Electric and magnetic dipole two-photon absorption in semiconductors

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Nonlinear spectroscopy of the exciton fine structure in GaAs has allowed us to measure simultaneously both magnetic dipole two-photon absorption and electric dipole one-photon absorption. The splitting of the excitonic ground state into the spin-allowed orthoexciton and the spin-forbidden paraexciton gives the electron-hole exchange energy directly. The peak assignment is proved by nonlinear magnetoabsorption. Utilizing electric dipole two-photon magnetoabsorption within the same experiment, a rich fine structure of the $2P$ exciton has been observed that has not been previously resolved. [S0163-1829(96)05820-1]

Nonlinear absorption spectroscopy has proved to be a powerful tool for understanding the optical and electronic properties of crystalline solids. A great number of two-photon absorption (TPA) experiments on bulk semiconductors such as ZnSe,[1] ZnTe, CdTe,[2] and GaAs (Refs. 2–4) have shown that this method can provide additional information to one-photon absorption (OPA) measurements due to different selection rules. In particular, the two-photon allowed $2P$ excitons, which cannot be observed in OPA spectra, have been studied extensively in the past.

A physical process of great importance in semiconductors is the electron-electron exchange interaction, responsible for the properties of the semiconductor at high excitation densities or in a magnetic field. This many-body effect is mostly neglected in the one-electron approximation, but has been found to influence excitonic levels in a magnetic field or under uniaxial stress.[5–8] Nevertheless, direct observation of a zero-field splitting of the $1S$-exciton level due to the exchange interaction is difficult for two reasons: first, the splitting is very small, typically one-tenth of the exciton binding energy, thus favoring materials with a large exciton binding energy; second, the transition to the lower $1S$-exciton state is electric dipole forbidden and therefore not accessible in OPA. For these reasons exchange energies of GaAs reported so far have been obtained only by extrapolation from experiments under high magnetic fields or uniaxial stress, which relax the selection rules. But the results for the exchange energy differ from each other by up to a factor of 40.[5–8]

In this paper we show that a combination of two different nonlinear absorption processes within one experiment, namely, TPA and self-absorption of second-harmonic generated light, can yield detailed information about the excitonic fine structure of semiconductors, which is not accessible by linear techniques, thus allowing a direct and precise determination of the analytical electron-hole exchange energy Δ_{exch}.

The nonlinear absorption experiments have been performed on bulk GaAs. The sample consisted of a 57-μm GaAs layer with a carrier mobility of 200.000 $\mathrm{cm}^2/\mathrm{V\,s}$ at 77 K ($n=1.4\times10^{13}\ \mathrm{cm}^{-3}$), grown by liquid phase epitaxy on a Si-doped (100)-oriented GaAs substrate. Ohmic contacts were made by evaporating AuGe on the surface and alloying at 450 °C for 4 min. The absorption processes at 1.4 K have been investigated by measuring the photoconductive response of the sample under intense linearly polarized near infrared light[9] with a photon energy of $\hbar\omega\approx E_g/2$, where E_g is the gap energy of GaAs (1.519 eV at 4.2 K). Magnetic fields between 0 and 6 T in the Faraday configuration have been applied.

In Fig. 1 the spectrum of the sample for zero magnetic field is shown. The photoconductive response is plotted versus the two-photon energy $2\hbar\omega$. The spectrum exhibits a strong increase of absorption at 1.518 eV with a clear maximum at $1.5189\pm0.000\,02$ eV. Furthermore, a double-peak structure is observed at $1.515\,17\pm0.000\,01$ and $1.515\,55\pm0.000\,01$ eV, denoted by $1S_O$ and $1S_P$, respectively.

