Optical Dephasing in Disordered Semiconductors

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We demonstrate that optical dephasing in disordered semiconductors does not require quasiparticle interaction but can be solely caused by disorder. We show that localization effects strongly influence the optical-dephasing signal by calculating the nonlinear polarization, taking into account disorder nonperturbatively. Decay times of the order of fs to ps can be expected depending on the ratio of diagonal disorder and intersite coupling. It follows that dephasing experiments performed on disordered semiconductors cannot be analyzed simply in terms of quasiparticle interactions.

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The interaction of carriers with phonons determines most of the steady-state and transient properties of disordered semiconductors (for a recent review, see, e.g., Ref 1). This interaction also governs the energy relaxation of excited carriers in a nonequilibrium situation, e.g., under optical excitation. The underlying processes can be described successfully in terms of hopping in the band tails on a time scale much larger than picoseconds. On the other hand, the investigation of the very fast processes immediately following an excitation with a short light pulse is still the subject of considerable experimental work. In particular, in the case of amorphous semiconductors like *a*-Si:H pump and probe experiments (see, e.g., Ref. 2) have been widely employed to study the energy relaxation of carriers close to the mobility edge on a picosecond and subpicosecond time scale.

Alternatively, the interaction of excitations with phonons can also be studied by photon echo[3,4] or transient four-wave-mixing experiments[5,6] in the stimulated photon echo configuration. In these experiments the sample is excited by two very short laser pulses with a time separation τ and k vectors $\mathbf{k}_1$ (first pulse) and $\mathbf{k}_2$ (second pulse). A photon echo then is observed at a time 2τ with respect to the first pulse in the case of an inhomogeneously broadened spectral line. In the four-wave-mixing experiment a third probe pulse is diffracted by the grating produced by the first two excitation pulses. In both experiments the resulting signal is asymmetric with respect to $\tau=0$ in the direction $2\mathbf{k}_2-\mathbf{k}_1$, in the case of an inhomogeneously broadened transition, since then the diffracting grating corresponds to a phased array.[5] The amplitude of the signal is proportional to the nonlinear polarization $\langle P(2\tau)\rangle$ and typically decays according to $\exp(-2\tau/T_2)$, with T_2 the dephasing time. This dephasing time is usually related to quasiparticle interactions like scattering with phonons or other excitations.

The interpretation of the dephasing process in terms of quasiparticle interaction is justified if the sample under consideration can be taken as an ensemble of mutually noninteracting two-level systems (as in the classical photon echo experiments on ruby[3]). The same is true for the case of a perfectly ordered crystalline semiconductor. A crystal can be described by an ensemble of two-level systems characterized by k vectors if the time scale is short enough to neglect the intraband interaction between carriers. The question arises whether disorder, which renders the classification of states in terms of k vectors meaningless, leads to a decay of the photon echo or diffraction signal even if quasiparticle interactions can be neglected, which would correspond to an infinitely long dephasing time in the case of a crystalline semiconductor. The problem can be formulated slightly differently starting from a tight-binding description: Does a quantum mechanical coupling between two-level systems result in a decay of the coherence of the optically created excitations?

Root and Skinner[7] have calculated the photon echo signal in the so-called $\pi/2$-π pulse configuration and considered excitons as excitation. The internal motion of the exciton has been assumed to be not affected by disorder. The Hamiltonian then is formally equivalent to the case of a single-band Anderson model.[8] They found from a perturbative treatment (strong disorder, localized regime) and for intermediate times τ that for the particular case of short-range correlated disorder a nonzero coupling between sites, represented by J, indeed results in a finite dephasing rate $\tilde{T}_2^{-1}\simeq 24fJ^2/W$. The disorder is characterized by a width W of the site energy distribution and f is the fractional occupancy of the absorbers in the host lattice. Hegarty and Sturge,[9] on the other hand, argue that elastic scattering transfers a nonzero $\mathbf{k}$ to the optically excited excitons, which can then no longer couple to the external photon field and thus lead to a decay of the nonlinear polarization.

