

Specific Recording Kinetics as a General Property of Unconventional Photorefractive Media

Martin Fally,^{1,2,*} Mirco Imlau,¹ Romano A. Rupp,² Mostafa A. Ellabban,² and Theo Woike³

¹*Fachbereich Physik, Universität Osnabrück, Barbarastrasse 7, D-49069 Osnabrück, Germany*

²*Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria*

³*Institut für Mineralogie und Geochemie, Universität zu Köln, Zùlpicherstrasse 49b, D-50674 Köln, Germany*

(Received 19 January 2004; published 8 December 2004)

We introduce a model for the kinetics of grating formation during holographic recording in optically excitable two-state systems. An unexpected characteristic time dependence of the diffraction efficiency is found. We show that it originates from a nonlinear transformation of the light interference pattern into a refractive-index profile. Our findings strongly resemble and explain by nature the experimental data of two-state systems in general, here represented by two examples: sodium nitroprusside and terbium gallium garnet.

DOI: 10.1103/PhysRevLett.93.243903

PACS numbers: 42.65.Pc, 42.40.Eq, 42.70.Ln

Photorefractive materials, i.e., media that change their refractive index upon exposure with light, are of particular interest in the field of technical optics [1]. In such substances the kinetics of hologram recording—a fingerprint for the system under investigation—has ever been a subject of intensive studies. For photorefractive electro-optic crystals the temporal evolution of a light-induced spatially modulated refractive-index change is understood and explained by the famous Kiev equations [2] that fit the experimental data excellently, e.g., in $\text{LiNbO}_3 : \text{Fe}$. A number of theories dealing with various aspects of recording gratings and their kinetics was developed [3,4]. Such models and corresponding experiments discussed the occurrence of transient energy transfer [5], the exposure dependence of photochromic materials [6] or the existence of multiple phase-shifted gratings [7]. As a matter of fact, these models succeed to describe the hologram kinetics for a dominating fraction in the overall field of photosensitive media. However, it is realized that several photosensitive systems have been discovered and extensively studied within the last several years, for which the temporal behavior of hologram recording cannot be explained by those models [8–10]. Astonishingly the kinetics of these new materials at first glance reveals similar characteristics, but the origin of their photosensitivity is entirely different. Thus we classify them as *unconventional photorefractive media*. They can be characterized by the following criteria: occurrence of photorefractive in spite of their centrosymmetry so that a linear electro-optic effect is forbidden, a transient kinetics of the diffraction efficiency for recording with mutually parallel polarization, and the particular possibility to record holograms with orthogonally polarized waves [11,12].

Here, we focus on this class of photorefractive media having in common *one* essential property: the existence of two states that can be optically excited. This class comprises media with completely different origins of the photorefractive response such as, e.g., photorefractive

garnets [8,13–15], nitroprussides [9,16], or crystals with DX center defects [10,17,18]. Although the recording of holograms has been investigated intensively in these media a convincing description of the respective kinetics is still missing and cannot be explained by the well-known models. Here, we show that the existence of two optically sensitive states is the key property for understanding the holographic grating formation and develop a model as follows. Starting from a general optically sensitive system with two states we derive an equation for the diffraction kinetics during grating formation, fit the corresponding function to experimental data of selected systems, and address the far reaching predicted consequences. The strength of the model is the validity for a wide range of different photosensitive media and its generality due to only three assumptions: (1) the existence of photoactive centers with the probability to occupy two states, (2) a photoreaction of first order, and (3) that a deexcitation does not occur, i.e., the excited state is sufficiently stable. It is obvious that these presuppositions are fulfilled by a number of different systems, e.g., $\text{Tb}_3\text{Ga}_5\text{O}_{12}$ (TGG), $\text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12}$, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (SNP), $\text{CdF}_2:\text{Ga}$, $\text{AlGaAs}:\text{Te}$, or $\text{CdZnTe}:\text{Cl}$. We emphasize that a detailed microscopic knowledge about the photosensitive effect is not required, thus facilitating the treatment of the problem and additionally retaining the model's general validity.

