)},
\]

(4.26)

which is derived from (2.66) † with \( E_D = 0 \) and assuming that the mobilities of the two carrier species are very different so that one of the recombination fields can be neglected. In Eq. (4.26) \( E_R \) is the largest of the recombination fields and the scaling factor \( R \) is introduced to account for the fact that the observed space-charge fields are smaller than the theoretical predictions.

For the shown fit curves only the scaling factor \( R \) is slightly changed in the range \( 0.45 < R < 0.49 \), while the other parameters \( (\mu, \gamma_{dir}) \) are the same for the three curves. Qualitatively, there is a satisfactory agreement between the measurements and the fitted curves obtained with the free carrier model. This suggests that near the crystal surface the refractive index is modulated by free charges.

† The absolute sign of the space-charge field cannot be obtained from Bragg diffraction experiments.

‡ The fact that in Fig. 4.30 the grating was approximated better by a step than by an exponential profile is not in contradiction with this observation. In the longitudinal geometry the read-out beam is not focused and its intensity is lower than \( I = 0.1 \) W/cm\(^2\). Therefore the trap components are not erased.

† We used Eq. (2.66) instead of (2.67) to get an analytical relationship between the light intensities and the fields \( E_{gf} \) and \( E_R \).
Measurements of the dependence of the photorefractive effect on the depth also allows the determination of the crystal absorption constant. The idea is to adjust the incident intensity in such a way that the same diffraction efficiency (or the same time response) is observed for different depths $d$. The required intensity $I_o$ is related to the depth by the relation

$$I_o \propto \exp\left(\frac{\alpha d}{\cos \theta}\right).$$

The values of the absorption constant $\alpha$ determined in this way have been already summarized in Table 4.5; one set of measurements is shown in Fig. 4.33.

**Fig. 4.33:** Determination of the absorption constant by photorefractive measurements. The intensity needed to obtain a constant diffraction efficiency is plotted as function of the read-out depth. The fitted absorption constant is $\alpha = 1870 \pm 100 \text{ cm}^{-1}$.

### 4.3.3.3 Robustness of the grating

A requirement for any efficient control device is the ability to control strong signals with weak signals. In conventional photorefractive effects with light of comparable wavelength for write and probe beams the latter erases the photorefractive grating. This forces the pump waves to have intensities equal to or larger than the probe wave. This limitation can be overcome using methods for fixing the photorefractive gratings (see section 4.1) at the expense of the speed of response. An alternative is to use different wavelengths for recording and probing. If the crystal is much less sensitive to the probe than to the recording light a real time control device can be realized. Particular interesting is our present case where only the recording light induces band-to-band phototransitions.

Recently, such kind of photorefractive experiments performed in GaAs/AlGaAs quantum wells has demonstrated that a probe beam being about 10 times more intense than the pump beams can be diffracted without a strong erasure of the information [8]. The authors called these gratings 'robust gratings'.

Two experiments demonstrating the robustness of the gratings recorded with interband photoexcitation were already presented in this chapter. In the experiment in the transversal geometry shown in Fig. 4.29 the intensity of the focused probe beam ($\lambda = 633 \text{ nm}$) was $I_{inc} = 1 \text{ W/cm}^2$ and was much higher than the one of the UV recording beams $I_o = 2-60 \text{ mW/cm}^2$. Nevertheless, a high diffraction efficiency of $\eta = 60 \%$ is obtained. A second experiment where one sees the grating robustness is the one shown of Fig. 4.32.
It is evident that the grating component close to the crystal surface is not influenced by the read-out light.

The maximum probe-to-pump ratio in the mentioned experiments was $I_{\text{read-out}}/I_o = 2 \times 10^4$ (Fig. 4.32). To see if even larger ratios can be used we tested the dependence of the diffracted intensity $I_{\text{diff}}$ on the incident intensity $I_{\text{inc}}$ of the probe beam. The experiments were performed in the longitudinal configuration. For read-out we used green light ($\lambda = 514$ nm) where KNbO$_3$ is more sensitive than in the red. Fig. 4.34 shows such a measurement. The power $I_{\text{inc}}$ is varied up to the maximum of $\approx 100$ W/cm$^2$, while the ultraviolet recording intensity is kept fixed at the low value $I_o = 0.32$ mW/cm$^2$. Although $I_o$ is small, the intensity $I_{\text{diff}}$ diffracted by the photorefractive grating is increases ($\partial I_{\text{diff}}/\partial I_{\text{inc}} > 0$) until $I_{\text{inc}}/I_o > 3 \times 10^5$. This is much better than the results reported in MQW's where the diffracted intensity decreases for $I_{\text{inc}}/I_o > 10^{-5}$ [8]. Similar dependencies as the one shown in Fig. 4.34 have been observed in the same crystal at other intensities, wavelengths and polarization of the ultraviolet beams. In all cases the slope efficiency $\partial I_{\text{diff}}/\partial I_{\text{inc}}$ was positive over the whole experimental range.

Fig. 4.34: Dependence of the diffracted intensity (left hand scale) on the intensity $I_{\text{inc}}$ of the incident read-out wave ($\lambda = 514$ nm) measured in the longitudinal geometry. The asymptotic diffraction efficiency (dashed line) corresponds to the slope efficiency of the solid line. The inset is an enlargement of the low intensity behaviour. The ultraviolet recording intensity ($\lambda = 364$ nm, Pol. II b) is constant, $I_o = 0.32$ mW/cm$^2$. No decrease of the diffracted intensity is observed up to the maximum incident intensity reached, $I_{\text{inc}}/I_o > 3 \times 10^5$. (Crystal KNbO$_3$:216, P1S-2).
One sees in Fig. 4.34 that for large read-out powers the differential diffraction efficiency \( \partial I_{\text{diff}}/\partial I_{\text{inc}} \) assumes a constant value (straight line), corresponding to an asymptotic value of the diffraction efficiency (short dashed line). As observed in all experiments, the grating component responsible for this diffraction is not affected by the green light and there are no experimental indications that it could be erased by green beams with intensities larger than 100 W/cm\(^2\). This grating component is probably related to the one seen in Fig. 4.34 near the surface. We already suggested its identification with modulated free carriers. In contrast, the component being more active at low green powers (inset) is partially erased by stronger illumination and thus the diffraction efficiency decreases. This component has to be attributed to trapped charges.\(^{\dagger}\)

The relatively small values of \( \eta \) shown in Fig. 4.34 have three reasons. (1) the small UV intensity (small depth of the grating), (2) the absence of an applied electric field, and (3) the use of the longitudinal geometry. While in the longitudinal geometry the optimized diffraction efficiency is around \( \eta \approx 1 \% \), in the transversal one values larger than 60 \% are obtained (Fig. 4.29). Considering the ratio \( I_{\text{inc}}/I_{0} \) mentioned above, this means that mW power beams can control transversally propagating kW power beams.