To understand the observed features one has to consider the band structure of GaAs at the Γ point near $k=0$. Following the model of Cho[10] and additionally neglecting the spin-orbit split-off Γ_7 valence band, the ground state of the exciton is a linear combination of eight electron-hole pair states

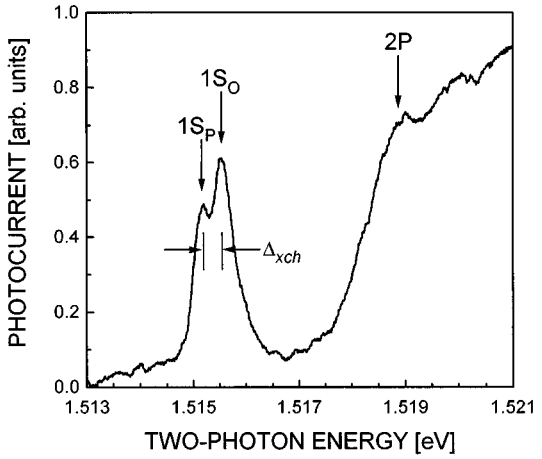

FIG. 1. Two-photon absorption spectrum of GaAs at 1.4 K in the excitonic region. The different $1S$- and $2P$-exciton transitions are indicated by arrows. Also shown is the exchange energy Δ_{exch}.

that can be formed by the twofold Γ_6 conduction-band electron state with $s=\frac{1}{2}$ and the fourfold Γ_8 valence-band hole state with $j=\frac{3}{2}$. The eight electron-hole pair states can be classified according to the system's total angular momentum $J=j\pm s$ and its z component M_J.

The electron-electron exchange interaction of the many-body system transforms to an additional but repulsive interaction between electron and hole, called electron-hole exchange interaction in the two-particle system, which reduces the Coulomb interaction. Taking into account only the isotropic electron-hole exchange interaction, which may be written as[11]

$$H_{\mathrm{exch}}=\tfrac{1}{8}\Delta_{\mathrm{exch}}(3-4\boldsymbol{\sigma}\cdot\mathbf{J})+\Delta_{\mathrm{LT}}\delta_{J1}(1-M_J^2),$$

where σ is the spin vector of the electron, $\mathbf{J}$ is the angular momentum vector of the hole, and Δ_{LT} is the longitudinal-transversal splitting, the short-range part of the exchange effect gives rise to a splitting of the exciton ground state into the $J=1$ singlet-triplet mixed state named orthoexciton, which is electric dipole allowed, and the $J=2$ pure triplet state named paraexciton, which is electric dipole forbidden. The energy difference between these two states is the so-called analytical exchange energy Δ_{exch}.

Despite the different spin multiplicity of the para- and orthoexciton making the simultaneous observation impossible in linear spectroscopy, transitions to both states can be induced in the present nonlinear experiment due to different types of dipole transitions (electric and magnetic) induced by the illumination of the sample by strong laser light with a photon energy of half of the band-gap energy of the semiconductor.

It is well known that compound semiconductors such as GaAs exhibit second-harmonic generation (SHG) when illuminated by nonresonant high-intensity light, due to the lack of inversion symmetry of the crystal lattice.[12] If the exciting laser frequency ω is chosen so that the energy of the SHG wave $E_{\mathrm{SHG}}=2\hbar\omega$ is in resonance with a transition energy of the semiconductor, part of the SHG wave can be reabsorbed within the crystal if the transition obeys the one-photon selection rules.[9] This second-order process gives rise to a peak at the position of the one-photon dipole-allowed $1S$ orthoexciton. This transition can clearly be identified in the spectrum in Fig. 1 where it is denoted by $1S_O$.

On the other hand, the high-intensity laser light induces two-photon transitions according to TPA selection rules whenever the two-photon energy $E_{\mathrm{TPA}}=2\hbar\omega$ equals the energy of a two-photon dipole-allowed transition. In zinc-blende semiconductors with a p-like valence band conservation of parity implies two-photon electric dipole transitions to even-parity states such as the $2P$ exciton, which can be detected at 1.5189 eV in the spectrum. Due to the small binding energy of the $2P$ exciton in GaAs this feature appears more as a maximum on the background of the higher excitonic states and the continuum absorption than as a distinct peak.

