Excitonic and free-carrier quantum beats created by femtosecond excitation at the band edge of GaAs

Markus Joschko, Michael Hasselbeck, Michael Woerner, and Thomas Elsaesser
Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Rudower Chaussee 6, D-12489 Berlin, Germany

R. Hey, H. Kostial, and K. Ploog
Paul-Drude-Institut für Festkörperelektronik, D-10117 Berlin, Germany
(Received 11 March 1998)

The coherent optical response of bulk GaAs is studied after ultrafast excitation close to the band edge. Pump-probe experiments with 20-fs pulses demonstrate that coherent polarizations between heavy- and light-hole continuum states make a strong contribution to the nonlinear optical response. The beat frequency is determined by the heavy-hole–light-hole energy splitting in the spectral probe window. In addition, excitonic heavy-hole–light-hole quantum beats are observed in the slightly strained GaAs crystal. The different contributions are separated via their polarization selection rules. [S0163-1829(98)02340-6]

Coherent polarizations govern the nonlinear optical response of semiconductors on ultrafast time scales and provide direct insight into the fundamental nonequilibrium dynamics of elementary excitations. In bulk and low-dimensional direct-gap semiconductors, excitonic polarizations at photon energies close to the band gap have been investigated in detail by ultrafast spectroscopy.[1] In quasi-two-dimensional quantum wells and strained bulk materials, the heavy-hole (HH) and light-hole (LH) excitons are energetically separated. Phase-coherent excitation of both these resonances by a short optical pulse gives rise to excitonic quantum beats that have been monitored in different experiments.[2–4] In addition to excitonic HH-LH quantum coherence, oscillatory signals due to a distribution of excitonic transition frequencies, i.e., polarization interference,[5] and/or the perturbed free induction decay of excitonic polarizations[6] have been found.

Recently, HH-LH quantum beats were observed in pump-probe experiments where 20-fs pulses excited *exclusively continuum states* in bulk GaAs.[7] Both the HH and LH to conduction-band transitions at a specific **k** vector are excited in a phase-coherent manner by the broad spectrum of a single optical pulse, thereby creating a coherent polarization between HH and LH states. This inter-valence-band polarization oscillates at a frequency determined by the HH-LH energy splitting and leads to oscillations on the pump-probe signals.

So far, this interesting type of HH-LH quantum coherence has only been studied with excitation in the band-to-band continuum to avoid excitonic contributions to the nonlinear response. When exciting near the band gap with optical pulses of sufficient bandwidth, however, both excitonic and continuum polarizations occur. HH-LH beats in the continuum as well as from excitonic states should contribute to the nonlinear response. In this paper, we report an observation of continuum HH-LH quantum beats in bulk GaAs with excitation at the band gap. Temporally and spectrally resolved pump-probe experiments with 20-fs pulses display a variation of beat frequencies within the spectrum of the probe pulses, depending on the HH-LH splitting in the optically coupled range. Different polarization selection rules for excitonic and continuum quantum beats allow a clear separation of the different effects.

We study a slightly strained bulk GaAs sample (thickness 500 nm clad between $Al_xGa_{1-x}As$ layers) that was grown by molecular-beam epitaxy. The absorption spectrum measured at a lattice temperature of 10 K is shown with a solid line in Fig. 1(a). Strain develops during sample preparation and/or at low temperature, and leads to a splitting of the excitonic transitions by $\Delta E_x = 8$ meV and a slight redshift of the absorption edge.[8] The spectrally and temporally resolved pump-probe studies are performed with bandwidth-limited 20-fs pulses from a mode-locked Ti:sapphire laser. The spectrum of the pump pulses [dashed line in Fig. 1(a)] is centered below the band gap, and excites both excitonic and free-carrier transitions. The probe pulses are spectrally resolved after passing through the sample and time-resolved data are recorded for different spectral positions E_{det} within the probe spectrum (resolution 4 meV). We detect ultrafast transients in four different pump-probe polarization geometries: parallel linear, perpendicular linear, cocircular, and countercircular. The excited density of electron-hole pairs is about 2×10^{15} cm^{-3}, as estimated from the incident pump intensity and the absorbance of the sample.

