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S.W. KOCH[1], H. HAUG[2] and M. LINDBERG

Optical Sciences Center, University of Arizona, Tucson, AZ 85721, U.S.A.

Résumé - Nous discutons la théorie des nonlinéarités optiques transitoires et stationnaires dans les semiconducteurs et présentons une analyse unifiée des processus physiques en jeu.

ABSTRACT - The theory of transient and steady state optical nonlinearities in semiconductors is discussed and a unifying analysis of the involved physical processes is presented.

1 - INTRODUCTION

In this paper we discuss near-bandedge optical nonlinearities of laser-excited semiconductors in two distinctively different time domains. In the first, ultrafast regime the semiconductor is in a state where the dynamics of the excitation is still relevant. The pump-probe times are shorter than, or at least comparable to the carrier-carrier scattering times. For this case, we analyze transient transmission oscillations as precursers of spectral hole burning and optical Stark shift. In the second, quasi-steady state or hydrodynamic regime we are dealing with times which are long in comparison to the characteristic carrier scattering times. Hence, it is reasonable to assume that the rapid intraband scattering of electrons and holes established quasi-thermal Fermi distributions of the carriers within their bands. The electronic optical nonlinearities in this quasi-equilibrium regime are dominated by many-body effects,[1] such as renormalization of the bandgap, bleaching of the exciton resonance with increasing excitation density, plasma screening, and band filling.

2 - EQUATIONS OF MOTION

To analyze transient and quasi-steady state optical nonlinearities, we compute the dynamic evolution of the expectation values[2,3]

$$f_e(k) = \langle a_k^\dagger a_k \rangle \tag{1a}$$

$$f_h(k) = \langle b_{-k}^\dagger b_{-k} \rangle \tag{1b}$$

$$P(k) = \langle a_k^\dagger b_{-k}^\dagger \rangle \tag{1c}$$

where a_k (b_k) is the destruction operator of an electron (hole) in the conduction (valence) band, and P(k) gives the polarization of the medium. Using a quantum mechanical projection technique,[4] we derive the equations of motion

$$\frac{\partial}{\partial t} f_{e/h}(k) = i\left[\mu_k E(t) + \sum_{q\neq 0} V(q)P^*(q+k)\right]P(k) + \text{c.c.} + \frac{\partial}{\partial t} f_{e/h}(k)\Big|_{\text{coll}} \tag{2a}$$

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[1] Jointly with Physics Department, University of Arizona

[2] Permanent address : Institut für Theoretische Physik, Universität Frankfurt, Frankfurt-am-Main, F.R.G.

$$\left[\frac{\partial}{\partial t} - i\Delta\epsilon_{eff}(k)\right] P(k) = \frac{\partial}{\partial t}P(k)\Big|_{coll} - i\left[\mu_k^* E(t)^* + \sum_{q\neq 0} V(q)P(k+q)\right][1 - f_h(k) - f_e(k)] , \quad (2b)$$

where μ_k is the dipole matrix element, E(t) is the light field, V(q) is the Coulomb potential, and $\partial f/\partial t|_{coll}$ and $\partial P/\partial t|_{coll}$ denote the contributions from the carrier collision processes. The renormalized transition energy $\Delta\epsilon_{eff}$ is

$$\Delta\epsilon_{eff}(k) = \epsilon_e^0(k) + \epsilon_h^0(k) - \sum_{q\neq 0} V(q)[f_e(k+q) + f_h(k+q)] . \quad (3)$$

Equations (2a) and (2b) can be regarded as generalized Bloch equations for semiconductors. They include a variety of many-body effects such as bandgap renormalization and state filling. As limiting cases, the generalized Bloch equations reproduce well-known results from quantum optics and semiconductor physics. Neglecting all Coulomb-interaction terms one obtains the undamped Bloch equations used in atomic spectroscopy of inhogeneously broadened systems. In semiconductors, the inhomogeneous broadening is an intrinsic consequence of the energy dispersion. Keeping the Coulomb interactions, but assuming just one electron-hole pair and no optical field, the effective Bloch equations reduce to the Wannier equation of the exciton.