Typical holographic recording experiments are performed by illuminating a photosensitive sample with two plane light waves of intensity I_R and I_S , the so-called two-wave mixing setup. The beams are interfering at the position of the sample under a crossing angle θ_B and thus result in a sinusoidal interference pattern $I(x) = I_0[1 + m \cos(Kx)]$ [see inset Fig. 3(a)]. Here, $I_0 = I_R + I_S$ denote the total intensity, $m = 2\sqrt{I_R I_S}/I_0$ the intensity modulation, and $K = 2\pi/\Lambda$ the spatial frequency with Λ the grating spacing. In a photorefractive substance the spatially modulated light is transformed into a spatial refractive-index pattern, i.e., a hologram is recorded.

Now we consider a photorefractive system that is characterized by the existence of exactly two optically active states A, B , i.e., that the change in the population fraction $p_{A,B}$ of the states linearly depends on the illumination with light. Moreover, the system is *fully bistable* so that $p_A + p_B = 1$. Illumination of the system with light of intensity I will result in a population and depopulation of the two states, respectively. In the simplest case of first order kinetics the rate equations are governed by

$$\frac{dp_i}{dt} = (-\gamma_i p_i + \gamma_j p_j)I, \quad i \neq j = \{A, B\}. \quad (1)$$

Here γ_i denote the reaction constants and I the intensity of the light. The solution of this system of differential equations yields a simple monoexponential time dependence of the population fraction

$$p_A(t) = \Delta p \exp(-\gamma t) + p_\infty, \quad (2)$$

with three parameters that characterize the particular system: $p_\infty = p_A(t = \infty)$, $\Delta p = p_A(t = 0) - p_\infty$, and $\gamma = \sum \gamma_i$. The reaction constants in general are wavelength dependent.

Let us assume the special case that we expose the system to a sinusoidal light interference pattern. Then the kinetics of the population fraction, expanded in a Fourier series, obey

$$\begin{aligned} p_A(t, x) &= 1 - p_B(t, x) \\ &= \Delta p e^{-q} \left[I_0(mq) + 2 \sum_{s=1}^{\infty} (-1)^s I_s(mq) \right. \\ &\quad \left. \times \cos(sKx) \right] + p_\infty \end{aligned} \quad (3)$$

with the convenient abbreviation $q = tI_0\gamma$ and I_s the modified Bessel function of order s . Here, q is a dimensionless quantity, the reduced exposure, that relates to the experimentally defined exposure by $Q = q/\gamma = qQ_0$. It is evident that the sinusoidal light interference pattern is transformed into a time dependent population fraction pattern that deviates more and more from a simple sinusoidal form with ongoing time. Thus, Fourier coefficients of higher harmonics become increasingly important. A simulation of the population fraction $p_B(t, x)$ at various times is shown in Fig. 1. It can be seen that in the photostationary state $p_B(t \rightarrow \infty, x)$ approaches spatial homogeneity again.

The key in understanding the kinetics of grating formation during holographic recording is given by inspecting the first harmonic's Fourier coefficient $p_B^{(1)}(q, m)$ of the function Eq. (3)

$$p_B^{(1)}(q, m) = 2\Delta p e^{-q} I_1(mq). \quad (4)$$

Therefore, we will shortly discuss the general properties of $p_B^{(1)}$ from Eq. (4). For $0 < m \leq 1$ the function increases, passes a maximum at a value q_{\max} , and decays to zero. In Fig. 2 a contour plot of the kinetics demon-