Pump-probe signals are presented in Figs. 1(b) and 2. The change of transmission $(T-T_0)/T_0$ is plotted as a function of the delay time between pump and probe pulses for different detection energies E_{det} around the absorption edge depicted by vertical arrows in Fig. 1(a). T and T_0 represent the transmission of the sample with and without excitation, respectively. For $E_{\mathrm{det}} = 1.494$ eV in the excitonic absorption region, we obtain the solid and dashed curves shown in Fig. 1(b) for parallel linear and perpendicular linear pump-probe polarizations, respectively. The transients display (i) a step-like transmission increase and (ii) an oscillatory component. The oscillations strongly depend on the polarization geometry. In particular, the phase of oscillation shifts by π when

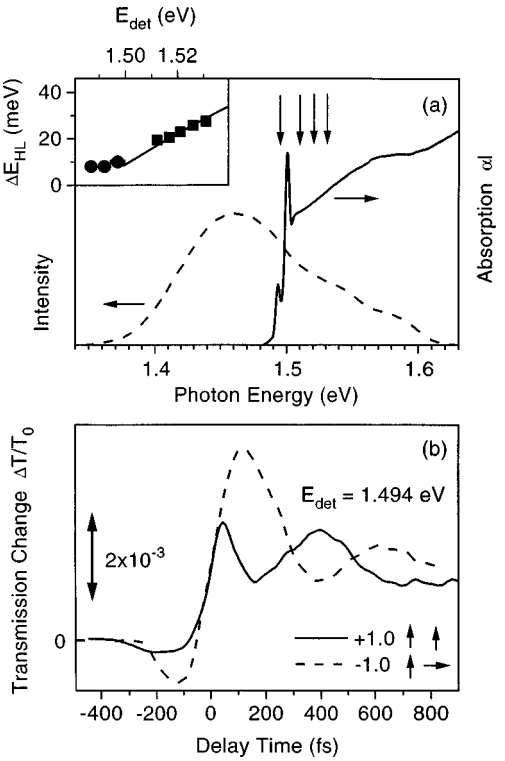

FIG. 1. (a) Solid line: absorption spectrum of the strained GaAs sample at $T=8$ K. Dashed line: spectrum of the 20-fs pulses overlapping both excitonic and free-carrier transitions. Arrows: detection energies E_{det} in the spectrally resolved pump-probe experiments. Inset: oscillation energies derived from the pump-probe data plotted vs detection energy E_{det} (circles: excitonic quantum beats, squares: continuum quantum beats). Solid line: calculated HH-LH splitting ΔE_{HL} for the (110) direction in k space. (b) Spectrally dispersed transmission changes $(T-T_0)/T_0$ at $E_{\mathrm{det}}=1.494$ eV as a function of delay time between pump and probe (T and T_0: transmission with and without excitation). Solid line: parallel linear polarizations of pump and probe. Dashed line: perpendicular linear polarizations.

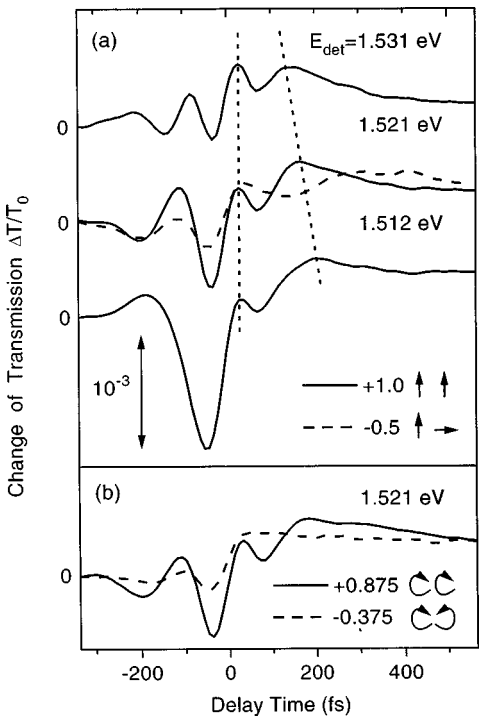

FIG. 2. Pump-probe transients at detection energies E_{det} in the free-carrier continuum. (a) Solid lines: parallel linear polarizations. Dashed lines: perpendicular linear polarizations. (b) Cocircular (solid line) and countercircular (dashed line) polarizations. The oscillations at positive delay are HH-LH hole quantum beats with a frequency determined by the respective HH-LH splitting ΔE_{HL} (cf. the inset of Fig. 1). Dotted lines connect points of identical phase.

the pump-probe polarizations are changed from parallel linear (solid line) to perpendicular linear (dashed line). For cocircular or countercircular pump and probe (not shown) pulses, the oscillations are completely absent.