A third nonlinear absorption of intense laser light in a semiconductor is due to another two-photon process, reported by Fröhlich, Itoh, and Pahlke-Lerch[13] for the case of alkali halides. In contrast to regular TPA, where two consecutive electric dipole transitions of a valence-band electron to an even-parity exciton states take place, there exists a TPA process where the electric dipole transition to an intermediate spin-allowed state of odd parity is followed by a magnetic dipole transition to a spin-forbidden odd-parity final state. Utilizing this third mechanism, Fröhlich, Itoh, and Pahlke-Lerch[13] were able to study the anisotropic exchange interaction in alkali halides via TPA, which directly influences the energy levels of the $1S$ paraexciton. They also determined the isotropic exchange energy, although, as stated by the authors, this was subject to large errors due to the uncertainty of the energy of the transverse orthoexciton gained from an independent measurement of three-photon absorption.

By applying a nonlinear spectroscopy in the photoconductive mode to extremely-high-purity GaAs samples we have been able to identify the spin-forbidden $1S$ paraexciton at $B=0$ T, which gives a distinct contribution denoted $1S_P$ on the lower-energy side of the orthoexciton in the spectrum in Fig. 1. As both the para- and the orthoexciton can be seen simultaneously in the experiment, one can directly determine the isotropic exchange energy Δ_{exch} in GaAs from the energy difference of the two peaks to a great accuracy. A value of $\Delta_{\mathrm{exch}}=0.38\pm0.01$ meV is obtained.

This value is in good agreement with the variational calculations of Abe,[14] taking into account three valence and two conduction bands and neglecting k linear terms in the Hamiltonian. However, there is a wide spread in experimental results obtained previously by indirect methods. A value of 0.37 meV was obtained by Gilleo, Bailey, and Hill,[5] extrapolated from piezoreflection measurements. Nam *et al.*[6] extrapolate the positions of the magnetoexcitonic $1S$-exciton fine structure to $B=0$ T using a peak assignment by line intensity estimations. This leads to a value $\Delta_{\mathrm{exch}}=0.16$ meV. Sell *et al.*[7] state an upper limit of the exchange energy of 0.1 meV, derived by polarization-dependent reflectivity measurements under stress. Ekardt, Lösch, and Bimberg[8] fit a theoretical model for the dependence of the exchange interaction on the oscillator strength of the transitions to their experimental data at medium magnetic fields, giving a value of 0.02 meV. All the experimental results were obtained by one-photon spectroscopy and therefore need extrapolation from high magnetic fields or stress as the paraexciton cannot be detected in principle within this technique without external perturbations. The broad variation of Δ_{exch} gives evidence for the difficulty in determining the exchange energy in this way.

The assignment of the peaks is perfectly confirmed by a two-photon magnetoabsorption measurement. In Fig. 2 TPA spectra of the sample in the range of the $1S$ exciton are shown at magnetic fields between 0 and 6 T, in steps of 0.5 T, in the Faraday configuration ($\mathbf{k}\|\mathbf{B}$) at $T=1.4$ K. The photoconductive signal is plotted versus the two-photon energy $2\hbar\omega$. For clarity, all spectra are normalized and in addition cut on the high-energy side of the $1S$ exciton features.

Following the structure of the $1S$ exciton from 0 to 6 T, one can see the development of the double structure at 0 T, already shown in Fig. 1, into a fine structure of five main transitions at 6 T. The $1S$ orthoexciton exhibits a splitting into two peaks above 0.5 T, which are separated from each other by 0.35 meV at 6 T. As a guide to the eye the peak positions are indicated by solid arrows.

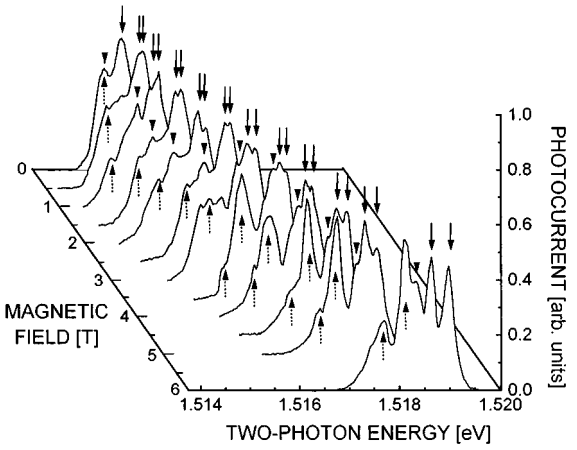

FIG. 2. Two-photon magnetoabsorption spectra of GaAs in the range of the $1S$ exciton at magnetic fields between 0 and 6 T in steps of 0.5 T in the Faraday configuration at 1.4 K. Solid arrows indicate $1S$-orthoexciton transitions, dotted arrows and triangles indicate $1S$-paraexciton transitions.

