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Citation: Applied Physics Letters **55**, 2307 (1989); doi: 10.1063/1.102046

View online: http://dx.doi.org/10.1063/1.102046

View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/55/22?ver=pdfcov

Published by the AIP Publishing

Resonant excitonic optical Stark effect in GaSe

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(Received 14 July 1989; accepted for publication 25 September 1989)

The time-resolved nonlinear transmission of bulk ϵ-GaSe has been studied in the femtosecond regime when resonantly exciting the material in the vicinity of the exciton at room temperature. Two regimes are evidenced. At early time delay, a blue shift of the exciton with no linewidth broadening can be related to optical Stark effect, while at longer time delay the usual exciton screening and band-gap renormalization due to real electronic transitions is observed. At resonance, a dependence of the Stark shift with the amplitude of the exciting field is obtained, as predicted by a simple "dressed-atom" model.

In the past few years, a great wealth of results has been obtained in the field of optical Stark effect. Most of the interest was focused on the off-resonance study of III-V multiquantum well structures as far as semiconductors are concerned.[1–4] We report here on resonant excitonic excitation in bulk GaSe.

Gallium selenide, in its ϵ form, crystallizes in the D^1_{3h} symmetry and has a layered structure. The electronic band structure in the center of the first Brillouin zone is quite flat; the reduced electron-hole mass is five times larger than that in GaAs.[5] The exciton bound to the gap has, therefore, a strong binding energy of 20 meV. The phonon broadening of the exciton at room temperature is of the order of 10 meV, so that it is easily observed in an optical transmission experiment.[6] This feature is more commonly found in multiple quantum well structures due to confinement effects. The exciton energy, as measured from the top of the valence band, is 2 eV, coincident with the central photon energy of the laser used in this work.[7] The first excitonic excited state lies 20 meV above the ground state. In the D^1_{3h} group the dipolar transition is forbidden in our transmission geometry $E \perp C$, where C is the optical axis orthogonal to the layers. However, excitonic absorption is partly allowed due to spin-orbit coupling, and its oscillator strength is one order of magnitude less than in allowed geometries. For all these aspects, GaSe is a very good candidate when one is interested in room temperature, excitonic resonance of nonlinear optical properties.[8]

The GaSe sample was prepared using the Bridgman method and was not intentionally doped. A small part of a 1×1 cm^2 platelet of ϵ-GaSe was carefully peeled down and its thickness measured using a white light interferometric technique in the transparency regime, combined with the optical index data available in the literature[9–11] and was found to be 15 ± 1 μm.

We could not achieve antireflection coating of the sample using our currently available evaporation techniques. This unfortunate situation is related to the complete bound saturation of the layers.

Our experiments were performed using a transmission pump-prope technique. Light pulses are generated by a dispersion compensated colliding pulse mode-locked dye laser[12] whose duration is adjusted to ~ 150 fs in order to match the spectral bandwidth to the exciton width. These pulses are amplified up to 3 μJ through a two-stage amplifier pumped by a 20 Hz repetition rate, doubled Nd:YAG laser. The six-pass preamplifier has been described elsewhere[13] and the second stage is a 3-cm-long, transversally pumped cell. By changing the dye in the latter cell from kyton red to sulforhodamine 101, in water we are able to downshift the central photon energy of the pulses by 9 nm. The pulses were split into two. One pulse was used as a pump having a maximum energy of 1 μJ; the other one was passed through a 2-cm-long monomode fiber to generate a continuum. After recompression through a prism-based double-pass dispersive delay line, the duration of the continuum was of the order of 20 fs, and the spectral full width at half height was of the order of 40 nm. This method eliminates spurious effects due to spectral chirps in the continuum. Pump and probe were orthogonally polarized to allow for elimination of the pump light scattered by the sample before spectral analysis by an optical multichannel analyzer.

The probe spectra transmitted through the sample showed the usual Perot–Fabry fringe pattern due to the high reflectivity ($\sim 25\%$) of the air-sample interfaces. A Fourier analysis of the transmitted spectra clearly shows in the time domain the various reflections of the probe pulse inside the Perot–Fabry cavity, as well-separated contributions delayed by ~ 300 fs. By eliminating these multireflected pulses, we were able to get rid of the fringes after inverse Fourier processing.