### 4.3.3.4 Grating time response

In section 4.3.3.2 we saw that the grating amplitude is not constant over the depth. The response time depends even more strongly on the position in the crystal than the grating strength. In the transversal geometry this depth dependence of the time response can be measured, while in the longitudinal geometry one measures a mixture of different response times because the probe beam is testing the grating at all depths.

Fig. 4.35 shows the diffraction efficiency vs. time in the transversal geometry. The read-out beam probes the grating close to the crystal surface (\( d \approx 10 \mu m \)). The recording beams are switched on and off by an acousto-optical modulator placed before the beam splitter of the holographic set-up. The UV beam is focused in the modulator, allowing switching times of about 0.1 \( \mu \)s. The grating is erased by switching off both recording beams (from the first order diffraction of the modulator) and switching on simultaneously a homogeneous illumination at the same wavelength (zeroth order beam of the modulator).

The grating response in Fig. 4.35 is not given by a single exponential term. This may be due to the complicated mechanisms of formation of the interband photorefractive gratings. We identify two grating components with different response time both for the recording and erasure stage. The amplitude of the faster component (\( \tau = 20 \mu s \)) is about 2/3 of the total one. The dashed lines show a single exponential fit (limited to the fast component) for the recording and a double exponential for the erasure. The data points drawn below the erasure

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\(^{\dagger}\) One can imagine that experiments like the one described here, but performed by changing the wavelength of an intense erasing beam using spectral lamps, could be of interest for the study of trap spectroscopy in photorefractive crystals.
curve are obtained by subtracting a single exponential function for the slow erasure component ($\tau = 130 \mu s$) from the original data. They follow quite well an exponential decay.

![Graph](attachment:image.png)

**Fig. 4.35:** Recording-erasure cycle of interband photorefractive grating in KNbO$_3$. A fast and a slow component can be identified. The dashed lines are fits following a single (recording) or a double exponential function (erasure). The points drawn below the measured curve at time $t = 180-230 \mu s$ show only the fast grating component. (Recording intensity = 0.35 W/cm$^2$, Erasure intensity = 0.25 W/cm$^2$, depth $d = 10 \mu m$, $I_{\text{read-out}} = 10$ W/cm$^2$).

Fig. 4.36 shows the intensity dependence of the erasure time measured 10 $\mu m$ below the surface of the crystal at $\lambda = 351$nm with $b$-polarized recording beams. The data were obtained from measurements like the one shown in Fig. 4.35. The recording intensity was kept approximately constant ($I_0 \approx 0.4$ W/cm$^2$) in all the measurements while the erasure intensity was changed. Only the fast erasure component was used to obtain the exponential decay time $\tau_2$ of the space-charge field.

For intensities larger than 50 mW/cm$^2$ the time constant follows the square root dependence $\tau_2 \propto I^{-1/2}$ quite well (Fig. 4.36). In the case where $E_{\text{of}} > E_D$ (large grating spacing) the free carrier model predicts that the time constant is inversely proportional to the carrier concentration $n_0 \propto I^{1/2}$, which is consistent with the observations. Thus we suggest that the fast component of the grating is composed by free carriers.

Measurements performed using other UV wavelengths gave similar results. In most of the cases a region of linear dependence $\tau_2 \propto I^{-1}$ was observed for $I < 5$ mW/cm$^2$. This transition from a linear to a sublinear regime for increasing intensities is fully analog to the one observed in photoconductivity. In the measurement of Fig. 4.36 the linear regime is not resolved because for small $I$ the time constant of the fast grating component saturates at $\tau_2 \approx 700 \mu s$ measured in the dark. Obviously, beside the reduction of the intensity the increase of the read-out depth also results in longer response times. For instance, at $\lambda = 364$
nm and c-polarization we have measured values of $\tau_2$ between 150 $\mu$s and 30 ms for depths between 0 and 125 $\mu$m ($I = 72$ mW/cm$^2$ at the surface).†

As was pointed out by Yeh [115], there is a simple lower limit for the time response of photorefractive gratings, this is the time needed to photoexcite the charges to be redistributed. For a carrier modulation amplitude $N$ this lower limit can be expressed as

$$\tau_{\text{min}} = \frac{N}{gI_o} = \frac{Nh\nu}{\alpha I_o}.$$  (4.27)

As an example, for $N = 10^{15}$ cm$^{-3}$, $\alpha = 5000$ cm$^{-1}$, $I_o = 1$ W/cm$^2$ and $h\nu = 3.5$ eV we expect for the minimum time constant $\tau_{\text{min}} \approx 0.1$ $\mu$s. Shorter times are not possible without increasing the light intensity. In practice, slower times have to be expected due to the effect of recombination (see section 2.5.4). In our experiment, for an intensity of 1 W/cm$^2$, the time constant is about 10 $\mu$s, corresponding roughly to the minimum time needed to photoexcite $10^{17}$ carriers per cubic centimeter. At 1 W/cm$^2$ the concentration of free charges can approach this number if the constant for direct recombination $\gamma_{\text{dir}}$ is not larger than $10^{-18}$ m$^3$s$^{-1}$ (Eq. (2.49)). This limit for $\gamma_{\text{dir}}$ is supported by a further argument. In chapter 2.5.4 we mentioned that the response time for free carrier gratings is given approximately by $T_{\text{dir}} = (gI_o\gamma_{\text{dir}})^{1/2}$. Considering that deep traps are not playing any important role the above dynamics becomes much more complex than shown in Fig. 4.35. This is due to the great importance of trap gratings (cf. subsection a).
experimental results are consistent only with $\nu_{\text{dir}} \leq 10^{-18} \text{m}^3\text{s}^{-1}$ and mobilities smaller than $10^{-9} \text{m}^2\text{V}^{-1}\text{s}^{-1}$. Otherwise the response would be faster and the space-charge field could not build-up due to too small recombination fields $E_{R\text{e}}$ and $E_{R\text{h}}$ and too small free-carrier limited field $E_{Qf}$.