Transients recorded at detection energies in the free-carrier continuum are shown in Fig. 2. At the low excitation density of 2×10^{15} cm^{-3}, the data display a weak steplike increase of transmission and strong oscillations. For higher excitation densities (not shown), the steplike increase of transmission becomes more pronounced. The oscillations in Fig. 2 are observed for negative and positive time delays of up to several hundreds of fs, and show a frequency, amplitude, and phase distinctly different from the excitonic signals in Fig. 1(b) [note the different abscissa scales of Figs. 1(b) and 2]. The oscillations at negative delay times and around delay zero are caused by detuning from the band edge and the probe-induced perturbed free induction decay discussed in Ref. 6. In the following, we concentrate on the oscillatory signal at positive time delays. This time domain is influenced by the different polarization geometries, and gives information on the physical mechanism driving the quantum beats.

The data shown as solid lines in Fig. 2(a) are taken with parallel-linear polarizations of pump and probe pulses at the detection energies E_{det} in the continuum marked in Fig. 1(a). The oscillation frequency increases with detection energy E_{det}, as is evident from the dotted lines connecting points of identical phase. The phase of the oscillations changes by about π when we switch from parallel to perpendicular-linear polarizations of pump and probe [dashed line in Fig. 2(a)] pulses. In Fig. 2(b), data are shown for cocircular (solid line) and countercircular (dashed line) polarizations at the detection frequency $E_{\mathrm{det}}=1.521$ eV. We observe oscillations for cocircular but not countercircular polarizations. This behavior is in contrast to the excitonic transients, where oscillations are absent for both circular polarization geometries, and points to different polarization selection rules (PSR's) governing transitions to excitonic states or the continuum.

We now discuss the ultrafast transmission changes measured in our spectrally and temporally resolved experiments. At all detection energies, two prominent features are observed on the signals. First, there is a steplike increase of transmission that rises within the time resolution of the experiment followed by a slower decay at later times. This is due to state filling by electron-hole pairs, and is influenced by correlated many-body effects such as screening and enhancement of the interband dipole matrix elements. At later times, the bleaching represents an incoherent signal determined by the transient carrier distribution and Coulomb correlations. The second feature is the oscillations superimposed on the bleaching signal at positive delay times due to quantum coherence between HH and LH states. For detection energies E_{det} in the range of the excitonic resonances, one

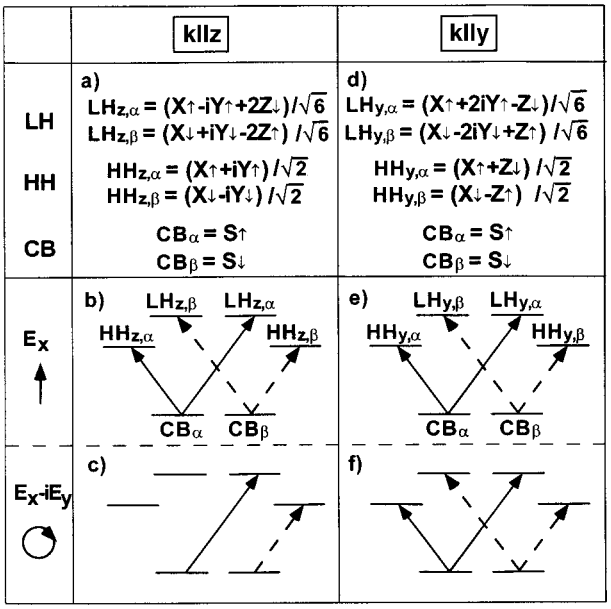

FIG. 3. Polarization selection rules for the coupling of pump and/or probe pulses to different transitions in bulk GaAs. (a) and (b) Orientations of orbitals (X,Y,Z) and spins (up $\uparrow$ and down $\downarrow$ with regard to the z direction) of light hole (LH), heavy-hole (HH), and conduction, band (CB) cell periodic wave functions for $\mathbf{k}$ vectors parallel to z and y directions, respectively (light propagates along z direction). (c) and (d) Coupling scheme of linearly polarized light to transitions at $\mathbf{k}$ vectors with $k\|z$ and $k\|y$, respectively. (e) and (f) Coupling of circularily polarized light to transitions with $k\|z$ and $k\|y$.

observes excitonic HH-LH quantum beats[2] induced by the phase-coherent excitation of both HH and LH excitons within the bandwidth of the pump pulse. This corresponds to an impulsive excitation of a three-level system with a common state in the conduction band (CB), making an additional contribution to the third-order nonlinear polarization in the sample. The excitonic polarization oscillates at a frequency determined by the strain-induced splitting of the excitonic transitions ($\Delta E_x = 8$ meV) seen in the spectrum of Fig. 1(a). These oscillations are transferred to the pump-probe signal via interaction with the probe field.

