

Charge Carrier Photoexcitation and Two-Wave Mixing in Dichroic Materials

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We give experimental and theoretical evidence that two-wave mixing light amplification in electro-optic and photoconductive materials is dramatically influenced by an anisotropic photoexcitation cross section of mobile charge carriers. An enhancement of the two-wave mixing gain is predicted and an increase of 90% is observed in a dichroic Ni doped KNbO_3 crystal in a geometry with large angles between the two wave propagation directions. The enhancement is possible because in anisotropic materials the photogeneration can lead to higher modulation depths as compared to the depth of light intensity modulation. [S0031-9007(97)04316-0]

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In dichroic photoconductive materials the photoexcitation of a charge carrier from a localized to a mobile state depends on the polarization of the incident light. One is led to expect that this anisotropy influences the formation of dynamic space-charge gratings (photorefractive gratings) generated in these materials as a result of the interference of two light waves [1–3]. In electro-optic media such gratings give rise to interesting nonlinear optical effects already for light intensity as low as a few mW/cm^2 [4–7]. In this Letter, for the first time to our knowledge, we give experimental and theoretical proof that the anisotropy of the photoexcitation of mobile carriers influences dramatically the strength of the resulting optical nonlinearity. For the experimental demonstration we measure the coherent amplification of a signal wave at the expense of a pump wave in a process which is called two-wave mixing or two-beam coupling [6]. Two-wave mixing amplification is probably the most unique and useful phenomenon induced by photorefractive gratings and provides the basis for a number of applications involving optical oscillators [8], laser beam cleanup [9], and phase conjugation [10]. The knowledge of the expected amplification gain in given configurations is of primary importance for such applications.

We present new theoretical predictions for the exponential two-wave mixing gain. Our model considers the anisotropy of photoexcitation and introduces the so called “usefully” dissipated energy, that is, the optical energy which is locally dissipated for the photogeneration of mobile charge carriers. The experimental results are in excellent agreement with the new expressions and cannot be described by the conventional theory used up to now for these phenomena [4]. This fact also demonstrates that the light intensity, e.g., the optical energy flow per unit area, which is conventionally used as the quantity driving the charge redistribution process, is not directly related to the

physics of the problem. For dichroic materials the spatial distributions of light intensity and usefully dissipated energy can differ strikingly. Therefore, in some geometries two-wave mixing gains are largely enhanced with respect to what is expected from the light intensity modulation depth.

There are numerous arguments contradicting the use of light intensity for describing the process under investigation here. The light intensity $I(\vec{r})$ as a measure of energy flow per unit surface can be best calculated using the Poynting vector $\vec{S}(\vec{r})$ of the wave [11]. In an optical anisotropic material the vector $\vec{S}(\vec{r})$ associated with the superposition of two plane waves changes direction as a function of position. One cannot find any scalar quantity to insert in the photoexcitation rate equations used conventionally [4]. Furthermore, two plane waves of equal intensity which are exactly counterpropagating in a medium can create a space-charge modulation [12,13] even though $\vec{S}(\vec{r}, t) = \vec{0}$ and no spatial modulation of intensity exists.

We demonstrate experimentally below that the primary quantity that governs the formation of space-charge gratings is the dissipated energy density $w(\vec{r})$ which is used to generate free charges; therefore, it is dissipated in a useful way for the process of interest. It is expressed as

$$w(\vec{r}) = \frac{1}{2} \epsilon_0 [\vec{E}(\vec{r}) \cdot \vec{\kappa} \cdot \vec{E}^*(\vec{r})], \quad (1)$$

where ϵ_0 is the permittivity of vacuum and $\vec{E}(\vec{r})$ is the complex amplitude of the total optical electric field obtained by the coherent superposition of optical waves. The second-rank tensor $\vec{\kappa}$ describes the anisotropy of the photoexcitation processes and is related to the imaginary part $\vec{\epsilon}''$ of the material dielectric tensor $\vec{\epsilon} = \vec{\epsilon}' + i\vec{\epsilon}''$. We define the tensor elements as

$$\kappa_{kl} = \phi_{kl}(\epsilon'')_{kl}, \quad (2)$$

where the quantities ϕ_{kl} describe the light polarization dependence of the quantum efficiency, that is, the probability that an absorbed photon of given polarization produces a photoexcited mobile carrier. In Eq. (2) no summing over equal indices is performed. In the case of 100% quantum efficiency the usefully dissipated energy $w(\vec{r})$ equals the locally dissipated energy $u(\vec{r}) = \frac{1}{2}\epsilon_0[\vec{E}(\vec{r}) \cdot \vec{\epsilon}'' \cdot \vec{E}^*(\vec{r})]$ [14].