In this work we investigate the role of elastic disorder scattering in optical-dephasing experiments. We do not employ a perturbational approach with respect to disorder, characterized by $\eta=W/J$. In particular, we demonstrate for the first time that in contrast to the linear response the nonlinear response is strongly influenced by Anderson localization. The present theory is applicable to semiconductors with either strong static disorder like

a-Si:H or with small disorder like mixed crystals, quantum wells, and superlattices. It correctly describes both limiting cases, $\eta \rightarrow 0$ and $\eta \rightarrow \infty$, where no dephasing occurs. In addition our approach allows for a calculation of $\langle P(2\tau)\rangle$ for arbitrary τ. A result analogous to that of Root and Skinner, however, in the delocalized regime, is found for the envelope to the decay curve. We estimate the decay time $\tilde{T}_2$ to be of the order of some 10 fs if, e.g., typical parameters for hydrogenated amorphous silicon[1,10] are used. Our results clearly demonstrate that dephasing experiments do not necessarily provide information about the interaction of excitations with quasiparticles, but, instead, the static disorder has to be taken into account as a cause of decay.

In order to emphasize the role of static disorder we do not consider any interaction between excitations and quasiparticles. We also neglect the interband electron-hole coupling and treat the excitations as mutually independent electron-hole pairs. For a simple tight-binding model we calculate the polarization to third order in the exciting electric field as a function of pulse separation τ. This treatment predicts[5] the asymmetric diffraction signals which are often found.[6] The light pulses are assumed to be of $\delta(t)$ shape.

It is instructive to first consider the most simple model which allows us to study the simultaneous influence of both static disorder and quantum-mechanical coupling: an ensemble of dimers.[11] For a single dimer the Hamiltonian describes two coupled two-level absorbers

$$H=\sum_{\alpha=v,c}\left\{\sum_{i=1,2}\epsilon_{\alpha i}n_{\alpha i}+J_\alpha(c_{\alpha 1}^\dagger c_{\alpha 2}+\text{H.c.})\right\}$$

and the polarization operator is taken to be

$$P=p\sum_i c_{vi}^\dagger c_{ci}+\text{H.c.} \tag{1}$$

The differences $\epsilon_{\alpha 1}-\epsilon_{\alpha 2}$ are assumed to be distributed randomly over a range W_α with zero mean. The relevant disorder parameter is $\eta_\alpha=W_\alpha/J_\alpha$. If $\eta_\alpha=0$ we have a symmetrical dimer with only two transitions connecting an antisymmetric with a symmetric state. Consequently, the symmetric dimer can be viewed as two uncoupled two-level systems. The total ensemble is then equivalent to an ensemble of two-level systems which does not show any dephasing. In the opposite extreme, i.e., for infinite disorder, $\eta_\alpha \rightarrow \infty$, we again have an ensemble of independent two-level systems without dephasing. In the intermediate case, the polarization is determined by terms like

$$\exp\{i[(\epsilon_{\alpha i}-\epsilon_{\alpha j})^2+J_\alpha^2]^{1/2}\tau\}+\text{const}\,,$$

which implies a decay for an ensemble with fluctuating energy differences $\epsilon_{\alpha i}-\epsilon_{\alpha j}$.

We find a general result that $\langle P(2\tau)\rangle$ decays towards a saturation value whenever optical transitions connect a particular initial state with more than just one excited state. This leads to a modulated signal for one particular absorber (the quantum beats[12]) and to a decay if the individual modulation frequencies of the ensemble of absorbers are distributed. The saturation value for large pulse separation τ is lower the more states are connected to a particular state by optical transitions.

An ensemble of two-level systems which are connected by nearest-neighbor interactions can be studied using the two-band model introduced by Abe and Toyozawa[13] which consists of two independent Anderson Hamiltonians,

$$H=\sum_{\alpha=c,v}\left\{\sum_i \epsilon_{\alpha i}n_{\alpha i}+J_\alpha\sum_{i\neq j}c_{\alpha i}^\dagger c_{\alpha j}\right\}.$$

For simplicity the polarization operator is again taken to be given by Eq. (1). The sites i,j are the nodes of a simple cubic lattice with lattice constant a. The relevant term for the third-order polarization contains a configurational average over four single-particle propagators,

$$\langle P(2\tau)\rangle \sim \langle \mathrm{Tr}(Pe^{-iH_v\tau}Pe^{-iH_c\tau}Pe^{iH_v\tau}Pe^{iH_c\tau})\rangle\,. \tag{2}$$