Finally, we mention also the response time observed in measurements performed in the longitudinal geometry in order to evaluate the potential for some applications. Also here it was possible to identify roughly two components in the dynamics. The faster component contributes about 3/4 of the total amplitude of the diffracted signal. The erasure time needed for the intensity diffracted to decrease to $e^{-2}$ of its initial value was measured for both components. We give these times for crystal KNbO$_3$:216(P1S-1) and illumination at $\lambda = 364$ nm (Pol. $\parallel$ b). At power levels of 100 mW/cm$^2$ one gets about 100-200 $\mu$s for the fast component and 1 ms for the slow component. The dark decay time is about 20 ms.

### 4.3.4 Ultraviolet two-beam coupling experiments

Interesting information can be gained from ultraviolet two-beam coupling experiments. Our investigations have been performed in a thin sample of undoped KNbO$_3$ (4A5, sample 144) with a thickness of 70 $\mu$m. We used the same set-up already used for measurements in Bi$_4$Ge$_3$O$_{12}$ (section 4.2.2.3) chopping the pump light at a frequency of about 15 Hz and recording the response of the signal beam with a storage oscilloscope. Both waves were used once as signal and once as reference wave. The result of all the measurements in the two signal directions were consistent (in absolute value) within 15 $\%$, indicating that phase coupling and not absorption coupling is the mechanisms underlying energy transfer. Thus we can relate the measured gain coefficients $\Gamma$ to the imaginary part of the space-charge field in the crystal.

Measurements made as function of the applied electric field have shown that $\Gamma$ is not influenced by the field in the range $0 \leq E_0 \leq 2.5$ kV/cm. The measured values are constant within $\pm20\%$ both for small ($\Lambda = 0.5$ $\mu$m) and large ($\Lambda = 9.7$ $\mu$m) grating spacings. In contrast, the grating spacing itself has a strong influence on the gain $\Gamma$ as shown in Fig. 4.37. The increase of $\Gamma$ at small grating spacing $\Lambda$ is steeper than linear. Such a behaviour is predicted by the free carrier model (cf. Fig. 2.17), therefore we can fit our data better using the expressions that include free carriers (full and dotted lines) than with the one for the conventional Kukhtarev model (dashed line). We interpret this fact as a further indication that free carriers are playing a major role in our crystals already at moderate intensities of few mW/cm$^2$.

The direction of beam coupling is shown in the inset, in the conventional case this coupling direction occurs if holes are the majority moving charges. For gratings formed only by free carriers this situation is valid in the case where $E_{R\text{e}} > E_{R\text{h}}$ (cf. (2.62), (2.63)). Eq. (2.66) (trap free model) and Eq. (2.70) (free carrier model with $n_0 \neq p_0$) both predict for this direction of the energy transfer that the electron mobility $\mu_e$ is smaller than the hole mobility $\mu_h$. This is possible when the electron mobilities are trap limited.
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Fig. 4.37: Grating spacing dependence of two-beam coupling gain in KNbO₃ for recording at λ = 364 nm with beams polarized in the plane of incidence. The inset shows the direction of the amplified beam. The solid line is the best fit to Eq. (4.26) (free carrier model for high intensities) while the dotted line is a fit to Eq. (2.67) (free carrier model for intermediate intensities). For comparison, the best fit with the conventional band model is also shown (dashed line, Eqs. (2.37)+(3.4)).

Crystal KNbO₃:4A5 (144), Pump Intensity = 6 mW/cm², E₀ = 0.

The values of the parameter obtained with the fits to the free carrier model have a large uncertainty, specially if one allows different concentrations for electrons and holes. The only parameter which is always quite stable is the recombination constant-mobility ratio γ(dir/μe). If we set n₀=p₀ we get γ(dir/μe) = (9.5±1.0)×10⁻¹⁰ Vm, and if n₀≠p₀ we get γ(dir/μe) = (6.8±1.5)×10⁻¹⁰ Vm. For the latter case we obtain concentrations n₀ and p₀ in the order of 10¹⁵ cm⁻³. However, the data can be fitted equally well with different sets of these two parameters and the ratio a = g/l(γ(dir)n₀p₀) (2.69) varies in the range 1.5 ≤ a ≤ 6. For the symmetric model (n₀=p₀) the best fit is obtained for a density n₀= 2.6×10¹⁵ cm⁻³, implying γ(dir) = 2×10⁻¹⁹ m³s⁻¹ if we use a mean intensity I = I₀(αd)⁻¹ in Eq. (2.49). The electron (trap limited) mobility is then μe = 2×10⁻¹⁰ m²(Vs)⁻¹. The effective electro-optic coefficient at λ = 364 nm resulting from the full line fit is r_eff = (90±10) pm/V.

4.3.5 Summary

In this chapter we have presented the first measurements of photorefractive effects in oxide crystals performed using band-to-band photoexcitation. KNbO₃ crystals and recording wavelengths between 334 and 364 nm were used and the experiments were done either in a longitudinal, or in a transversal recording geometry. The experimental results show that the mechanisms leading to the formation of this kind of photorefractive gratings is different than the conventional one.
By recording with an applied electric field, the diffraction efficiency reaches $\eta \approx 1.4\%$ in the longitudinal and $\eta \approx 65\%$ in the transversal geometry. The response time for transversal recording reaches $\tau = 10\,\mu s$ for an intensity of $1\,W/cm^2$. This is about 10 times faster than the shortest response times measured previously in reduced KNbO$_3$ at the same power level using visible light. The combination of these two results makes this kind of effects attractive for photorefractive beam steering applications or for fast optical spatial modulators or correlators. In contrast, the two beam coupling gain coefficients $\Gamma = 10\,cm^{-1}$ are not large enough to overcome the absorption losses ($\alpha = 500-6000\,cm^{-1}$ at $\lambda = 364-351\,nm$) occurring in the crystal sample, precluding applications for beam amplification in the UV. The gain coefficients could be enhanced if the Franz-Keldysh effect would increase the crystal nonlinearities in the UV. However, our investigations show that no enhancement of this kind is observed at $\lambda = 364\,nm$. Investigations performed using low power recording waves and high power signal waves ("robust gratings") indicate the presence of a grating component being immune to a strong visible erasure beam. Its differential diffraction efficiency shows no degradation up to signal to pump ratios $>3 \times 10^5$. Thus, the use of interband photorefractive effects constitutes an alternative to the fixing for nondestructive hologram read-out. We suggest the origin of the stable component to be a grating formed by a spatially modulated free carrier concentration.

