Spatial-diffusion measurements in impurity-doped solids by degenerate four-wave mixing

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A method is introduced that measures the spatial-migration rate of electronic excitation in condensed media over distances of the order of 0.1 μm. Two volume holographic gratings of widely differing modulation periods are simultaneously produced, using a phase-conjugate wave geometry of degenerate four-wave mixing. Spatial migration results in a reduced scattering efficiency of one grating and is observed as a polarization rotation of the backward-going output wave. Upper limits are placed on the diffusion constants in pink ruby and Nd^{3+}-doped silicate glass.

In this Letter we extend the analogy between degenerate four-wave mixing and holography to measure the spatial-migration rate of electronic excitation in impurity-doped solids. The production of holographic phase and absorption gratings in an absorbing medium has been well studied.[1–4] In these experiments it is the Bragg scattering of an optical beam from the grating produced by the interference of an image ($\mathbf{E}_i$) and reference beam ($\mathbf{E}_{\text{ref}}$) that produces an object beam ($\mathbf{E}_o$). Such a grating can arise from the modulation of the index of refraction that is due to the polarizability difference between optically excited ions and ions in their ground state. A process to produce and monitor two such gratings simultaneously has been discussed by Eichler[5] and, more recently, in a phase-conjugate wave-generation[6] context by several authors.[7,8] The formal analogy between conjugate-wave generation and holography has been discussed by Yariv.[9]

In this dual-grating configuration, one grating is produced by impurity-ion absorption of nearly copropagating beams and has a large grating spacing (~10 μm), while the other, produced by nearly counterpropagating beams, has a much smaller spacing (~0.2 μm). When spatial migration of the excited-state population density is absent or bottlenecked, the lifetime of both gratings is determined solely by the excited-state lifetime and will be independent of grating spacing. The effect of an active spatial-transport process is to make the lifetime of the grating depend on its spacing. Here we show how this dependence can be measured by observing the state of polarization of the scattered object wave rather than by studying the beam transients, as has been done previously.[3–5,8,10]

The experimental geometry is shown in Fig. 1. Three lightly focused (f = 50 cm) equal-pathlength beams from an argon laser operating at 514.5 nm (TEM_{00}) and 500 mW overlap in an absorbing sample. The wavevectors of the two exactly counterpropagating beams are $\mathbf{K}_+$ and $\mathbf{K}_-$ ($= -\mathbf{K}_+$), with associated electric fields $\mathbf{E}_+$ and $\mathbf{E}_-$, respectively. The image beam has wavevector $\mathbf{K}_i$ and electric field $\mathbf{E}_i$, and the phase-conjugate object wave, $\mathbf{K}_o$ ($= -\mathbf{K}_i$) and $\mathbf{E}_o$. The counterpropagating beams $\mathbf{E}_+$ and $\mathbf{E}_-$ are orthogonally polarized, and $\mathbf{E}_i$ is polarized at 45° to each. In general, the output-wave polarization will be at some different angle θ relative to the direction $\mathbf{E}_-$, and we interpret this angle in terms of grating lifetimes, as explained below.

By including the vector nature of the electric fields and extending the discussion of previous authors[3,4,7,8] we find that the electric field of the scattered object wave is proportional to $\tau_q(\mathbf{E}_j \cdot \mathbf{E}_k^*)\mathbf{E}_l$, where τ_q is the lifetime of the grating with wavevector $\mathbf{q} = \mathbf{K}_j - \mathbf{K}_k$. This output wave results from the scattering of $\mathbf{E}_l$ off the grating produced by $\mathbf{E}_j$ and $\mathbf{E}_k$. In our geometry there are two such phase-matched components, and the output wave is

$$\mathbf{E}_o = \frac{i}{2\hbar}\exp(-\beta l/2)\,[1-\exp(-\beta l/2)] \times Q(\Delta\alpha)\,[\tau_{\Delta k}(\mathbf{E}_+ \cdot \mathbf{E}_i^*)\mathbf{E}_- + \tau_{2k}(\mathbf{E}_- \cdot \mathbf{E}_i^*)\mathbf{E}_+], \quad (1)$$

where β is the ground-state absorption coefficient, l is the sample length, and Q is quantum efficiency. The quantity $\Delta\alpha$ is the complex polarizability difference between the excited and ground states of the absorbing ion. For the electric-field orientations indicated in Fig. 1, the output wave will be polarized at an angle