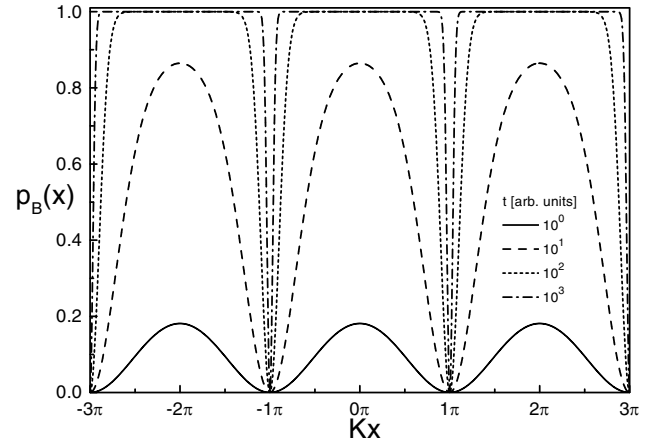


FIG. 1. Kinetics of the population fraction $p_B(x, t)$ for a sinusoidal light intensity distribution at different times (arbitrary units) with $\Delta p = 1$, $p_\infty = 0$, and $m = 1$.

strates this behavior. Note that the value q_{\max} at which the maximum occurs (dashed line) does not strongly depend on the modulation: $q_{\max}(m = 1) = 1.55$. In the limit of large q we find an asymptotic approximation for $p_B^{(1)}(q, m) \rightarrow e^{(m-1)q} / \sqrt{2\pi m q}$. Hence for the particular case of $m \equiv 1$, i.e., the recording beams have equal intensities $I_R = I_S$, the function decays proportional to $q^{-1/2}$. Note also that for $p_B^{(0)}(q, m)$ a monoexponential decay of the kinetics is expected only for homogeneous illumination, i.e., $m \equiv 0$.

At this point the photorefractive response must be included. In principle any dependence of the light-induced refractive-index changes $n_{li}(x)$ on the population fraction $p_B(x)$ can be accounted for. The case of photochromic materials with an exponential dependence of the light-induced absorption on exposure was studied in

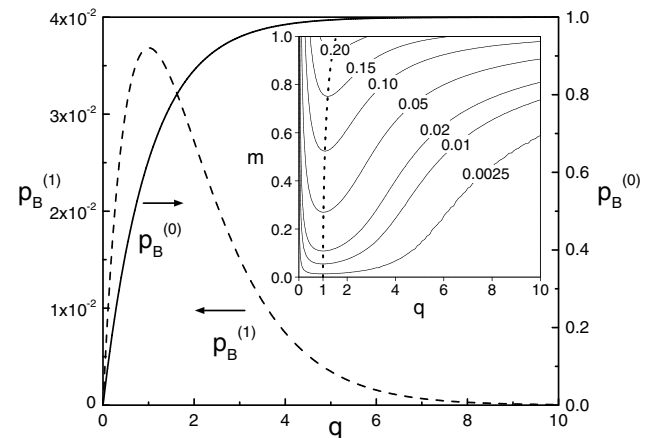


FIG. 2. Kinetics of the zeroth (solid line, right scale) and first (dashed line, left scale) order Fourier coefficients $p_B^{(0)}(q, 0.1)$, $p_B^{(1)}(q, 0.1)$ for a modulation $m = 0.1$ and $\Delta p = 1$. The inset shows the full function $p_B^{(1)}(q, m)$ as a contour plot. Solid contour lines indicate constant values of $p_B^{(1)}(q, m)$; the dotted line marks the position q_{\max} of the maximum value.

Ref. [6]. In a good approximation, derived from the Clausius-Mossotti relationship, we assume that the changes of the refractive index depend linearly on the population changes, i.e., $n_{li}(t, x) = c p_B(t, x)$. This implies that the spatial variation of the refractive index resembles that of the population changes. Therefore also higher harmonics appear in a Fourier series expansion of the refractive-index changes $n_{li}(t, x) = n_0(t) + n_1(t)\cos(Kx) + n_2(t)\cos(2Kx) + \dots$. Hence, we can assign corresponding terms in the expansion of Eq. (3) to those of the refractive index. In experiments each Fourier coefficient is accessed by measuring the diffraction efficiency $\eta^{(s)} = I_D^{(s)} / (\sum_s I_D^{(s)})$ of order s at the corresponding angle $\theta_B^{(s)}$. This quantity relates theory and experiment. For thin gratings the efficiency of the first diffraction order reads [19]

$$\eta^{(1)}(q, m) = \left[\frac{n_1(q, m)\pi d}{\lambda \cos\theta_B^{(1)}} \right]^2. \quad (5)$$