Other investigations were performed with the aim of characterizing the shape of the refractive index gratings under different external conditions. A first component of the grating reaches its maximum close to the input surface and decreases towards the depth. A second (slow) component is centred deeper in the crystal and has a more uniform amplitude. This component disappears if the visible read-out intensity is high. We attribute the first component to the effect of free carriers and the second one to charges trapped in mid gap levels. In the longitudinal geometry, where the read out beams are not focused, the read-out intensity is low and the complex grating structure can be approximated better by a step profile than by a single exponential profile. The diffraction efficiency increases quadratically with the effective grating thickness $d^*$ which depends on the UV light intensity and wavelength. For an intensity of $20\,mW/cm^2$ the thickness of the assumed grating step profiles is between $d^* = 200\,\mu m$ ($\lambda = 364\,nm$, Pol. II c) and $d^* = 15\,\mu m$ ($\lambda = 351\,nm$, Pol. II b).

In chapter 2.5 we presented two theoretical models for free carrier gratings valid in the case where no spatially modulated charge density is stored in the traps. These models describe the measured results better than the conventional models. The free carrier grating model describes better the depth dependence of the grating strength, the grating spacing dependence of two-beam coupling gain, the intensity dependence of the grating response time, as well as the intensity dependence of the photocurrent and its time response. The experiments could be even better described by the model that allows different concentrations for free electrons ($n_0$) and free holes ($p_0$) (Eq. (2.67)). However, this model does not allow an analytical relationship between $n_0$, $p_0$ and the light intensity $I_0$, precluding the determination of many parameters. We could only estimate the order of magnitude of two of the key parameters of the models, the constant for direct recombination $\gamma_{dir}$ and the mobility $\mu$ of the slower carriers. We found that $\gamma_{dir}/\mu = 10^{-9}\,V m$ with $\gamma_{dir} = 10^{-19} - 10^{-18}\,m^3 s^{-1}$ and $\mu = 10^{-10} - 10^{-9}\,m^2(Vs)^{-1}$. The values are consistent with the grating response time, the
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grating spacing dependence of two beam coupling and the measured photocurrent. The fact that the constant $\gamma_{\text{dir}}$ is so small permits the generation of large free carrier concentrations already at mW/cm$^2$ power levels. As the mobility $\mu$ is small, the free carriers could be described by a combination of true free carriers in the conducting band and “quasi-free” carriers, i.e. carriers trapped for a short time at shallow trap levels (see section 4.1.3.3). Short pulse experiments in the UV could possibly clarify this point.

Future experiments in cw-interband photorefractive effect could be expanded to the investigation of doped K\textsubscript{NbO}\textsubscript{3} crystals. In doped crystals we expect a larger influence of traps, and thus slower responses.

The use of ultraviolet dynamic gratings for beam steering applications in K\textsubscript{NbO}\textsubscript{3} planar or channel waveguide [116, 117] would also be of great interest. Preliminary investigations have shown that for a constant UV intensity the photorefractive time response in the planar waveguides is more than a factor of 100 slower than in the underlying bulk, indicating that the He ion implantation may induce the creation of a large number of defect levels in the band gap.
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5. Conclusions

In the first part of this work we presented and analyzed new theoretical models for the photorefractive effect. The first (electron-ion model) deals with the situation occurring when in addition to the photoexcited electronic charges non-photoexcitable ionic charges can also move in the crystal. The second model (interband photorefractive effects) considers the case where the recording light induces interband phototransitions of electrons. Three slightly different modifications of the latter model were given. The theoretical predictions were discussed in detail and used later for the successful interpretation of the experiments.

The experimental investigations had the common aim of studying the production of photorefractive holograms which are not erased by the read-out optical waves. Two major approaches were taken.

In the first approach we developed a method to freeze-in the optical information carried by the signal wave in form of modulation of ionic charges in the crystal. For this purpose, volume hologram fixing in KNbO₃ using a thermal cycling method was demonstrated. Fixing is achieved by recording the photorefractive gratings at a temperature $T > 70 \, ^\circ C$ and subsequently cooling the crystal to room temperature. This process produces fixed holograms with a diffraction efficiency on the order 1% and storage times of some months. The underlying process corresponds to the electron-ion model. Its prediction that the combined effect of the primary (electronic) and secondary (ionic) charge carriers controls the dynamic evolution and the strength of the resulting phase grating was confirmed experimentally. The theory predicts that the handling time, i.e. the time for which the fixed grating can be read out, is longer for larger grating spacings and is shorter (but with larger diffraction efficiencies) when an electric field is applied. These predictions were confirmed experimentally and were used to determine a few material parameters. The ionic charges compensating the primary space-charge field are suggested to be oxygen vacancies with a mobility $\mu_i = 10^{-12} \, m^2/(Vs)$ at $T = 200 \, ^\circ C$ and a thermal activation energy of 1.0 eV for motion along the a or c crystallographic directions. In direction b the activation energy is lowered to 0.8 eV.

The second approach was to use two different wavelengths at which the crystals have different sensitivities for recording and read-out. We used ultraviolet light for recording, because of higher sensitivity and optical resolution, while for read-out we used visible light. The wavelength range in the UV was 305-365 nm. These investigations were performed in Bi₄Ge₃O₁₂ and KNbO₃.