In view of the above argumentations the density rate $\partial n(\vec{r})/\partial t$ of charge carriers that makes a transition from an immobile to a mobile state takes the form

$$\frac{\partial n(\vec{r})}{\partial t} = \frac{\epsilon_0}{4\hbar}[\vec{E}(\vec{r}) \cdot \vec{\kappa} \cdot \vec{E}^*(\vec{r})]\frac{N(\vec{r})}{N_0} + \beta N(\vec{r}), \quad (3)$$

where $N(\vec{r})$ is the density of photoexcitable carriers in the non mobile state and has an average value N_0 . β is the rate describing thermal transitions. In the framework of a model that assumes only one kind of energy level for the localized carriers the above equation has to replace the expression of the kind $\partial n(\vec{r})/\partial t = [sI(\vec{r}) + \beta]N(\vec{r})$ contained within the rate equations (1) in Ref. [4], where $I(\vec{r})$ is the light intensity and s is a photoexcitation constant describing optical transitions regardless of light polarization. Equation (3) should be combined with terms describing carrier transport and carrier recombination to the nonmobile state and with the Gauss equation that relates the static space-charge electric field to the charge distribution [4]. Linearizing all the equations in a similar way as in Ref. [4] one can calculate the expected amplitude of the resulting space-charge electric field E_{sc} . Finally, using also the vector wave equation one determines the energy exchange for two-wave mixing interaction between a pump P and a signal wave S . We give here only the final expression for the exponential gain Γ with which the intensity I_S of the signal wave is amplified in a two-wave mixing process. For the weak signal regime ($I_S \ll I_P$) one has $I_S(z) = I_S(z=0)\exp(\Gamma z - 2\alpha_S z)$ with $\alpha_S = \pi(\hat{e}_S \cdot \vec{\epsilon}'' \cdot \hat{e}_S)/[\lambda n_S(\hat{e}_S \cdot \hat{d}_S)|\cos\theta_S|]$ [3] and

$$\Gamma = \frac{2\pi}{\lambda} \frac{n_S n_P^2}{\cos\theta_S} (\hat{e}_P \cdot \hat{d}_P) \frac{(\hat{e}_S \cdot \vec{\kappa} \cdot \hat{e}_P)}{(\hat{e}_P \cdot \vec{\kappa} \cdot \hat{e}_P)} r_{\text{eff}} E_{sc,i}, \quad (4)$$

where λ is the vacuum wavelength of the light, n_S and n_P are the refractive indices for the waves S and P , respectively, θ_S is the angle between the Poynting vector of the wave S and the coordinate z normal to the entrance surface in the medium, $\hat{e}_S$ ($\hat{e}_P$) is the unit vector in the direction of the electric field for the wave S (P), $\hat{d}_S$, $\hat{d}_P$ are the corresponding unit vectors in direction of the electric displacement vectors, r_{eff} is an effective linear electro-optic coefficient valid for the particular experimental geometry [15], and $E_{sc,i}$ is the amplitude of the space-charge field component which is shifted by $\pi/2$ with respect to the fringes defined by Eq. (1) [3]. Equation (4) contains six terms on the right-hand side. The second and third term differ slightly from the expression used conventionally (see, for instance, Ref. [16]) because they now properly contain all the

corrections due to refractive index anisotropies. These corrections are particularly significant for materials with large optical anisotropy, such as organic crystals and liquid crystals. The fourth term contains the tensor $\vec{\kappa}$ and is responsible for the striking effects of photoexcitation anisotropy verified experimentally below. If $\vec{\kappa}$ is isotropic the fourth term on the right-hand side of Eq. (4) reduces to the conventional projection ($\hat{e}_S \cdot \hat{e}_P$) [4,5,16].