Here, d is the thickness of the grating, λ the wavelength of light, and $n_1 = c p_B^{(1)} = c \Delta p I_1(mq) e^{-q}$. It can be seen from Fig. 1 that in the photostationary state, i.e., in the limit $q \rightarrow \infty$, we end up with a *homogeneous* refractive index again which differs from that of an unexposed sample. The amplitude of the refractive-index change then is $\Delta n = n_0(q=0) - n_0(q \rightarrow \infty) = c \Delta p$ which can be evaluated from the experimental data. Inspecting Eq. (5) in combination with the exposure dependence of $p_B(q)^{(1)}$ presented in Fig. 2 it is evident that the first order diffraction efficiency increases, passes a maximum, and finally decays to zero as a function of exposure. Such a behavior is rather unusual for common (electro-optic) photorefractive materials. In case of appearance these kinetics is frequently attributed to compensating gratings [20]. We emphasize that for the particular case of SNP it was proven that this explanation was not consistent with the experimental findings [21]. The model discussed above and the equations developed here hence offer a new interpretation for such temporal behavior of hologram formation.

As an example for optically sensitive two-state systems with a photorefractive response we reinvestigated SNP [22]. To demonstrate the generality of the model we chose in addition a completely different substance, the garnet TGG:(Ce,Ca) (see Table I). In Fig. 3 the exposure dependence of the first order diffraction efficiency is shown during recording. As presented by the dashed lines in Fig. 3 we fitted the diffraction efficiency as a function of exposure for SNP and TGG by employing Eq. (5). The agreement between data and fit is quite satisfactory with reduced χ^2 values in the vicinity of 1. χ^2 is defined as the weighted sum of the quadratic deviations between the model function and the experimental data as usual. In addition the fitted physical parameters shown in Table II correspond well to the values derived experimentally

TABLE I. Experimental parameters of holographic recording for SNP and TGG with λ_p the recording wavelength, Λ the grating spacing, m the modulation, d the grating thickness, and T the temperature.

| Substance | λ_p [nm] | Λ [nm] | m | d [mm] | T [K] |
|-----------|------------------|----------------|-------|----------|---------|
| SNP | 514 | 752 | 0.089 | 0.15 | 100 |
| TGG | 458 | 4340 | 0.51 | 5.0 | 295 |

from other optical methods, e.g., $\Delta n = 1.2 \times 10^{-2}$ in [23]. Comparing the degree of modulation m obtained by the fit and that of the incident interference pattern differences are noticed. This can be due to the fact that the modulation of the interference pattern inside the crystal is reduced as compared to outside [24]. Another reason is that the minimum of the least-squares function along the m direction is shallow, i.e., a variation in this parameter does not significantly change the χ^2 value.

We now shortly discuss the strengths, limits, and consequences of the model. The strengths of the presented model are its generality and the consistent description of the kinetics with only three free parameters. We emphasize that the assumption of an optical two-state system shall be applicable to a lot of systems including photo-