The excitonic character of these quantum beats manifests itself in the observed PSR's: oscillations are observed for parallel and perpendicular linear polarizations with opposite phase, but not for cocircular and countercircular polarizations. In our bulk sample, the small strain polarizes the p orbitals of HH and LH states resulting in the PSR illustrated in the left column of Fig. 3.[4,9] Close to the band gap, the strain introduces a dominant quantization axis along the z direction [Figs. 3(a)–3(c)]. For circularly polarized light propagating along this axis, the HH and LH transitions in the different spin systems are completely decoupled [Fig. 3(c)]. In this case, it is not possible to create a coherent HH-LH polarization resulting in the absence of any quantum beats. For linearly x-polarized light propagating along the z axis, both HH-CB and LH-CB transitions are excited within each spin system, and quantum beats occur [Fig. 3(b)]. The PSR's are the same as for excitons in quantum wells.[4] A more detailed analysis (discussed below) shows that changing from a parallel linear polarization of pump and probe pulses to a perpendicular linear polarization results in a phase change of the beats by π with the same beat amplitude. Our data for E_{det} on the excitonic resonances [Fig. 1(b)] are in full agreement with these theoretical predictions.

In addition to excitons, the spectrally broad pump pulse excites HH and LH to CB transitions in the continuum. In the optically coupled range of k space, the pulses cover both interband transitions and HH-LH quantum coherence is generated. In contrast to the excitonic transitions, the HH-LH energy splitting varies continuously over this range and—consequently—the beat frequency observed in the pump-probe measurements varies continuously with detection energy E_{det}. The beat frequencies (squares in the inset of Fig. 1) are derived from the data by Fourier transformation of the oscillatory signal, and compare well with the HH-LH energy splitting derived from bandstructure calculations.[10] The observed dependence of the beat frequency on E_{det} directly rules out other possible mechanisms such as, e.g., (a) exciton–LO-phonon quantum beats,[11] (b) electron-polariton interactions,[12] or (c) propagation effects.[13] These phenomena would lead to a constant beat frequency that is independent on the detection scheme [mechanism (a)], and beats due to mechanisms (b) and (c) would occur on a distinctly different time scale of picoseconds.

The PSR's for the continuum HH-LH beats are different from the excitonic case. We observe strong oscillations for parallel linear and cocircular polarizations, but very weak beats of opposite phase for perpendicular linear polarizations. In the free-carrier continuum, the effect of strain is much weaker than for excitonic states.[7,9] Here the individual $\mathbf{k}$ vector acts as the dominant quantization axis, resulting in PSR's that are depicted schematically in the right column of Fig. 3. For any chosen polarization (linear or circular), there is always a direction in k space where the HH and the LH transitions are coupled via a common state in the conduction band. Our experiments demonstrate that selective excitation or probing of HH-CB or LH-CB transitions is not possible with circularly polarized light.

For a quantitative analysis, we explicitely calculate the optical matrix elements for transitions in the six-level system for each direction in k space. For simplicity, the so-called spherical approximation is used, in which warping of the energy surfaces is neglected. The orientation of the optical dipoles is determined by the corresponding p orbitals and spins in the cell periodic part of the Bloch wave functions, examples of which are given for $\mathbf{k}\|z$ and $\mathbf{k}\|y$ in Fig. 3). For a given k vector there are six dipole-allowed transitions, e.g., $CB\alpha \leftrightarrow LH\beta$ (cf. Fig. 3: α and β indicate different states within the twofold spin degeneracy), in the corresponding six-level system with the optical matrix elements[14]

$$\mathbf{M}_{CB\alpha\leftrightarrow HH\alpha}(\mathbf{k}) = M(k)\cdot[\mathbf{e}_\vartheta + i\cdot\mathbf{e}_\varphi]/\sqrt{2},$$

$$\mathbf{M}_{CB\beta\leftrightarrow HH\beta}(\mathbf{k}) = M(k)\cdot[\mathbf{e}_\vartheta - i\cdot\mathbf{e}_\varphi]/\sqrt{2},$$