We consider two simplified models which allow a treatment in terms of localization theory. First (model A), we assume that the coupling in the valence band vanishes, $\eta_v=\infty$ (i.e., an infinite mass in the crystalline case). From Eq. (2) we get[14]

$$\langle P(2\tau)\rangle \sim p^4\sum_{ij}[g(\tau)(1-\delta_{ij})+\delta_{ij}]\phi_{ij}(\tau)\,, \tag{3}$$

where

$$g(\tau)=\langle\exp\{-i(\epsilon_{iv}-\epsilon_{jv})\tau\}\rangle\,,\quad i\neq j\,,$$

and

$$\phi_{ij}(\tau)=\langle \mathrm{Tr}(|ci\rangle\langle ci|e^{-L_c\tau}|cj\rangle\langle cj|)\rangle\,.$$

This latter function is nothing else but a density-density correlation function for the conduction band,[7,15] while for uncorrelated site energies $g(\tau)$ is determined by the Fourier transform of the valence-band site energy distribution function. As compared to $\phi_{ii}(\tau)$ it, therefore, decays on a generally much shorter time scale W_v^{-1}. We can manipulate Eq. (3) using particle conservation, $\sum_j\phi_{ij}(\tau)=1$, and obtain

$$\langle P(2\tau)\rangle \sim Np^4\{[1-g(\tau)]\phi_{ii}(\tau)+g(\tau)\}\,; \tag{4}$$

i.e., the decay of the nonlinear polarization is directly related to the decay of the intraband electron density correlation function. The physical interpretation of this result is obvious. Our model assumption implies that the hole is localized at a particular site while the electron is able to move around. This propagation can be described in terms of the mean square displacement $\langle R^2(\tau)\rangle$ which is given by

$$\langle R^2(\tau)\rangle=(1/N)\sum_{i,j}R_{ij}^2\phi_{ij}(\tau)\,,$$

where R_{ij} is the separation of sites i and j. A mode-coupling treatment[7,16] of $\phi_{ij}(z)$ reveals all the known results related to the Anderson localization. In particular, in the localized regime ($\eta_c > \eta_{c\,\mathrm{crit}}$), $\langle R^2(\tau)\rangle \rightarrow \xi_{\mathrm{loc}}^2$ for $\tau \rightarrow \infty$, where ξ_{loc} is the localization length. We also find that $\phi_{ii}(\tau)$ approaches the finite long-time limit

$$\phi_{ii}(\tau) \rightarrow G_{ii}(1+a^2/\xi_{\mathrm{loc}}^2)a^2/\xi_{\mathrm{loc}}^2 . \quad (5)$$

Here $G_{ii}(E)$ is the diagonal element of a single-particle lattice Green's function at energy E, related to the ordered Hamiltonian $\frac{1}{6}\sum_{ij} c_{ic}^{\dagger} c_{jc}$ (with a band for $-1 < E < 1$). For weak localization, $\xi_{\mathrm{loc}} \rightarrow \infty$, Eq. (5) leads to $\phi_{ii}(\tau) \rightarrow 0$ while for vanishing localization length (uncoupled two-level absorbers) $\phi_{ii} = 1$, i.e., no dephasing. For intermediate cases $\langle P(2\tau)\rangle$ initially decays faster the larger $\eta_c^{-1} = J_c/W_c$, in rough agreement with the perturbational result of Root and Skinner for intermediate times. For large times we find a saturation value roughly proportional to ξ_{loc}^{-2}.

In the delocalized regime at intermediate times we obtain as a rough estimate for the envelope

$$\phi_{ii}(\tau) \simeq \exp(-6D\tau/a^2) , \quad (6)$$

where D is the dc-diffusion constant given by $D = 12J_c^2 a^2(1-\delta)/\pi W_c$ (for a box-shaped distribution of width W_c).[10] δ is the coupling constant of the Anderson localization problem, $\delta = (\eta_c/\eta_{c\,\mathrm{crit}})^2$, $\eta_{c\,\mathrm{crit}} = 11.8$. Thus the envelope described by Eq. (6) is characterized by a dephasing rate $\tilde{T}_2^{-1} \simeq 11.5(1-\delta)J_c^2/W_c$ which extends the result of Root and Skinner[7] to the delocalized regime. The numerical values for $\phi_{ii}(\tau)$ are plotted in Fig. 1 (full line, model A).