In Bi₄Ge₃O₁₂, the absorbed UV photons can induce only electron phototransitions from the valence band to mid gap defect levels or from such levels to the conduction band. We found that the first process is dominant in our undoped crystals. The results indicate that Bi₄Ge₃O₁₂ is at present the only material where the conventional photorefractive effect works well and permits an effective amplification of laser beams at wavelengths close to 300 nm. The main drawback of this material is its small electro-optic effect compared to other crystals. Quasipermanent holograms are obtained at room or elevated temperature using a procedure similar to the one used in KNbO₃. However, the secondary carriers are not of
Conclusions

Ionic nature and are slightly influenced by light. The increase of the handling time is only around a factor of 1000 compared to about $10^7$ in KNbO$_3$. The measured response times ($\approx 4$ ms at $\lambda = 305$ nm and $I = 0.25$ W/cm$^2$) and mobility-life time product $\mu\tau = 1.5\cdot10^{-8}$ cm$^2$/V indicate an efficient charge transport in this material. Therefore the principal potential applications of this material are for dynamic holography or coherent image amplification in the ultraviolet, where the optical resolution is enhanced.

In KNbO$_3$, in contrast, the ultraviolet photons have an energy large enough to induce direct phototransitions between the two bands. This is the process described by the models for interband photorefractive effects which were developed in this work and offers new interesting possibilities for fundamental research and for applications. Fundamental investigations profit from the fact that in the limit of large intensities the crystal behaviour does not depend on the presence of traps. For applications, interband photorefractive effects are of great interest in cases where the recording ultraviolet waves are only needed for controlling other beams. This includes fast photorefractive spatial light modulators, photorefractive real time optical correlators and photorefractive beam steering in bulk crystal or in optical waveguides. Our experiments showed that the space-charge fields are induced in large amount by a spatial modulation of free carriers. Since visible photons do not induce interband phototransitions, the component of the grating created by the free carriers is extremely robust with respect to strong visible read-out beams. Signal to pump ratios larger than $10^5$ can be used. Diffraction efficiencies of $\eta = 65\%$ were obtained in a transversal geometry where the read out beam propagates parallel to the input surface of the UV beams. Response times of $\approx 10$ $\mu$s at an intensity of 1 W/cm$^2$ were measured. This geometry seems to be particularly advantageous because the diffraction efficiency is limited only by the shape of the region illuminated by the UV beams or by the crystal dimensions. The response time, in contrast, is limited by the value of the constant $\gamma_{dir}$ describing the direct recombination processes. A comparison of the different measurements (photoconductivity, grating dynamics, two-beam coupling) with theoretical models suggests that this constant is on the order of $10^{-19}$-$10^{-18}$ m$^3$s$^{-1}$. With this value the direct recombination can balance the direct photoexcitation only when the free carrier densities are large, thus explaining why a large number of free carrier can be created with only a few mW/cm$^2$ of ultraviolet radiation.
6. Outlook

Future applications of hologram fixing in KNbO$_3$ include image storage devices for optical associative memories or for “novelty filters”, i.e. a device detecting what is new in a given scene. Permanent storage requires the thermal fixing procedure described in this work while novelty filters could make use of the observed difference in response time between the primary and the secondary grating components. Another possibility is to use the electron-ion charge compensation effects and the reported theoretical predictions as a tool for material characterisation. For instance, the reduction state of the crystal and the effective number of trap centers could be deduced from measurements of the charge compensation dynamics at elevated temperatures.

For Bi$_4$Ge$_3$O$_{12}$ the investigation of the effect of doping on its photorefractive properties in the ultraviolet could give additional information. Doping would increase the effective number of traps, and thus larger refractive index changes and gain coefficients can be expected at small grating spacings. However, we expect also a shorter carrier lifetime and thus a less efficient charge transport and longer response times. In addition, the photochromic effect, i.e. a light induced change in absorption constant, may be enhanced by doping the crystals. This effect constitutes an alternative to the photorefractive hologram recording.

More research can be performed in the new field of interband photorefractive effects. First, it is reasonable to believe that this effect should be observable also in other oxide materials like BaTiO$_3$, LiNbO$_3$ and SrTiO$_3$. The comparison of the effects in different undoped materials is easier for interband than for conventional photorefractive effects because the trap distribution has a less direct influence. Moreover, more investigations can be oriented to a better understanding of the fundamental physical mechanisms underlying the charge transport. For instance, one of the major open problems in cw photorefractive experiments is the determination of the value of the electron or hole mobility. The values determined with ps experiments cannot be used because of trapping effects, and the mobility seems to depend on the time scale in which the experiments are performed. From our investigations we deduced that the effective mobility of the slower carrier species is smaller than $\mu = 10^{-9}$ m$^2$(Vs)$^{-1}$ for KNbO$_3$. Ultraviolet short pulse investigations could give a more precise value because the theoretical relationships can be simplified. Furthermore, laboratory devices that use interband photorefractive effects can be made. These may include optical correlators or thin spatial light modulators.

The research field on the photorefractive effect is already in its adult stage. However, from time to time new ideas contribute to expand this field, like a tree getting a new branch. One day, one of these branches might produce the sweetest fruits. I hope that this work might have contributed in part to the creation of a new bud on the photorefractive tree.
Values of the crystal parameters and of the external conditions used for modeling the photorefractive response predicted by the electron-ion model

### Basic material parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoionization constant</td>
<td>$s_e = 0.03 \text{ m}^2(\text{Ws})^{-1}$</td>
</tr>
<tr>
<td>Dark generation rate</td>
<td>$\beta_e = 1 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Recombination constant</td>
<td>$\gamma_e = 10^{-15} \text{ m}^3/\text{s}$</td>
</tr>
<tr>
<td>Donor concentration</td>
<td>$N_{D_0} = 3 \times 10^{22} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Acceptor concentration</td>
<td>$N_A = 5 \times 10^{21} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Ion concentration</td>
<td>$N_{I_0} = 10^{24} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>$\mu_e = 10^{-6} \text{ m}^2(\text{Vs})^{-1}$</td>
</tr>
<tr>
<td>Ion mobility</td>
<td>$\mu_I = 2 \times 10^{-15} \text{ m}^2(\text{Vs})^{-1}$</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>$\varepsilon = 55$</td>
</tr>
</tbody>
</table>

### External parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light intensity during recording</td>
<td>$I_0 = 150 \text{ W/m}^2$</td>
</tr>
<tr>
<td>Light intensity during erasure</td>
<td>$I_0 = 100 \text{ W/m}^2$</td>
</tr>
<tr>
<td>Effective modulation index</td>
<td>$m' = 0.5$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T = 400 \text{ K}$</td>
</tr>
</tbody>
</table>