$$\mathbf{M}_{CB\alpha\leftrightarrow LH\beta}(\mathbf{k}) = M(k)\cdot[-\mathbf{e}_k]\cdot\sqrt{2/3},$$

$$\mathbf{M}_{CB\beta\leftrightarrow LH\beta}(\mathbf{k})=M(k)\cdot[\mathbf{e}_k]\cdot\sqrt{2/3},$$

$$\mathbf{M}_{CB\alpha\leftrightarrow LH\alpha}(\mathbf{k})=M(k)\cdot[\mathbf{e}_\vartheta-i\cdot\mathbf{e}_\varphi]/\sqrt{6},$$

$$\mathbf{M}_{CB\beta\leftrightarrow LH\alpha}(\mathbf{k})=M(k)\cdot[\mathbf{e}_\vartheta+i\cdot\mathbf{e}_\varphi]/\sqrt{6}. \quad (1)$$

$M(k)$ is the magnitude of the optical matrix elements, the orientation of which is expressed in the unit vectors of the polar coordinate system $\mathbf{e}_k$, $\mathbf{e}_\vartheta$, and $\mathbf{e}_\varphi$. Pump and probe pulses are assumed to propagate along the z direction, with polarizations aligned to x and/or y directions:

$$\mathbf{E}_x=E_0\cdot\mathbf{e}_x,\quad \mathbf{E}_y=E_0\cdot\mathbf{e}_y,$$

$$\mathbf{E}_{\sigma^+}=E_0\cdot[\mathbf{e}_x+i\cdot\mathbf{e}_y]/\sqrt{2}, \quad (2)$$

$$\mathbf{E}_{\sigma^-}=E_0\cdot[\mathbf{e}_x-i\cdot\mathbf{e}_y]/\sqrt{2}$$

for linear and circular polarizations, respectively. The amplitude $A_{pu,pr}(\vartheta,\varphi)$ of the HH-LH quantum beats in the pump-probe experiment depends on the direction of the respective $\mathbf{k}$ vector, and is directly proportional to the following sequence of interactions with the electric fields of pump and probe pulses:[15]

$$\begin{aligned}A_{pu,pr}(\vartheta,\varphi)=&B_{pu,pr,CB\alpha\leftrightarrow HH\alpha,CB\alpha\leftrightarrow LH\alpha}(\vartheta,\varphi)\\&+B_{pu,pr,CB\alpha\leftrightarrow HH\alpha,CB\alpha\leftrightarrow LH\beta}(\vartheta,\varphi),\\&+B_{pu,pr,CB\beta\leftrightarrow HH\beta,CB\beta\leftrightarrow LH\beta}(\vartheta,\varphi)\\&+B_{pu,pr,CB\beta,HH\beta,CB\beta\leftrightarrow LH\alpha}(\vartheta,\varphi), \quad (3)\end{aligned}$$

$$\begin{aligned}B_{pu,pr,i,j}(\vartheta,\varphi)=&[\mathbf{M}_i(\mathbf{k})\cdot\mathbf{E}_{pu}]\cdot[\mathbf{M}_j^*(\mathbf{k})\cdot\mathbf{E}_{pu}^*]\\&\times[\mathbf{M}_j(\mathbf{k})\cdot\mathbf{E}_{pr}]\cdot[\mathbf{M}_i^*(\mathbf{k})\cdot\mathbf{E}_{pr}^*]\\&/[M(k)\cdot E_0]^4.\end{aligned}$$

Finally, the beat amplitudes are averaged over all directions in k space:

$$QB_{pu,pr}=\frac{1}{4\pi}\int_0^\pi d\vartheta\int_0^{2\pi}d\varphi\ A_{pu,pr}(\vartheta,\varphi). \quad (4)$$

With the procedure described above, we obtain the following beat amplitudes for different polarization geometries:

$$\begin{aligned}&QB_{x,x}=+0.178=+1.0QB_0,\quad QB_{x,y}=-0.5QB_0,\\&QB_{\sigma^+,\sigma^+}=+0.875QB_0,\quad QB_{\sigma^+,\sigma^-}=-0.375QB_0.\end{aligned} \quad (5)$$

Here a minus sign represents a phase shift of π [also see numbers in Figs. 1(b), 2(a), and 2(b)]. The experimental results are in good agreement with this analysis, demonstrating that excitonic and free-carrier HH-LH quantum beats can be clearly separated via the PSR's. For countercircular polarizations the experimental data [dashed line in Fig. 2(b)] do not show the theoretically predicted weak HH-LH beats of opposite phase ($QB_{\sigma^+,\sigma^-}=-0.375QB_0$). This small discrepancy, which is close to the experimental accuracy, is probably due to the spherical approximation of our model (warping terms are neglected in the PSR's).