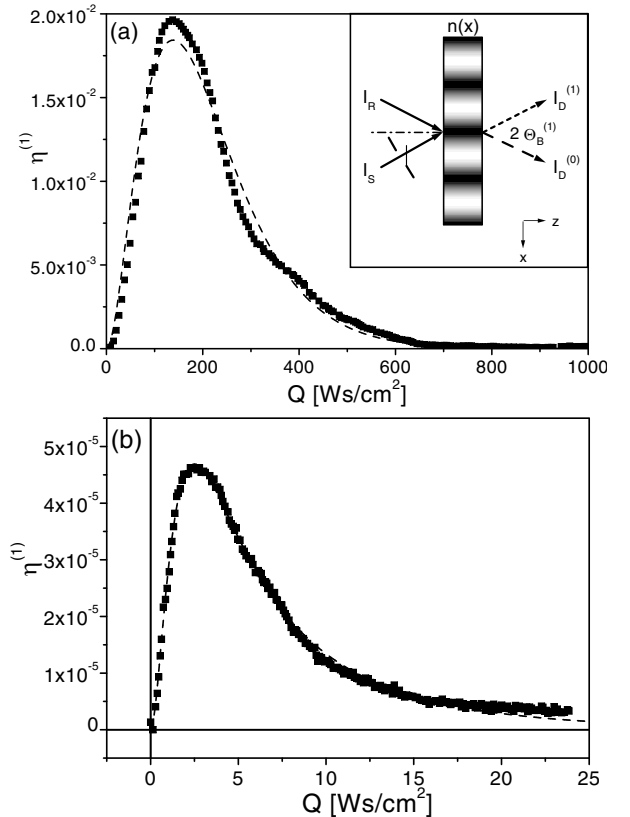


FIG. 3. Diffraction efficiency $\eta^{(1)}(Q = qQ_0)$ as a function of exposure during recording for (a) SNP [22] and (b) TGG. For details of recording see Table I. Inset: Scheme of a two-wave mixing setup. The solid lines are fits to the data using Eq. (5).

TABLE II. Fitting parameters for SNP and TGG with Δn the refractive-index change in the photostationary state, $Q_0 = 1/\gamma$ and m the modulation.

| Substance | Δn | $Q_0 = 1/\gamma$ [Ws/cm ²] | m |
|-----------|----------------------|--|-------|
| SNP | 1.5×10^{-2} | 138.3 | 0.020 |
| TGG | 5.2×10^{-7} | 1.84 | 0.914 |

chromic materials. Among the tentative candidates that we found by a first survey are a dye-doped polymer [25], Ca₃Mn₂Ge₃O₁₂ [11], CdF₂:Ga [26], AlGaAs:Te [27], CdZnTe:Cl [17], and the ferroelectric Bi₄Ti₃O₁₂ [20]. A limiting assumption of the presented model is the linear relation between the refractive-index change n_{ji} and the population fraction p_B . However, even if the dependence is more complex than assumed, Eq. (3) holds. Only the series expansion of the refractive index must be adapted. Moreover, to meet a regime of linearity is basically a question of choosing proper conditions, e.g., wavelengths.

Several important consequences are arising out of the model. Among them we expect a kinetics different from an exponential decay even for the transmitted beam. Moreover, the functional dependence of the kinetics strongly depends on the modulation of the interference pattern. Finally, the most exciting prediction is the mandatory existence of higher harmonics, i.e., diffraction orders, even for thick gratings ($m = 1$) that follow their own kinetics.

Summarizing, we proposed a general model to describe the temporal behavior of transmission and diffraction properties during holographic recording in optically excitable two-state systems with photorefractive response. To verify our model we chose two crystals with completely different origin of photorefraction and experimentally determined the kinetics of grating formation. We found that the diffraction efficiencies agree very well with the theoretical curves fitted according to Eq. (5). Moreover, the model mandatorily predicts higher diffraction orders and a noticeable dependence of the kinetics on modulation.

Financial support by the FWF (P-15642) and the DFG (IM 37/2-1) is acknowledged. One of the authors (M.F.) thanks the German Research Foundation for granting a visiting professorship in the Mercator Programme at the Universität Osnabrück (OS-55/12-1). We are indebted to L. Ackermann for providing us with the garnet crystals.

*Electronic address: Martin.Fally@univie.ac.at

[1] *Photorefractive Effects and Materials*, edited by P. Günter and J.-P. Huignard, Topics in Applied Physics Vol. 62 (Springer-Verlag, Berlin, Heidelberg, New York, 1987).