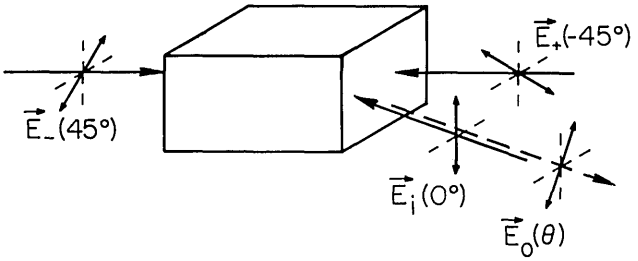

Fig. 1. The four beams have their electric fields along the indicated directions. The crossing angle between $\mathbf{K}_+$ and $\mathbf{K}_i$ is 1° (outside sample), and the polarization angle θ of $\mathbf{E}_o$ is measured from the normal of the scattering plane defined by $\mathbf{K}_+$ and $\mathbf{K}_i$.

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$$\theta = \arctan\left(1 - \frac{\tau_{2k}}{\tau_{\Delta k}}\right). \quad (2)$$

The grating decay rates can be written as $\tau_q^{-1} = \tau_0^{-1} + W(q)$, where τ_0 is the lifetime of the excited state and $W(q)$ represents the additional grating relaxation rate from spatial migration of the excitation among the impurity ions. Assuming an incoherent migration process and a mean step length much less than π/q, the spatial migration is then diffusive in character, and $W(q) = Dq^2$, where D is the diffusion constant.

It is also possible to measure τ_q by observing the temporal decay of $\mathbf{E}_o$ after $\mathbf{E}_+$ and $\mathbf{E}_i$ or $\mathbf{E}_-$ and $\mathbf{E}_i$ are turned off.[3-5,8,10] In situations in which the dynamics are in the nanosecond range, our polarization technique is especially attractive for observation of a spatial-migration process, since picosecond lasers and probe-pulse delay schemes are not required.

In particular, we have produced cw holograms in both Nd^{3+}-doped silicate glass and pink ruby and measured the polarization character of the scattered object wave. In the glass (2 wt% Nd_2O_3), the measured angle θ was less than 2°, indicating little diffusion over $\lambda/4n$ distances.[11] The radiative lifetime of the $^4F_{3/2}$ state of Nd^{3+} is about 0.3 msec, which gives an upper limit on the spatial diffusion constant of $D < 2 \times 10^{-9}$ cm^2/sec.

In the ruby, the birefringence of the Al_2O_3 host required careful attention to sample alignment because of phase-matching considerations and the possibility of elliptical field components inside the crystal. With the c axis along the direction of $\mathbf{K}_+$ and $\mathbf{K}_-$, the measured polarization angle θ again was less than 2° in samples containing 0.01 and 0.08 at% Cr^{3+}. This result indicates that the spatial migration of the ^2E excitation in ruby has a diffusion constant less than 1×10^{-10} cm^2/sec or is strongly bottlenecked because of trap sites or spatial inhomogenieties.[12] In similar and much higher (~1%) concentration ruby, measurements using a transient grating technique[5] have also shown no spatial migration over distances of the order of 0.1 μm.

The magnitude $|\Delta\alpha|$ of the difference between the complex polarizabilities of the excited and ground states can also be determined from the magnitude of the scattered object wave, as indicated in Eq. (1). At 514.5-nm wavelength, a power-reflection coefficient of 4% in ruby yielded a value of $|\Delta\alpha| \simeq 3 \times 10^{-25}$ cm^3, which is in near agreement with the recent measurement of Liao and Bloom.[8] In the Nd^{3+} glass, this reflection coefficient was 0.016%, which gives a similar value of $|\Delta\alpha| \simeq 2 \times 10^{-25}$ cm^3. From an oscillator strength calculation,[13] this polarizability difference has been estimated at 8×10^{-25} cm^3 for Nd^{3+}-doped glass.

We have discussed the use of wave polarizations in cw holography and phase-conjugate wave generation to measure directly the spatial migration of excitation in impurity-doped glasses and crystals. This technique can also be extended to exciton diffusion problems in organic systems and measurements of spatial dynamics in gases.

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