Our second model B considers an ordered conduction band, $\eta_c = 0$ with band structure $\epsilon_{\mathbf{k}}$. Equation (2) can then be expressed in k space and the self-consistent mode-coupling approach of Götze[17] and Prelovšek[18] is applied to calculate the intraband correlation function $\phi_{\mathbf{k}\mathbf{k}'}(\tau)$ for the valence band,

$$\phi_{\mathbf{k}\mathbf{k}'}(\tau) = \langle \mathrm{Tr}(|v\mathbf{k}\rangle\langle v\mathbf{k}|\, e^{-L_v\tau}\, |v\mathbf{k}'\rangle\langle v\mathbf{k}'|)\rangle ,$$

while Eq. (3) is replaced by

$$\langle P(2\tau)\rangle \simeq p^4 \sum_{\mathbf{k}\mathbf{k}'} \phi_{\mathbf{k}\mathbf{k}'}(\tau) \exp\{-i(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}})\tau\} \quad (7)$$

and Eq. (4) by

$$\langle P(2\tau)\rangle \sim Np^4\{[1-\Psi(\tau)]J_0^6(2J_c\tau) + \Psi(\tau)\} .$$

Here $\Psi(\tau)$ is the valence-band current-current correlation function, related to the conductivity. The case $\eta_v \rightarrow \infty$ ($J_v \rightarrow 0$, i.e., $\Psi = 0$) is given simply in terms of the Bessel function $J_0(x)$. It coincides with model A for the special case $\eta_c = 0$. For finite η_v the correlation function $\phi_{\mathbf{k}\mathbf{k}'}$ (or Ψ) can be calculated numerically on the basis of the approach of Götze[17] and Prelovšk.[18] The result is also plotted in Fig. 1. For a perfectly ordered system, $\eta_v = 0$, the current does not decay, $\Psi(\tau) = 1$, and we have no dephasing.

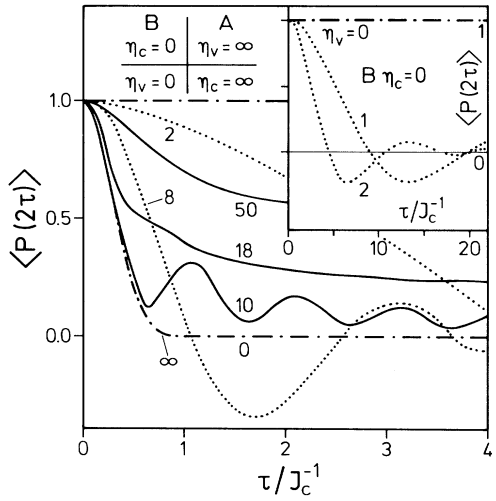

FIG. 1. Sequence of decay curves of the normalized nonlinear polarization. Model A (solid line); model B (dotted line). The dashed-dotted line applies for both models. $J_c = -2J_v$ in model B.

Equations (4) and (8) express the central result of this Letter. They show that in contrast to the optical linear response[19] the nonlinear response is drastically influenced by disorder effects. For a particular model system we have demonstrated that static disorder alone can lead to a decay of the third-order polarization $\langle P(2\tau)\rangle$ with increasing pulse separation τ. Our treatment predicts no dephasing in the two limiting cases of a perfectly ordered and a perfectly disordered ensemble. For a strongly localized valence band and for moderate disorder in the conduction band, the nonlinear polarization $\langle P(2\tau)\rangle$ decays to zero with a dephasing rate roughly proportional to the diffusion constant D for electrons. In the localized regime for the conduction band the signal reaches a saturation limit which is roughly proportional to the inverse square of the localization length ξ_{loc}. On the other hand, if one of the bands is completely ordered, disorder in the second band leads to a decay of $\langle P(2\tau)\rangle$, which is related to current relaxation.

It is evident that the experimental verification of the effects of disorder in nonlinear optics is difficult because of a number of unavoidable quasiparticle interactions. In particular, in weakly disordered semiconductors the dephasing rate due to excitation-excitation and excitation-phonon interactions[20] may lead to decay rates [of the order of $(10\ \mathrm{fs})^{-1}$] comparable to or even larger than those considered here. On the other hand, in more heavily disordered semiconductors these interactions may well be sufficiently suppressed and the disorder-induced dephasing will contribute considerably to the experimental signal. As an application we consider interband transitions excited with a typical photon energy of about 2 eV in amorphous silicon. The majority of excited elec-

trons will be delocalized. As an estimate we use Eq. (6) and take $D = 10^{-2}$ cm^2/s [21] and $a = 5$ Å.[1] This leads to a short decay time constant of $\tilde{T}_1 \simeq 160$ fs which may dominate the experimentally found decay. Extremely long decay times due to disorder are predicted if the optical excitation couples only localized states. This situation may be realized in mixed crystals like, e.g., $CdS_{1-x}Se_x$,[22] or in quantum well systems with compositional or structural disorder.

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