Also the $1S$ paraexciton splits into two peaks at 0.5 T. The lower one of the two lines (indicated from 0 T upward by a dotted arrow) runs through a minimum in transition energy at 1 T with increasing magnetic field before it bends up and runs parallel to the other transitions, at the same time gaining oscillator strength compared to the $1S$ orthoexciton and thus being the most prominent transition at 6 T. At 3 T an additional shoulder at the low-energy side of the paraexciton appears that forms a clear peak at 6 T (also indicated by a dotted arrow). It can be seen that the magnetic field increases the absorption strength of the paraexcitonic contributions compared to the orthoexcitonic ones. This is a direct consequence of the different transition processes. Whereas electric dipole transitions are weakly affected by a magnetic field, the probability of a magnetic dipole transition is enhanced proportional to B.

In Fig. 3 the transition energies of the observed $1S$-exciton lines are plotted against magnetic field. As a guide to the eye solid and dashed lines connect the measured transition energies of ortho- and paraexcitons, respectively. The dependence of the peak position on magnetic field is strongly nonlinear for fields lower than 3 T, leading to an asymmetric splitting of the paraexciton and a diamagnetic shift of all lines. The coupling between the $(J=1)$ and $(J=2)$ $1S$-exciton states results in a complicated development of the highest paraexciton transition.

The observed splitting reflects the theoretically predicted behavior of the $1S$-exciton substates in a magnetic field.[6] For the low-field region ($\gamma<1$ with $\gamma=\hbar\omega_C/2R_y$, ω_C is the cyclotron frequency and R_y the effective Rydberg energy of the exciton), where the magnetic field can be treated as a perturbation on the excitonic levels, the degeneracy of both the orthoexciton and the paraexciton is lifted due to the linear Zeeman effect.[8] This is illustrated in a diagram in Fig. 3, where the different $(J=1)$ and $(J=2)$ $1S$-exciton levels are indicated by M_J. In addition, a diamagnetic term in the exciton Hamiltonian shifts the transitions quadratically with magnetic field to higher energy. For $\gamma>1$ the magnetic field is stronger than the excitonic Coulomb interaction, giving

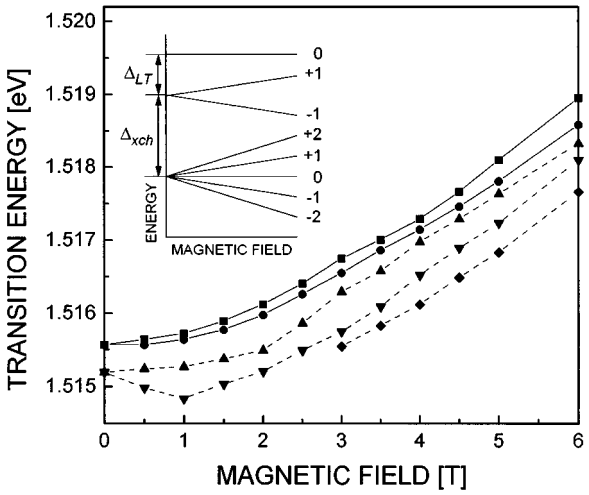

FIG. 3. The $1S$-orthoexciton and $1S$-paraexciton transition energies as a function of magnetic field for the Faraday configuration. As a guide to the eye the data points are connected by solid and dashed lines for the orthoexciton and paraexciton, respectively. The inset schematically shows the splitting of the $1S$ exciton due to the linear Zeeman effect. The different states are labeled by M_J.

rise to a Landau-level-like linear dependence of the transition energies on the magnetic field, as can be seen in the spectrum of Fig. 3.