### Derived parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron concentration (by $I_0 = 100 \text{ W/m}^2$)</td>
<td>$n_0 = 2 \times 10^{16} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Dielectric relaxation rate for electrons (by $I_0 = 100 \text{ W/m}^2$)</td>
<td>$\Gamma_{\text{die}} = 6.580 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Dielectric relaxation rate for ions</td>
<td>$\Gamma_{\text{dil}} = 0.658 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>Debye wavevector for electrons</td>
<td>$K_{De} = 6.306 \times 10^6 \text{ m}^{-1}$</td>
</tr>
<tr>
<td>Debye wavevector for ions</td>
<td>$K_{Dil} = 9.770 \times 10^7 \text{ m}^{-1}$</td>
</tr>
<tr>
<td>Inverse of diffusion length</td>
<td>$K_e = 1.204 \times 10^7 \text{ m}^{-1}$</td>
</tr>
</tbody>
</table>
Appendix B: Band models with electron and hole charge transport

The conventional band transport model of Kukhtarev et al. and the electron-ion model treated in section 2.3 consider a primary charge transport by electrons alone. However, in a general situation like the one shown in Fig. 2.1 the transport of charges can occur either by electrons in the conduction band or by holes in the valence band. The generalization of the single level Kukhtarev model to the case where a second kind of charge carriers can be photoexcited has been made by Strohkendl et al. [118] and Valley [107]. Valley considered also the case where the photoexcitation of electrons and holes takes place from different mid-gap defect levels. This last situation has been treated also by Kukhtarev et al. [106], Bashaw et al. [110] and Zhivkova and Miteva [119]. As these models are only indirectly related to this thesis we summarize their predictions in this appendix and add some expressions concerning the dynamic behaviour. In addition, we present new results applying in the situation where one kind of charge carriers (for instance holes) cannot be photoexcited.

B.1 Photoexcitation of electrons and holes

We distinguish between two models (Model 1 and Model 2) schematically depicted in Fig. B.1.

![Schematic representation of the models of the photorefractive effect giving rise to electron-hole competition.](image)

In Model 1 all the charge carriers are photo- (or thermally) excited from a single defect level $N_D$ while Model 2 considers two independent levels $N_D$ and $N_A$ in which carriers can be

---

For Model 2, $N_A$ does not correspond to the usual definition given in section 2.2 but gives the total density of defect sites of type A. $N_A^-$ is then the concentration of levels filled with one electron while $N_A-N_A^+$ is the number of ionized defects (that is, filled with a hole). It is our opinion that from the physical point of view the situation of Model 2 is not realistic if the crystal
trapped. For this reason, in Model 2 one can get a partial compensation between the space-charge fields produced by the charges trapped in the upper level and the ones trapped in the lower one. This is not possible in the case of Model 1. There is a second principal difference between the two models. Model 1 predicts a time dynamics that can be described by a single exponential time rate in cw-experiments, while for Model 2 two time rates are needed.

B.1.1 Steady-state space-charge fields

For Model 1 one can distinguish two limiting cases [118, 107]. The first one is found when the grating spacing $\Lambda$ is large compared to the carrier diffusion lengths $K_e^{-2}=\mu_e k_BT/e\gamma_e N_{D0}^+$ and $K_h^{-2}=\mu_h k_BT/e\gamma_h (N_D-N_{D0}^+)$. For no applied fields and negligible dark conductivity the space charge field is then given by

$$E_1 = \left(-im \frac{E_q E_D}{E_q + E_D} \frac{\sigma_e - \sigma_h}{\sigma_e + \sigma_h}\right) \quad \text{(B.1)}$$

where $\sigma_e = e_n \mu_e$ and $\sigma_h = e_n \mu_h$ are the electron and hole conductivities respectively, $m=I/I_0$ is the modulation ratio, and $E_q$ and $E_D$ are the same fields previously defined in section 2.3.1. In the opposite case of small $\Lambda$ or large diffusion lengths one gets

$$E_1 = \left(-im \frac{E_q E_D}{E_q + E_D} \frac{s_e(N_D-N_{D0}^+)}{s_h(N_D-N_{D0}^+)} \right) \quad \text{(B.2)}$$

Thus, the final effect of electron-hole competition is to reduce the value of the space-charge field $E_1$ by the factors given by the second term on right-hand side of Eq. (B.1) and (B.2).

For Model 2 the situation is slightly different. An inhomogeneous illumination modulates the charge distribution in both levels D and A. Since charge transfer between the two levels does not occur, two essentially independent space-charge field components can build up. The sum of these two components is

$$E_1 = \left(-im \frac{E_D (E_{qe} - E_{qh})}{E_D + E_{qe} + E_{qh}} \right) \quad \text{(B.3)}$$

where, in analogy with (2.9), $E_{qe}=(e/e\varepsilon_0 K)(N_{D0}^+ (N_D-N_{D0}^+)/N_D)$ is the limiting field for electrons and $E_{qh}=(e/e\varepsilon_0 K)(N_{A0}^- (N_A-N_{A0}^-)/N_A)$ is the corresponding one for holes. $N_{D0}^+$ and $N_{A0}^-$ are the densities of empty electron-acceptors and empty hole-acceptors in the dark, respectively (Fig. B.1). Equation (B.3) shows that the sign of the space-charge field depends on whether $E_{qe}$ or $E_{qh}$ is larger.

---

is initially in thermal equilibrium. In that case the presence of two partially filled levels in the band gap is possible only if they are energetically very close to each other (within few $kT$).
B.1.2 Time rates

For cw-illumination Model 1 predicts a simple exponential time evolution of the space-charge field given by Eq. (2.38) for the recording process and (2.39) for the optical erasure process. In this case the time rate $\Gamma_2$ is

$$\Gamma_2 = \Gamma_{\text{die}} \begin{bmatrix} 1 + \frac{K^2}{K_0^2} \\ 1 + \frac{K^2}{K_\infty^2} \end{bmatrix} + \Gamma_{\text{dih}} \begin{bmatrix} 1 + \frac{K^2}{K_0^2} \\ 1 + \frac{K^2}{K_\infty^2} \end{bmatrix},$$

where $K_0 = K_{\text{oe}}$ is the Debye wavevector defined in (2.22). The dielectric rate $\Gamma_{\text{dih}}$ and the inverse diffusion length $K_h$ for holes are obtained by substituting the suffix $e$ with $h$ in (2.5a) and (2.24).