Figure 1 shows absorption spectra (αd) of ϵ-GaSe under resonant excitation for various time delays between pump and probe and an intensity of 8 GW/cm^2, correspond-

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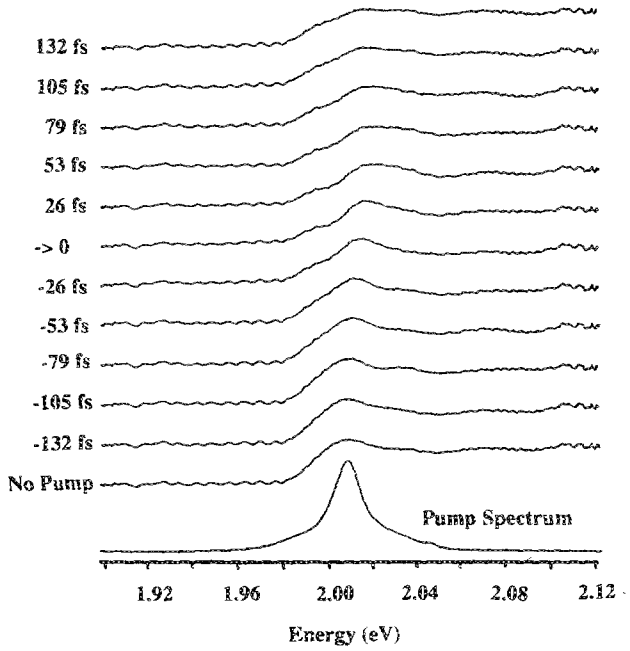

FIG. 1. Absorption spectra (αd vs energy) of ϵ-GaSe for various pump-probe time delays.

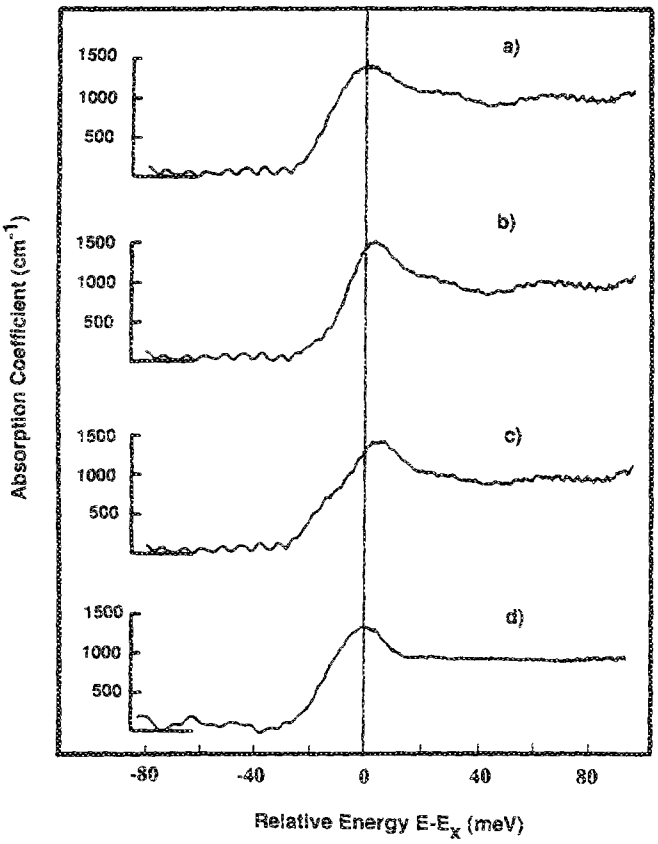

FIG. 2. Exciton shift for different detunings for the same time delay (-- 70 fs) and comparable pump intensities (a) reference spectrum, (b) excitation 9 meV below the exciton, (c) exitation at resonance, and (d) excitation 14 meV above the exciton.

ing to a maximum carrier density of $4\times10^{17}\,\mathrm{cm}^{-3}$. The excitonic blue shift is so large under such conditions—up to 10 meV—that there is no need for any differential technique. The bottom spectrum is an unperturbed reference absorption of the sample. One can easily distinguish two regimes in Fig. 1. At early times the exciton peak undergoes a blue shift with no relevant broadening. We propose here to interpret this early shift as being due to optical Stark effect. At longer time delays, the excitonic and free-carrier populations generated by the real electronic transitions induced by the pump photons strongly affect the absorption spectrum. The exciton is further shifted toward the blue due to screening effects by both excitons and free carriers. It eventually broadens and disappears due to ionization and scattering. At even longer time delays (>300 fs) band-gap renormalization takes place. These later features are long lasting because real electronic populations are responsible for them.