3 - THEORY OF TRANSIENT OPTICAL NONLINEARITIES

In this section we summarize the theory[5] of transient ultrafast effects in pump-probe-type spectroscopy, where the strong pump pulse excites the medium polarization which is measured by the weak probe pulse. We analyze the situation where the semiconductor material is illuminated by two light pulses which are temporally delayed with respect to another by a time difference t_p. One of the pulses usually has a relatively low intensity, it is spectrally broad and acts as probe pulse, $E_p(t)$, whereas the other pulse, the pump pulse $E_L(t)$, is spectrally narrow and has a high intensity. For reference, we choose the peak of the pump pulse as origin of time, t = 0. If the probe pulse arrives at the sample before the peak of the pump pulse, we have a negative time delay, $t_p < 0$.

In the experiments one typically measures the changes in the transmission spectrum of the probe pulse (differential transmission spectrum, DTS)

$$\delta T(\omega) = \frac{|E_p(L,\omega)|^2_{pump\ on} - |E_p(L,\omega)|^2_{pump\ off}}{|E_p(L,\omega)|^2_{pump\ off}}, \quad (4)$$

where $E_p(L,\omega)$ is the amplitude of the probe field, after it has travelled through the sample of length L. For the situation when the pump-induced changes δE_p are small in comparison to the total transmitted probe field, one can approximate δT as

$$\delta T(\omega) \cong \frac{2\ \mathrm{Re}\left[E_p^*(L,\omega)|_{pump\ off}\ \delta E_p(L,\omega)|_{pump\ on}\right]}{|E_p(L,\omega)|^2_{pump\ off}} \quad (5)$$

which shows that in this case the DTS can be viewed as measuring the frequency interference between the unperturbed transmitted probe field and the pump-induced change in the transmitted probe field.

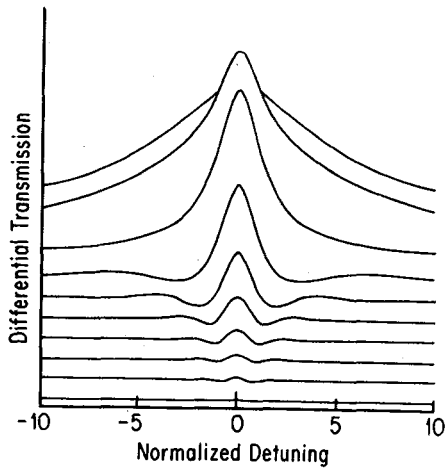

Fig. 1: Differential transmission spectra calculated for interband excitation. The central pump frequency Ω_L is assumed to be well above the semiconductor bandgap. The detuning is normalized to σ^{-1} = 120/2ℓn2 fs. The temporal FWHM of the pump pulse is 120 fs and the damping constants have been taken as γ = 0.035 fs^{-1} and Γ = 1/200 fs^{-1}. Various curves are for different time delays t_p between pump and probe. The bottom curve is for t_p = -400 fs and the top curve is for t_p = 50 fs.

In Ref. 5 we have evaluated the transmission spectra for the conditions where i) the differential transmission changes around the central frequency of the pump pulse are recorded for resonant interband excitation, and ii) where the transmission changes are measured around the exciton resonance but the excitation occurs below the exciton frequency. For the case i) our result is

$$\delta T(\omega) = B\,\mathrm{Re}\Big[\int_0^\infty dt\; e^{i(\omega-\Omega_L)t}(e^{-2\gamma t}\int_0^\infty dt'\; e^{-\Gamma t'}\,E_L(t_p-t')\,E_L^*(t_p-t'-t) + e^{-\Gamma t}\int_0^t dt'\; e^{-(2\gamma-\Gamma)t'}\,E_L(t+t_p-t')\,E_L^*(t_p-t')\Big)\Big] , \quad (6)$$

where B is a combination of constants and γ and Γ are the damping constants of the polarization and the carrier population, respectively. Evaluating Eq. (6) yields the results plotted in Fig. 1 for different t_p. The computed DTS exhibit oscillatory structures around the central frequency of the pump for large negative t_p, i.e., when the probe pulse comes during the rising part of the pump pulse. The period of the oscillations is inversely proportional to t_p. The origin of the observed oscillatory structures is a transient population grating generated by the pump and probe pulses together.