It is interesting to note that the HH-LH quantum beats in the free-carrier continuum are observed for relatively long delay times of up to 500 fs (Fig. 2). This indicates that dephasing times of the coherent HH-LH polarizations are substantially longer than for excitation of similar carrier concentrations at higher excess energies.[7] When exciting high in the continuum, carrier-optical phonon scattering and carrier-carrier (Coulomb) scattering represent the main dephasing mechanisms. For excitation close to the band edge, both photogenerated heavy and light holes are well below the energy threshold for optical phonon emission. In this case, phonon scattering makes a minor contribution to the dephasing of the coherent HH-LH polarization. For the moderate excitation density of 2×10^{15} cm^{-3}, Coulomb scattering times among the photoexcited carriers are known to be in the range of several hundreds of femtoseconds,[16,17] similar to the dephasing times found here.

In conclusion, we studied ultrafast HH-LH quantum beats of excitons and free carriers in a slightly strained GaAs crystal in spectrally and time-resolved pump-probe experiments in the vicinity of the fundamental absorption edge. Different polarization selection rules allow us to separate the two effects. We demonstrated that HH-LH quantum beats of free carriers make an important contribution to the ultrafast nonlinear response of bulk III-V semiconductors when excited at the band edge.

M.H. was supported by the Alexander von Humboldt Foundation.

[1] For a review, see J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer, Berlin 1996), Chap. 2.

[2] K. Leo, T. C. Damen, J. Shah, E. O. Göbel, and K. Köhler, Appl. Phys. Lett. **57**, 19 (1990).

[3] B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog, Solid State Commun. **74**, 1279 (1990).

[4] S. Schmitt-Rink *et al.*, Phys. Rev. B **46**, 10 460 (1992).

[5] M. Koch, J. Feldmann, E. O. Göbel, P. Thomas, J. Shah, and K. Köhler, Phys. Rev. B **48**, 11 480 (1993).

[6] J. P. Likforman, M. Joffre, G. Cheriaux, and D. Hulin, Opt. Lett. **20**, 2006 (1995).

[7] M. Joschko, M. Woerner, T. Elsaesser, E. Binder, T. Kuhn, R. Hey, H. Kostial, and K. Ploog, Phys. Rev. Lett. **78**, 737 (1997).

[8] The crystal was glued on a fused silica window and the GaAs substrate was removed by etching to allow transmission measurements.

[9] P. Enders, A. Bärwolff, M. Woerner, and D. Suisky, Phys. Rev. B **51**, 16 695 (1995).

[10] The influence of strain on the HH-LH energy splitting in the continuum is weak, so splitting is close to that in the unstrained material (Ref. 9).

[11] L. Banyai, D. B. Tran Thoai, E. Reitsamer, H. Haug, D. Steinbach, M. U. Wehner, M. Wegener, T. Marchner, and W. Stolz, Phys. Rev. Lett. **75**, 2188 (1995).

[12] V. V. Travnikov, S. O. Kognovitskii, Ja. Aaviksoo, and I. Re-

imand, in *The Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 1, p. 357.

[13] D. Kim, J. Shah, D. A. B. Miller, T. C. Damen, W. Schäfer, and L. Pfeiffer, Phys. Rev. B **48**, 17 902 (1993).

[14] See *Optical Orientation*, edited by F. Meier and B. P. Zakharchenya (North-Holland, Amsterdam, 1984).

[15] W. T. Pollard, S. L. Dexheimer, Q. Wang, L. A. Peteanu, C. V. Shank, and R. A. Mathies, J. Phys. Chem. **96**, 6147 (1992).

[16] A. Leitenstorfer, A. Lohner, T. Elsaesser, S. Haas, F. Rossi, T. Kuhn, W. Klein, G. Boehm, G. Traenkle, and G. Weimann, Phys. Rev. Lett. **73**, 1687 (1994).

[17] F. Rossi, S. Haas, and T. Kuhn, Phys. Rev. Lett. **72**, 152 (1994).