We verify Eq. (4) using a dichroic photorefractive KNbO₃ crystal. It was a Ni doped crystal with dimensions $a \times b \times c = 4.6 \times 5.8 \times 6.0$ mm³. The dopant level in the melt used to produce the raw boule contained Ni and Nb in an atomic ratio of 0.003. The orthorhombic point group symmetry $mm2$ of KNbO₃ allows for three different diagonal elements of the tensors $\vec{\epsilon}'$, $\vec{\epsilon}''$, and $\vec{\kappa}$ [14]. All experiments were performed using Ar⁺-laser light at the wavelength $\lambda = 514$ nm for which the absorption constants were measured to be $\alpha_a = 0.77$ cm⁻¹, $\alpha_b = 2.43$ cm⁻¹, and $\alpha_c = 0.89$ cm⁻¹. The two-wave mixing experiments described below were performed with p -polarized beams propagating in the crystal bc plane (see Fig. 2). Therefore we are interested only in the ratio $\alpha_b/\alpha_c = 2.7$ that corresponds to a ratio $(\epsilon'')_{22}/(\epsilon'')_{33} = 3.0$ for the imaginary dielectric tensor.

It is important to verify if and how the anisotropy of $\vec{\epsilon}''$ translates into an anisotropy of the photoexcitation tensor $\vec{\kappa}$. The tensor element κ_{ii} is proportional to the density n_0 of mobile charges photoexcited by light polarized along the crystalline axes i . The density n_0 is directly proportional to the photoconductivity $\sigma_{ph} = e\mu n_0$, with e being the elementary charge and μ being the carrier mobility. Because the photoconductivity ratio for different light polarizations can be precisely determined experimentally, we can use this ratio to determine the ratio between the diagonal elements of $\vec{\kappa}$. We have performed photoconduction experiments using a holographic technique similar to the one in Ref. [17]. The time constant for photoerasure of a space-charge grating under the influence of an erasing beam polarized either along the b - or c -crystal axis direction was measured. The space-charge field decay was monitored by diffracting off the grating a 633 nm He-Ne laser beam. Care was taken that in all the volume probed by the He-Ne readout beam the erasing light intensity was the same. The decay of the space-charge grating was found to be single exponential. The exponential time constant τ is inversely proportional to the photoconductivity [7]. Figure 1 shows the results of the grating photoerasure experiments. We find a linear dependence of the inverse erasure time τ^{-1} on light intensity. However, b -polarized light erases the grating much faster. From the two slopes we extract the anisotropy ratio $\kappa_{22}/\kappa_{33} = 3.4 \pm 0.1$. This number is close to the one found above for the anisotropy of $\vec{\epsilon}''$ and suggests that in our sample the quantum efficiency for photoexcitation of mobile charges deviates only little from isotropy.

Figure 2 shows our experimental geometry for two-wave mixing. This interaction geometry is relevant from

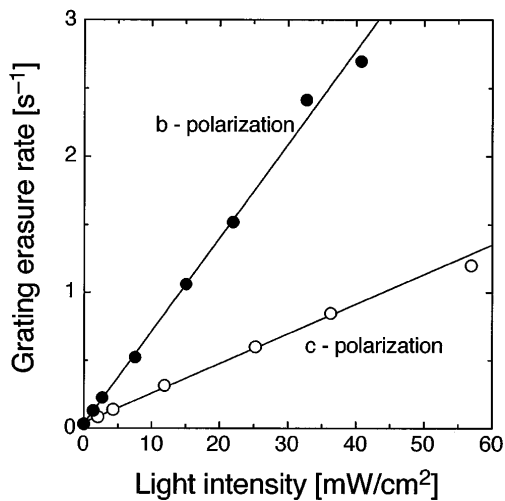


FIG. 1. Inverse erasure time τ^{-1} vs the local intensity I of the grating erasure beam ($\lambda = 514$ nm). The two sets of experimental points are valid for b and c polarization of the erasure light, respectively. From the slopes of the straight lines one determines $\kappa_{22}/\kappa_{33} = 3.4 \pm 0.1$.

a technological point of view because it is used in important applications [9]. The signal beam S enters through the c surface of the crystal under an external angle α with the surface normal. The pump beam enters through the b surface under an angle β . Both beams are horizontally polarized (bc plane). The pump beam is collimated in the horizontal direction to a width of 0.95 mm at the entrance face and is $150\times$ more intense than the signal beam.