In case ii), i.e. for non-resonant excitation energetically below the exciton resonance e, we obtain the DTS as

$$\delta T(\omega) \propto 2\,\mu^4 \left[\frac{2\upsilon}{\upsilon^2 + \Delta^2} \mathrm{Re}\left\{ \int_{-\infty}^{t_p} dt \int_{-\infty}^{t} dt'\, E_L(t)\, E_L^*(t')\, e^{i(e-\Omega_L)(t-t')} \right\} \right.$$

$$\left. + \mathrm{Re}\left\{ \frac{1}{\upsilon - i\Delta} \int_0^{\infty} dt\, E_L(t+t_p)\, e^{(i(\omega-\Omega_L)-\upsilon)t} \int_{-\infty}^{t+t_p} dt'\, E_L^*(t')\, e^{i(e-\Omega_L)(t_p-t')} \right\} \right] \qquad (7)$$

where $\Delta = \omega - e$ is the probe detuning from the exciton resonance and υ denotes the exciton linewidth. Examples of the results obtained from Eq. (7) are reproduced in Fig. 2, where again t_p is varied. As in the case i) discussed above, oscillatory structures are observed for negative values of t_p, however, this time not around the central pump frequency but around the exciton resonance. Since the pump laser is detuned with respect to the exciton resonance, the oscillatory structures are not symmetric as in the case of the interband transitions. When the delay time approaches zero, the oscillatory structures disappear leaving a differential transmission which has an almost dispersive shape. This dispersive shape indicates that the exciton resonance has been shifted to higher energies (increased transmission on the low-energy side and decreased transmission on the high-energy side). This is the so-called optical Stark shift of the exciton. Hence, our results show that the coherent oscillations evolve continuously into the optical Stark shift. The results presented in Figs. 1 and 2 are in good qualitative agreement with recent femtosecond experiments.[6]

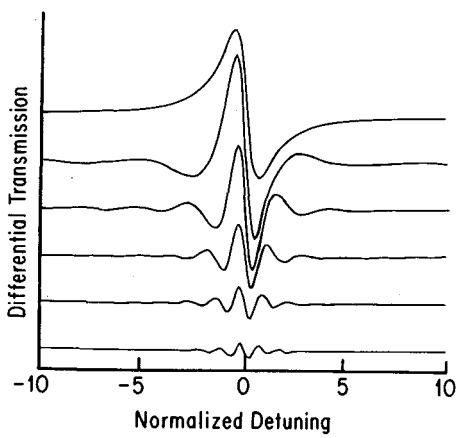

Fig. 2: Differential transmission spectra calculated in the spectral vicinity of the exciton resonance ω_X. The central pump frequency Ω_L is assumed to be detuned by -10σ and the temporal FWHM of the pump pulse is 120 fs. The curves are for different time delays t_p with 100 fs intervals, starting from the bottom at -500 fs to the top curve which is for 0 fs.

4 - THEORY OF STEADY STATE OPTICAL NONLINEARITIES

If a semiconductor is excited with pulses whose duration is long in comparison to the carrier intraband relaxation time, the rapid carrier-carrier scattering effects, i.e. the terms $\partial/\partial t\ \langle ... \rangle|_{coll}$ in Eqs. (2), establish a

quasi-thermal equilibrium in the laser-generated system of elementary excitations. Typically this situation is reached in resonant pump-probe experiments on the timescale of several hundred femtosceonds up to a few picoseconds. The originally nonthermal distributions of electrons and holes within their bands evolve into quasi-Fermi distributions, where the respective chemical potentials are defined within each band and the electronic temperature may be higher than the lattice temperature. The chemical potentials are determined by the numbers of excited electrons and holes and the plasma temperature is mainly determined by the excess excitation energy with respect to the bandgap. In this hydrodynamic quasi-equilibrium regime the details of the electron-hole generation process are considered unimportant and only the total number of electron-hole pairs plays a significant role. Under these conditions the optical semiconductor nonlinearities are determined mainly by the density of the generated carriers[1,2] and the scattering terms in Eq. (2) become negligible, $\partial/\partial t \; <...>|_{coll} \cong 0$. In other words, the scattering events occur on a much faster timescale than the explicitly discussed processes, thus keeping the system in the quasi-equilibrium state.