- [2] N.V. Kukhtarev, V. B. Markov, S. G. Odulov, M. S. Soskin, and V. L. Vinetskii, *Ferroelectrics* **22**, 949 (1979).
- [3] R. Magnusson and T. K. Gaylord, *J. Appl. Phys.* **47**, 190 (1976).
- [4] V. L. Vinetskii, N.V. Kukhtarev, S. G. Odulov, and M. S. Soskin, *Sov. Phys. Usp.* **22**, 742 (1979).
- [5] N. Kukhtarev, V. Markov, and S. Odulov, *Opt. Commun.* **23**, 338 (1977).
- [6] W. J. Tomlinson, *Appl. Opt.* **14**, 2456 (1975).
- [7] A. E. Attard and T. X. Brown, *Appl. Opt.* **25**, 3253 (1986).
- [8] B. Sugg, H. Nürge, B. Faust, E. Ruža, R. Niehüser, H.-J. Reyher, R. A. Rupp, and L. Ackermann, *Opt. Mater.* **4**, 343 (1995).
- [9] T. Woike, S. Haussühl, B. Sugg, R. A. Rupp, J. Beckers, M. Imlau, and R. Schieder, *Appl. Phys. B* **63**, 243 (1996).
- [10] R. A. Linke, T. Thio, J. D. Chadi, and G. E. Devlin, *Appl. Phys. Lett.* **65**, 16 (1994).
- [11] B. Sugg, Ph.D. thesis, Univ. Osnabrück, 1996 (Shaker Verlag, D-52013 Aachen, ISBN 3-8265-1760-1).
- [12] M. Imlau, T. Woike, R. Schieder, and R. A. Rupp, *Europhys. Lett.* **53**, 471 (2001).
- [13] V. A. Bedarev and S. L. Gnatchenko, *Low Temp. Phys.* **20**, 124 (1994).
- [14] A. B. Chizhik, I. I. Davidenko, A. Maziewski, and A. Stupakiewicz, *Phys. Rev. B* **57**, 14366 (1998).
- [15] V.V. Eremenko, S. L. Gnatchenko, I. S. Kachur, V. G. Piryatinskaya, M. B. Kosmyna, B. P. Nazarenko, and V. M. Puzikov, *Appl. Phys. Lett.* **79**, 734 (2001).
- [16] T. Woike, M. Imlau, S. Haussühl, R. A. Rupp, and R. Schieder, *Phys. Rev. B* **58**, 8411 (1998).
- [17] T. Thio, J.W. Bennett, D. Chadi, R. A. Linke, and P. Becla, *J. Cryst. Growth* **159**, 345 (1996).
- [18] A. I. Ryskin, A. S. Shcheulin, and D. E. Onopko, *Phys. Rev. Lett.* **80**, 2949 (1998).
- [19] H. J. Eichler, P. Günter, and D.W. Pohl, *Laser-Induced Dynamic Gratings* of Springer Series in Optical Sciences Vol. 50 (Springer, Berlin, 1986).
- [20] X. Yue, J. Xu, F. Mersch, R. A. Rupp, and E. Krätzig, *Phys. Rev. B* **55**, 9495 (1997).
- [21] M. Imlau, S. Haussühl, T. Woike, R. Schieder, V. Angelov, R. A. Rupp, and K. Schwarz, *Appl. Phys. B* **68**, 877 (1999).
- [22] M. Imlau, T. Woike, R. Schieder, and R. A. Rupp, *Phys. Rev. Lett.* **82**, 2860 (1999).
- [23] M. Imlau, T. Woike, D. Schaniel, J. Schefer, M. Fally, and R. A. Rupp, *Opt. Lett.* **27**, 2185 (2002).
- [24] U. Van Stevendaal, K. Buse, H. Malz, H. Veenhuis, and E. Krätzig, *J. Opt. Soc. Am. B* **15**, 2868 (1998).
- [25] N. Menke, B. Yao, Y. Wang, Y. Zheng, M. Lei, G. Chen, Y. Chen, M. Fan, Y. Han, and X. Meng, *Acta Photonica Sin.* **32**, 819 (2003).
- [26] A. I. Ryskin, A. S. Shcheulin, E. V. Miloglyadov, R. A. Linke, I. Redmond, I. I. Buchinskaya, P. P. Fedorov, and B. P. Sobolev, *J. Appl. Phys.* **83**, 2215 (1998).
- [27] R. A. Linke, A. S. Shcheulin, A. I. Ryskin, I. I. Buchinskaya, P. P. Fedorov, and B. P. Sobolev, *Appl. Phys. B* **72**, 677 (2001).