In a first set of two-wave mixing experiments we keep the angle γ between the two beams constant and change α and β simultaneously by rotating the sample. Figure 3 shows the measured exponential gain Γ as a function of α for $\gamma = 60^\circ$. The dotted curve (no anisotropy in the tensor $\vec{\kappa}$) corresponds with the predictions of the scalar theory [4,5], which fully disagree with the measurements. In contrast, the solid line describes the measurements very well. This curve is plotted using

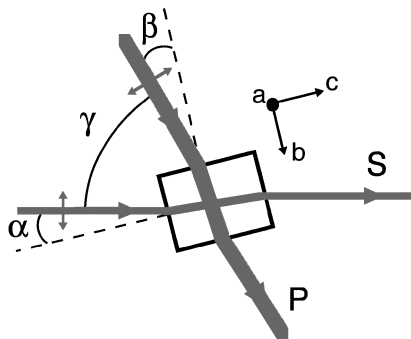


FIG. 2. Experimental configuration for two-wave mixing in dichroic KNbO_3 . The pump wave P amplifies the signal wave S . As drawn here the angles α , β , and γ are taken to be all positive so that $\alpha + \beta + \gamma = 90^\circ$.

Eq. (4) and the anisotropy $\kappa_{22}/\kappa_{33} = 3.4$ determined above, and with the value of the space-charge electric field $E_{sc,i}$ calculated using the known material properties, i.e., the effective number of traps $N_{\text{eff}} = 5.3 \times 10^{16} \text{ cm}^{-3}$, measured previously for this crystal [18]. No parameters were adjusted to plot the solid curve. Our theory predicts correctly the point at which the gain crosses zero, which is a well defined characteristic of the dichroism. While for the conventional models the crossing point should occur whenever the electric field vectors of the two waves are orthogonal (point B in Fig. 3), in reality we find it in accordance with Eq. (4) at the angle for which $\hat{e}_S \cdot \vec{\kappa} \cdot \hat{e}_P = 0$ (point A). In order to clarify this point further we have drawn schematically in the inset in Fig. 3 the relative orientation of the important vectors for the crystal orientations corresponding to points A and B.

In the previous experiment the fringe spacing Λ of the interference pattern was almost constant. We want to test our theory also in the case where the grating period varies significantly. This was done in a second set of experiments for which the angle $\alpha = -30^\circ$ and the crystal orientation were kept fixed while the pump wave angle β was changed. Figure 4 compares again the results of both theories. The dotted curve gives again the exponential gain Γ predicted by the scalar theory ($\kappa_{22}/\kappa_{33} = 1$). It clearly fails to describe the measurements satisfactorily. The solid curve is plotted using the same parameters as in Fig. 3 and reproduces well the gain crossing point and the measured data. The

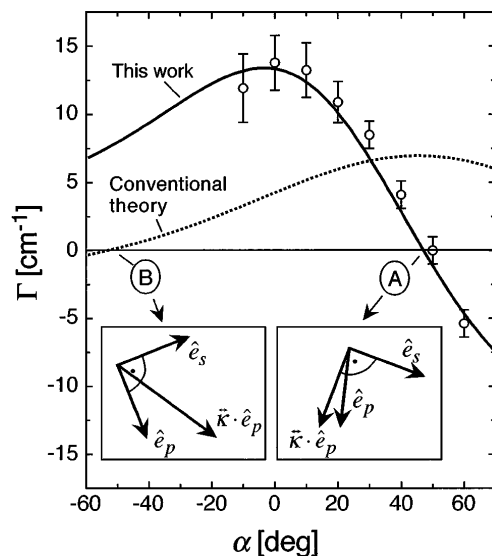


FIG. 3. Measured two-wave mixing gain Γ (circles) as a function of the angle α for $\gamma = 60^\circ$ (fixed). Dotted curve: Prediction of conventional theory [Eq. (4) with $\kappa_{22}/\kappa_{33} = 1$]. Solid curve: Prediction of Eq. (4) with $\kappa_{22}/\kappa_{33} = 3.4$ determined from the experiment in Fig. 1. Both curves are plotted using an effective density of traps $N_{\text{eff}} = 5.3 \times 10^{16} \text{ cm}^{-3}$ found in Ref. [18]. The insets show the orientations of the relevant vectors (all in the same plane) for the two gain zero-crossing points A and B.