A proper analysis of the excitation dependent absorption spectrum of a semiconductor in steady state should include effects such as screening, phase space filling, band filling, and bandgap renormalization.[1,2] To describe the dynamics of the screening, one has to consider the spatial rearrangement of electrons and holes and the local population fluctuations. These effects are neglected in our present treatment, but if one simply postulates a fully developed quasi-equilibrium state, the screening can be described in the usual self-consistent approximation. In our treatment, this amounts to replacing the unscreened Coulomb potential by a screened one $V \rightarrow V_s$ which has a reduced interaction strength especially at long distances and which adds the Debye shift to the transition energy

$$\Delta\epsilon_{eff}(k) = \epsilon_e^0(k) + \epsilon_h^0(k) + \sum_{q\neq 0} [V_s(q) - V(q)] - \sum_{q\neq 0} V_s(q)[f_e(k+q) + f_h(k+q)] \; . \tag{8}$$

Following the argumentation of Ref. 3 we obtain the absorption as

$$\alpha(\omega) = C \sum_{\lambda} \text{sign}\langle \eta_\lambda | S | \eta_\lambda \rangle \; | \langle x=0 | S | \eta_\lambda \rangle |^2 \; \delta(\epsilon_\lambda - \omega) \; , \tag{9}$$

where C is a constant. Here S is the inversion operator and $|\eta_\lambda>$ and ϵ_λ are the eigenstates and eigenenergies of Eq. (2b) in the quasi-equilibrium limit. The sign function occurs because the operator S is not positive definite. Physically, the sign describes gain (minus) or absorption (plus) at the corresponding states.

Eq. (9) has several well-known limiting cases. For the unexcited situation when the electron and hole populations are zero, S is the unit operator and the η_λ are the eigenfunctions of the pure Coulomb problem (Wannier equation). Under this condition, Eq. (9) reduces to the original Elliott formula.[7] On the other hand when the Coulomb potential is ignored, $V \rightarrow 0$, the problem is diagonalized in a plane wave basis yielding the usual free-particle result. The absorption formula used by Banyai and Koch[8] is obtained by ignoring the phase space filling corrections in the generalized Wannier equation. The resulting expression for the absorption has been evaluated for many different semiconductor materials[9] including room temperature GaAs, CdS, semiconductor microcrystallite doped glasses, and ZnSe. As an example, the theoretical results for the absorption

spectrum of CdS at T=60K is shown in Fig. 3. The low-density absorption curve (0) is the spectrum of the unexcited crystal. It exhibits peaks which are caused by the 1s and 2s-exciton lines. For higher plasma densities these peaks gradually vanish as a consequence of the plasma screening which weakens the attractive Coulomb interaction between electron and hole. The 1s-exciton ionizes at the critical (Mott) density. This causes a decreasing absorption around the energetic position of the exciton line. The effect of bandgap renormalization is clearly visible at higher excitation densities causing the absorption to increase with carrier density in the spectral region below the exciton resonance.

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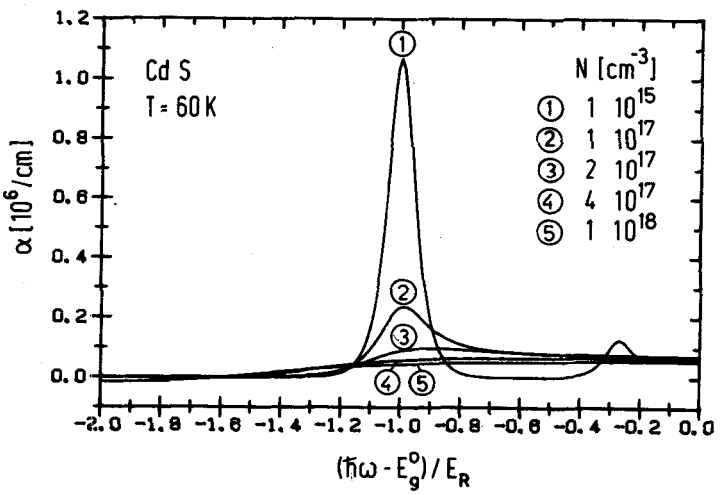

Fig. 3: Computed absorption spectra for CdS at T=60 K for different plasma densities N. Here, E_g^o = 2.583 eV is the unrenormalized bandgap and the exciton Rydberg is E_R = 27 meV.

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