Allowed transitions occur for both the transversal orthoexcitons with $J=1$, $M_J=\pm1$ due to self-absorption of the SHG light and the transversal paraexcitons with $J=2$, $M_J=\pm1$ due to magnetic dipole TPA. For magnetic fields with $\gamma>1$ the field-induced mixing of the states leads to the observation of the paraexcitonic components with $M_J=\pm2$. Transitions to longitudinal excitons ($M_J=0$) are only allowed in Voigt geometry[10] and therefore cannot be detected in our spectra. From this analysis we assign the observed features at 6 T in order of increasing energy to the $|2,-2\rangle$, $|2,-1\rangle$, $|2,+1\rangle$, $|1,-1\rangle$, and $|1,+1\rangle$ $1S$ excitons, respectively.

To emphasize the powerfulness of the nonlinear spectroscopy technique presented here, Fig. 4 shows the TPA spectrum of the sample in the range of the $2P$ exciton at a mag-

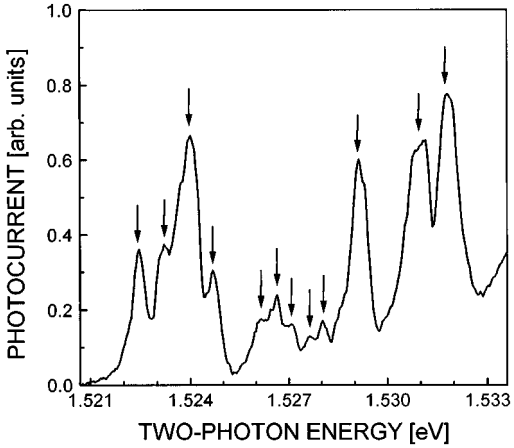

FIG. 4. Two-photon magnetoabsorption spectrum of GaAs in the range of the $2P$ exciton at 6 T in the Faraday configuration. Observed transitions are indicated by arrows.

netic field of 6 T in the Faraday configuration. Due to the compression of the excitonic wave function in the presence of a magnetic field, the oscillator strength of the $2P$-exciton contribution is strongly enhanced. Whereas at 0 T the influence of envelope-hole coupling is too weak to observe a splitting of the $2P$ exciton as in other materials,[15] it strongly affects the spectrum at 6 T. A complete lifting of the 12-fold degeneracy of the $2P$ exciton at 0 T (neglecting the spin degeneracy) in a magnetic field beyond Zeeman splitting could be observed in GaAs, giving rise to 12 peaks in the spectrum. This fine structure has been reported for ZnTe and CdTe by Neumann, Nöthe, and Lipari.[2] Both materials have a large exciton binding energy and very sharp absorption lines, with well-resolved fine structure. In GaAs, where, on the one hand, the linewidth of the exciton lines is about four times larger than in CdTe and, on the other hand, the binding energy of the $2P$ exciton is about two times smaller, they were not able to resolve this additional splitting of the various $2P$-exciton states. With our high-sensitivity nonlinear photoconductive measurement a detailed analysis of the $2P$ exciton in a magnetic field, and therefore the determination of the spherical parameter[16] that defines the strength of the envelope-hole coupling, is possible.

In conclusion, we have shown that three different nonlinear absorption processes take place in the sample due to irradiation by intense laser light with an energy of half of the band gap of GaAs, namely, self-absorption of SHG light, electric dipole and magnetic dipole TPA. Because of the different selection rules it was possible to observe both a zero-field $1S$-exciton splitting due to the electron-hole exchange interaction and the $2P$ exciton. From the energy separation between the $1S$ ortho- and paraexciton we could directly and accurately determine the electron-hole exchange energy. The assignments of the peaks were proved by nonlinear magnetoabsorption where a Zeeman splitting of the ortho- and paraexciton could be observed, leading to a fine structure of five peaks at 6 T. In addition, we reported a rich fine structure of the $2P$ exciton in a magnetic field beyond Zeeman splitting due to envelope-hole coupling, showing the universal powerfulness of nonlinear spectroscopy to investigate the excitonic fine structure.

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