In Fig. 2, the behavior of the exciton is shown as a function of the detuning between the exciting pump pulse and the unperturbed exciton. The three curves were obtained at the same time delay (-70 fs) and comparable pump intensity (≈10 GW/cm^2). As mentioned earlier, the pump excitation below the exciton was achieved by using sulforhodamine 101 in the second stage of the amplifier and in that case the detuning $\Omega = E_x - \hbar\omega = 9$ meV. At resonance, kyton red was used as a dye. The curve corresponding to above resonance excitation was obtained with kyton red and by slightly heating the sample ($T\approx35$ °C), which shifts the exciton toward low energies by 14 meV. The central photon energy of the pump is then above one half-width of the exciton and almost coincident with the $n=2$ first excited state of the exciton.

When going from Fig. 2(b) to Fig. 2(c), one can observe an increase of the excitonic shift which points out the resonant behavior of the optical Stark effect. When exciting above the exciton [Fig. 2(d)], no shift is observed under our experimental conditions. However, in the latter case, the exciton undergoes a blue shift for higher pump intensity and/or larger time delays and it is then not easy to distinguish between the Stark effect and exciton screening effects.

In the very simple "dressed atom" model (1), one considers a two-level electronic system with ground state E_0 and one photon $\hbar\omega$ and an excited state E_1. When the photon is coupled to the material system via dipolar interaction the shift of the two-level system is given by

$$\Delta E = \sqrt{\Omega^2 + 4P^2\epsilon^2} - \Omega. \tag{1}$$

Here $\Omega = E_1 - E_0 - \hbar\omega$ is the detuning and ϵ is the electromagnetic field amplitude. The dipolar coupling constant P includes excitonic parameters such as the modulus squared of the exciton envelope function at $r=0$ and the parameter describing the excitonic nonlinearity due to the underlying Fermi statistics.[14,15]

Far from resonance, $\Omega \gg 2P\epsilon$, Eq. (1) gives the usual expression for the optical Stark shift:

$$\Delta E \approx 2P^2\epsilon^2/\Omega\,, \tag{2}$$

showing the dependence of the shift upon the electromagnetic field intensity and the resonant behavior.

At resonance, $\Omega = 0$, expression (1) reduces to

$$\Delta E = 2P\epsilon\,, \tag{3}$$

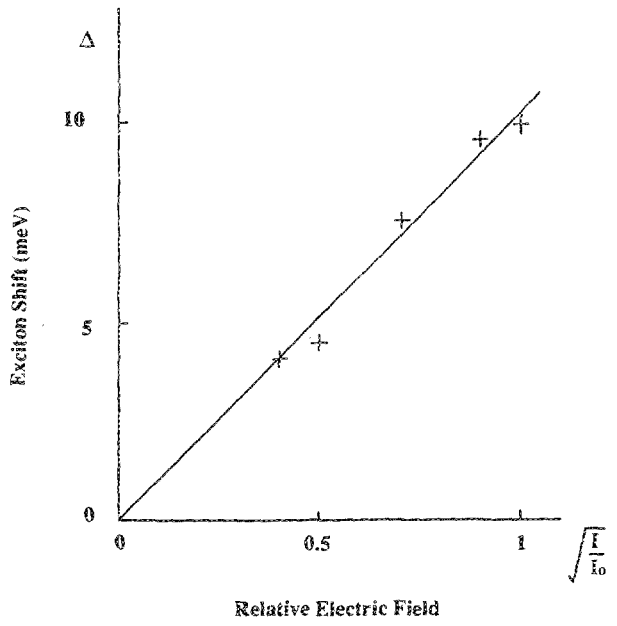

FIG. 3. Exciton shift at resonance vs the relative pump-field amplitude at the same time delay ($-$ 70 fs).

in which the exciton shift depends only on the field amplitude, i.e., the square root of the pump intensity.

A test of this prediction is shown in Fig. 3 where the variation of the exciton shift is plotted versus the square root of the relative pump intensity. The experimental points were obtained by measuring the shift of the exciton peak maximum for various attenuations of the pump always at the same time delay of $-$ 70 fs between pump and probe. As can be seen, the result confirms the behavior given by Eq. (3) and gives support to the interpretation of the resonant exciton shift at early time delays in terms of optical Stark effect.

Expression (2) predicts a red shift of the exciton when exciting above resonance $\Omega < 0$ which is not observed, but the model involved is too simple to be fully realistic. A model for the resonant optical Stark effect has not yet been established in which the full coupling of the light field with the total electronic system would be considered. More, collective interactions of the carriers and excitons created by the photon should be added.

We have explored, in bulk ϵ-GaSe, the absorption changes induced by intense 150 fs light pulses whose photon energy is close or equal to the unperturbed exciton. It has been found that, at early times in the pump envelope, the observed large shift for the exciton can be interpreted as due to optical Stark effect.

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