For Model 2 no explicit solutions for the time rates were reported so far. As the problem is analogous to the one treated in section 2.3.2 we indicate here only the main steps needed to find such solutions. The starting point is a set of equations of the type (2.1a-2.1f) describing the physics of Model 2. From this, four coupled differential equations similar to (2.4a-2.4c) are obtained. Here the independent variables are $N_{D1^+}, n_1, N_{A1^-}$ and $p_1$, where $p(x) = p_0 + p_1 \exp(iKx)$ is the hole concentration in the valence band. In analogy to (2.13), the general solution of this set of equation is a sum of four exponential terms with time rates $\Gamma_0, \Gamma_1, \Gamma_2$ and $\Gamma_3$. These time rates fulfill a fourth rank polynomial equation of the type (2.14). Again, two of these time rates (we call them $\Gamma_0$ and $\Gamma_1$) are very large and are connected with small amplitudes. The other two time rates are given in first order approximation by

$$\Gamma_2 \equiv \frac{\Gamma_2}{\Gamma_0^3}, \quad \text{and}$$

$$\Gamma_3 \equiv \frac{\Gamma_3}{\Gamma_0^4},$$

where

$$\Gamma_0^2 = (\Gamma_{\text{Re}} + \Gamma_{\text{De}})(\Gamma_{\text{dih}} + \Gamma_{\text{lh}} + \Gamma_{\text{dh}} + \Gamma_{\text{Rh}}) + (\Gamma_{\text{De}} + \Gamma_{\text{Rh}})(\Gamma_{\text{die}} + \Gamma_{\text{le}}),$$

and

$$\Gamma_2 = \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{die}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{die}} \Gamma_{\text{Re}} \Gamma_{\text{le}} \Gamma_{\text{Re}}$$

$$+ \Gamma_{\text{die}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{die}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}}$$

and

$$\Gamma_3 = \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}}$$

and

$$\Gamma_4 = \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}} + \Gamma_{\text{Re}} \Gamma_{\text{dih}} \Gamma_{\text{le}} \Gamma_{\text{Re}}.$$
Here $\Gamma_{\text{die}}$, $\Gamma_{\text{le}}$, $\Gamma_{\text{Re}}$ and $\Gamma_{\text{De}}$ are the time rates defined in Eqs. (2.5a)-(2.5d) and $\Gamma_{\text{dih}}$, $\Gamma_{\text{h}}$, $\Gamma_{\text{Rh}}$ and $\Gamma_{\text{Dh}}$ are corresponding time rates for holes. Using (B.5) and (B.6) and assuming that the diffusion and recombination rates are larger than all other rates one gets

$$
\begin{align*}
\Gamma_2 &= \Gamma_{\text{dih}}\left[1 + \frac{K^2}{K_{oh}^2}\right] + \Gamma_{\text{die}}\left[1 + \frac{K^2}{K_h^2}\right] \\
\Gamma_3 &= \Gamma_{\text{dih}}\left[1 + \frac{K^2}{K_h^2}\right] + \Gamma_{\text{die}}\left[1 + \frac{K^2}{K_e^2}\right]
\end{align*}
$$

for the faster of the two rates, and

$$
\begin{align*}
\Gamma_3 &= \Gamma_{\text{dih}}\left[1 + \frac{K^2}{K_h^2}\right] + \Gamma_{\text{die}}\left[1 + \frac{K^2}{K_e^2}\right]
\end{align*}
$$

for the slower one. The new wavevectors $K_{oh}$ and $K_h$ appearing in (B.10) and (B.11) are defined as

$$
K_{oh}^2 = \frac{e^2 N_A^0 (N_A - N_A^0)}{\varepsilon \varepsilon_0 k_B T N_A}
$$

for the square of the Debye-wavevector for the holes, and

$$
K_h^2 = \frac{e \gamma h N_A^0}{\mu_k k_B T}
$$

for the square of the inverse diffusion length for holes.

The time rate $\Gamma_2$ in Eq. (B.10) differs from the one obtained for Model 1 (B.14) only by the appearance of two different Debye-wavevectors. In contrast, the time rate $\Gamma_3$ do not exist in Model 1. As in the case of the electron-ion model its value can be much smaller than the dielectric rates $\Gamma_{\text{die}}$ and $\Gamma_{\text{dih}}$. The grating spacing dependence described by Eq. (B.11) is essentially the same as the one predicted by the electron-ion model (Eq. (2.21), Fig. 2.5). In particular, for small spatial frequency $K$ a quadratic dependence of $\Gamma_3$ on $K$ is expected.

### B.2 Photoexcitation of electrons, thermal excitation of holes

We consider now the case where one kind of charge carriers (for instance holes) are excited only thermally. For Model 1 of Fig. B.1 this situation is not specially interesting. For no applied field the effect of hole thermal excitation results mainly in a reduction of the modulation index $m'$ with respect to the conventional single carrier Kukhtarev case.
The case of Model 2 is different. Here an effective hole-charge modulation can be stored in the level A. Putting $s_h=0$ we can solve the initial set of equations in a way similar to the one described in section 2.3. For no applied field, the resulting space-charge field $E_1$ is

$$E_1 = -im' \frac{E_D E_{qe}}{E_D + E_{qe} + E_{qh}}$$

(B.14)

where $m'$ is equal to $s_e I_1/(s_e I_0 + \beta_e)$. By substituting $E_{qh}$ with $E_{qf}$ this result is fully equivalent to (2.12a) which was obtain in the electron-ion model. Therefore, charge compensation effects like the ones shown in Fig. 2.6 - Fig. 2.8 can be explained also by this model if the condition $E_{qh} \gg E_{qe}$ is fulfilled, that is the number of hole-acceptors $N_{A0}$ and of hole-donors $N_A$ should be much larger than $N_D$ and $N_{D0}$.