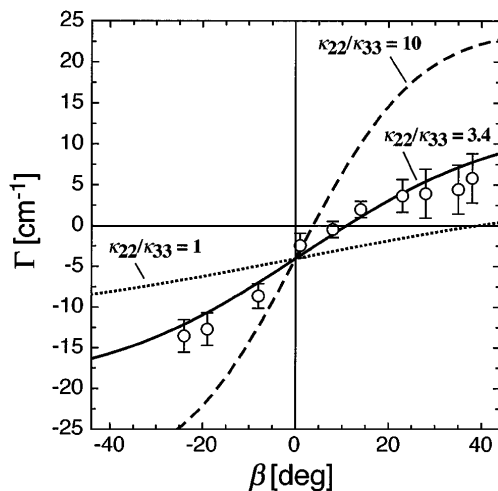


FIG. 4. Two-wave mixing gain Γ (circles) as a function of the angle β for $\alpha = -30^\circ$. The theoretical curves are plotted according to Eq. (4) with $\kappa_{22}/\kappa_{33} = 1$ (dotted line), $\kappa_{22}/\kappa_{33} = 3.4$ (solid line, determined in Fig. 1), and $\kappa_{22}/\kappa_{33} = 10$ (dashed line). The latter curve shows the possible gain enhancement for larger anisotropy.

dashed line illustrates the predicted gain if the anisotropy was $\kappa_{22}/\kappa_{33} = 10$.

The two experiments of Figs. 3 and 4 also indicate that the absolute values of the two-wave mixing gain can exceed what is expected from scalar models. This is possible because in our geometry the density rate of carrier photoexcitation $\partial n(\vec{r})/\partial t$ [Eq. (3)] has a higher spatial modulation than the light intensity. Therefore, a control of the material dichroism can lead to a large and important enhancement of two beam coupling gains. For instance, if our crystal would have a ratio $\kappa_{22}/\kappa_{33} = 34$ ($10\times$ larger than our present material), we could expect a peak gain coefficient of 70 cm^{-1} in the geometry of Fig. 3. The maximum possible according to the conventional theory is 7 cm^{-1} .

While in the configuration of Fig. 2 the anisotropy has the dramatic consequences seen in Figs. 3 and 4, in a geometry with both beams entering the sample from the same surface (transmission geometry) one finds quantitative but not qualitative differences. This is a possible reason why the effects of dichroism have been overlooked so far. Let us consider the example of our crystal in a symmetric transmission geometry with fringe spacing of $\Lambda = 0.4 \mu\text{m}$. If the beams enter through the b crystal face, the grating vector is directed along the c axis, and both beams are p polarized; the gain coefficient is reduced by about 37% for $\kappa_{22}/\kappa_{33} = 3.4$ with respect to the isotropic case. This reduction factor changes only slowly with the beam interaction angle. Therefore, previous manifestations of the effects of dichroism on two-wave mixing might have been erroneously interpreted in terms of electron-hole competition [19,20], incomplete crystal poling, or partial grating erasure due to surface reflections [12]. Most materials showing strong two-wave

mixing effects, such as BaTiO_3 and $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ are strongly anisotropic and are expected to show similar behavior as shown in this work for KNbO_3 .

In conclusion, the basics of two-wave mixing in electro-optic and photoconductive material have been rediscussed. We have proven experimentally that the usefully dissipated energy $w(\vec{r})$, and not the local light intensity $I(\vec{r})$, is the quantity driving the formation of space-charge electric field gratings. The new insights presented here might give important guidance to material researchers for improving coherent two-wave mixing light amplification by means of a control of the material dichroism.

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