It is interesting to compare the result (B.14) with the one obtained for the case of allowed hole-photoexcitation (B.13). There $E_1$ is proportional to $(E_{qe} - E_{qh})$. A complete compensation in the steady state would therefore only be possible if $E_{qe} = E_{qh}$, that is, if the effective number of electron-acceptors equals the one of hole-acceptors. If $E_{qh}$ is larger than $E_{qe}$ the space-charge field $E_1$ can change sign during the recording process because the holes can be moved in an active way. In contrast, in the present case the redistribution of holes is driven only by the presence of the field generated by the electronic charges. Therefore, the hole contribution to the space-charge field cannot reach a magnitude larger than the one of the electronic contribution. This gives rise to the compensated space-charge field given in Eq. (B.14).

For Model 2 in absence of hole photoexcitation the time rates $\Gamma_2$ and $\Gamma_3$ are given by the same expressions that we have derived in (B.10) and (B.11). However, here the dielectric relaxation rate $\Gamma_{dih}$ for the holes does not depend on light intensity but only on temperature. This was also the case for the dielectric relaxation rate for the ions $\Gamma_{dii}$ in (2.21). Therefore, the present model leads generally to the same predictions then the electron-ion model in the limit of a large number of defects of type A (Fig. B.1). In the case of a reduced number of hole traps there is a minor difference in the grating spacing dependence of the dynamics due to the terms containing $K_h^2$ in (B.10) and (B.11) which have no correspondence in (2.20) and (2.21).
Appendix C: Crystals

Bi$_4$Ge$_3$O$_{12}$

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Samples</th>
<th>Dimensions $^\circ$ $x_1,x_2,x_3$ [mm$^3$]</th>
<th>Polished surfaces</th>
<th>Effective number of traps $N_{\text{eff}}$ [$10^{15}$ cm$^{-3}$]</th>
<th>Majority carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG1</td>
<td>BGO 1/1</td>
<td>4.9x5.0x5.3</td>
<td>(110)</td>
<td>2.1±0.3</td>
<td>$h^+$</td>
</tr>
<tr>
<td></td>
<td>BGO 1/2</td>
<td>5.0x5.7x5.0</td>
<td>(001)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BG2 (FA717)</td>
<td>BGO 4</td>
<td>9.8x9.4x6.9</td>
<td>(110)</td>
<td>0.25±0.1</td>
<td>$h^+$</td>
</tr>
<tr>
<td></td>
<td>BGO 5</td>
<td>9.8x9.4x6.9</td>
<td>(110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>BGO 6</td>
<td>21.6x13.7x12.8</td>
<td>(110),(001)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

KNbO$_3$

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Doping$^\dagger$</th>
<th>Samples</th>
<th>Dimensions $^\ddagger$ $a$$b$$c$ [mm$^3$]</th>
<th>Polished surfaces</th>
<th>$N_{\text{eff}}$ [$10^{15}$ cm$^{-3}$]</th>
<th>Majority carriers</th>
</tr>
</thead>
<tbody>
<tr>
<td>216 (00.0188)</td>
<td>pure</td>
<td>P1S-1</td>
<td>1.4x4.6x4.4</td>
<td>a</td>
<td>1.2±0.3</td>
<td>$e^-$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P1S-2</td>
<td>1.4x4.6x7.3</td>
<td>a</td>
<td>9±3</td>
<td>$e^-/h^+$</td>
</tr>
<tr>
<td>3A5</td>
<td>pure</td>
<td>138</td>
<td>7.5x2.7x6.4</td>
<td>a, (b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A5</td>
<td>pure</td>
<td>137</td>
<td>0.025x6.5x6.3</td>
<td>a</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>139</td>
<td>2.0x2.4x6.6</td>
<td>a, (b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>144</td>
<td>0.07x5.5x6.5</td>
<td>a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (224.62.a(67))</td>
<td>Fe, 150 ppm</td>
<td>224/an</td>
<td>7.2x0.8x3.1</td>
<td>b</td>
<td>150±30</td>
<td>$h^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>224/cat</td>
<td>7.2x0.8x0.6</td>
<td>b</td>
<td>15±3</td>
<td>$e^-$</td>
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<tr>
<td>Rb</td>
<td>Rb 1%</td>
<td>#1</td>
<td>3.2x6.5x3.6</td>
<td>a</td>
<td>2.6±0.3</td>
<td>$h^+$</td>
</tr>
<tr>
<td>Ta</td>
<td>Ta 1%</td>
<td>#6</td>
<td>4.2x3.1x3.7</td>
<td>b</td>
<td>1.2±0.3</td>
<td>$e^-$</td>
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<tr>
<td>LiNaFe1 (247/85.2)</td>
<td>$|$</td>
<td>247</td>
<td>4.0x1.5x5.1</td>
<td>b</td>
<td>11±3</td>
<td>$h^+$</td>
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<tr>
<td>LiNaFe2 (2A2.4.190)</td>
<td>$||$</td>
<td>104</td>
<td>5.8x6.5x6.2</td>
<td>b</td>
<td>55±20</td>
<td>$h^+$</td>
</tr>
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$^\circ$ $x_1 = [110], x_2 = [\overline{1}0], x_3 = [001]$

$^\dagger$ Melt atomic concentrations

$^\ddagger$ Annealed in water reach atmosphere at $T= 800^\circ$C for 24 hours (slightly reduced).

$^\|$ Sample 224/an is cut near the anode of an inhomogeneous reduced crystal, 224/cat near the cathode.

$\|$ Li 2.5 %, Na 2.5 %, Fe 0.1 %

$\|\|$ Li 10 %, Na 5 %, Fe 0.1 %
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Curriculum vitae

Name: Germano Luigi Montemezzani

Born: June 21, 1963 in Locarno, Ticino (Switzerland)

1969-1974: Elementary school in Magadino (TT)

1974-1979: Ginnasio Cantonale in Giubiasco (TT)


June 1982: Scientific “Matura”, typus C.


April 1987: Graduation with a diploma in experimental physics (Dipl. Phys. ETH)

1987-1992: PhD. student in the group of Prof. Dr. P. Günter in the Laboratory of Nonlinear Optics at the Institute of Quantum Electronics (Swiss Federal Institute of Technology, Zürich), where this work has been written.

Zürich, November 1992

G. Montemezzani