Excitonic electroabsorption spectra and Franz-Keldysh effect of $In_{0.53}Ga_{0.47}As/InP$ studied by small modulation of static fields

A. Jaeger and G. Weiser
Department of Physics and Center of Material Sciences, University of Marburg, D-35032 Marburg, Germany
(Received 13 February 1998)

The influence of electric fields on excitons and band states of a bulk semiconductor grown lattice matched to an *n*-InP substrate is studied by measuring absorption and differential electroabsorption spectra, i.e., by weak modulation of static fields. At small fields, field broadening of light- and heavy-hole excitons, split by residual strain, determines the shape of the electroabsorption spectrum. At slightly larger fields Franz-Keldysh oscillations of the band states develop, the discrete exciton lines disappear in the absorption spectrum and their electroabsorption signal becomes part of the response of the continuum. The transition from excitonic electroabsorption to the Franz-Keldysh effect is clearly resolved and both regimes are compared with theoretical models. The observable range of Franz-Keldysh oscillations increases linearly with the field which corresponds to a constant mean free path of free carriers of 160 nm and to a collision rate that increases with the square root of energy. Different reduced mass of light- and heavy-hole transitions leads to beat in the spectrum. For static fields above 10 kV/cm the electroabsorption spectra, in particular, the decay of the amplitude with increasing energy, is quantitatively described by the one-electron theory if an energy-dependent scattering rate accounts for a field-independent mean free path. [S0163-1829(98)04639-6]

I. INTRODUCTION

The fundamental absorption edge of semiconductors is significantly modified by the Coulomb interaction of electrons and holes that gives rise to discrete states below the band gap E_g and to an enhanced continuum absorption above the gap.[1] It dominates the distribution of excited states and their oscillator strength with respect to the ground states in materials with large exciton binding energy but is important even in high-mobility semiconductors where a small reduced mass and large dielectric constant leads to very small exciton binding. Static electric fields change also the absorption edge of a semiconductor and produce an exponential absorption tail, first described by Franz[2] and Keldysh[3] as field- and photon-assisted tunneling from the valence to the conduction bands. Based on the wave function of an electron in a constant electric field the Franz-Keldysh effect was generalized to states above the gap[4,5] and electroreflectance became a valuable tool to study the band structure of semiconductors. Mixing of band states by the field, however, leads not only to broadening of the absorption edge but also to oscillatory changes of the absorption above the gap. These Franz-Keldysh oscillations are difficult to observe because high-quality samples providing a long lifetime of carriers and sufficiently homogeneous fields are necessary. Theory predicted quite early that the discrete exciton states should respond even more sensitively to an electric field than the band states[6–9] but the experiments, measuring usually field-induced changes of the reflectivity could not separate the response of excitons and band states. In high mobility semiconductors the exciton binding energy was too small to avoid strong mixing of exciton and band states by the relatively large fields near the surface while in the case of larger binding energy only an excitonic response was observed and Franz-Keldysh oscillations did not develop.[10–12]

Modern epitaxy improved the experimental situation by growing thin single crystals of high quality. If grown on a transparent substrate field-induced changes of the transmission can be studied which depends little on a surface field and employs the relatively homogeneous field inside a sample. Electroabsorption spectra of $In_{1-x}Ga_xAs_yP_{1-y}/InP$ epilayers have been used to determine the variation of the field with applied voltage in laser structures, to measure the exciton linewidth[13] and the mean free path of free carriers.[14] Electroreflectance and the related photoreflectance[15] are now frequently applied to characterize III-V heterostructures. We present a study of field-induced changes at the absorption edge of a semiconductor over a wide range of fields that reveals distinctly different effects for low and high field. The results are compared with theoretical models that are reviewed in the next section to summarize the relations needed for the evaluation of the data. After a brief description of the experimental procedure we present and discuss the experimental results.

II. THEORETICAL MODELS

The absorption at the direct gap of a semiconductor where weak Coulomb interaction leads to Wannier excitons is given by[1]

$$\alpha(\hbar\omega)=\frac{A}{nc\omega}2\pi\sqrt{R}\left\{\sum_{n=1}^{\infty}\frac{2R}{n^3}\delta\left(\hbar\omega-E_g+\frac{R}{n^2}\right)+\frac{\mathcal{H}(\hbar\omega-E_g)}{1-\exp\left(-2\pi\sqrt{\frac{R}{\hbar\omega-E_g}}\right)}\right\}. \quad (1)$$

 © 1998 The American Physical Society

The sum accounts for absorption into discrete states which line up in a hydrogenlike series while the second expression with the Heaviside step function $\mathcal{H}(\hbar\omega - E_g)$ describes the absorption by the continuum. R and a_B are the binding energy and Bohr radius of the exciton

$$R = \frac{\mu e^4}{2(4\pi\varepsilon_o\hbar)^2}\frac{\mu}{\varepsilon^2}, \quad a_B = \frac{4\pi\varepsilon_o\hbar^2}{e^2}\frac{\varepsilon}{\mu} \tag{2}$$

and μ is the reduced mass of electron and hole the Coulomb interaction of which is reduced by the dielectric constant ε. The absorption strength A is determined by the momentum matrix element p_{cv} between the valence and conduction band:

$$A = \frac{e^2}{4\pi\varepsilon_o m_o^2}|p_{cv}|^2\left(\frac{2\mu}{\hbar^2}\right)^{3/2}. \tag{3}$$

The continuum absorption that in Eq. (1) is expressed on an energy scale normalized to R approaches for high energy the same square-root dependence as obtained for vanishing Coulomb interaction ($R=0$):

$$\alpha(\hbar\omega) = \frac{A}{nc\omega}\mathcal{H}(\hbar\omega - E_g)\sqrt{\hbar\omega - E_g}. \tag{4}$$

The acceleration of an electron by an electric field leads to new eigenstates that within the one-electron theory are described by replacing the plane-wave envelope for motion along the field F by the Airy function:

$$\varphi = \frac{1}{2\pi}\exp(ik_x x)\exp(ik_y y)\frac{\sqrt{eF}}{\hbar\Theta}\mathrm{Ai}(\zeta), \quad \zeta = \frac{\hbar\omega - E_g}{\hbar\Theta}. \tag{5}$$

The argument of the Airy function $\mathrm{Ai}(\zeta)$ is the kinetic energy of the hole and electron normalized to an electro-optic energy $\hbar\Theta$ that accounts for the interaction with the electric field along z:

$$\hbar\Theta = \left(\frac{eF\hbar}{\sqrt{2\mu_z}}\right)^{2/3}. \tag{6}$$

The resulting absorption spectrum is described by the Airy function and its derivative with respect to ζ (Ref. 4) and oscillates around the spectrum for the field-free case [Eq. (4)].

$$\alpha(\omega,F) = \frac{A}{nc\omega}\sqrt{\hbar\Theta}\,\pi[\mathrm{Ai}'^2(\zeta) - \zeta\cdot\mathrm{Ai}^2(\zeta)]. \tag{7}$$

The field-induced change $\Delta\alpha$ of the interband absorption, the electroabsorption spectrum, therefore consists of a series of peaks that shift with increasing field to higher energy. This shift is a consequence of the scaling of the kinetic energy to $\hbar\Theta$ and leads to a relation of peak position E_ν and peak number ν that delivers the field in the sample from optical data once the reduced mass is known.[16]

$$(E_\nu - E_g)^{3/2} = \frac{3ehF}{8\sqrt{2\mu_z}}\cdot\nu. \tag{8}$$

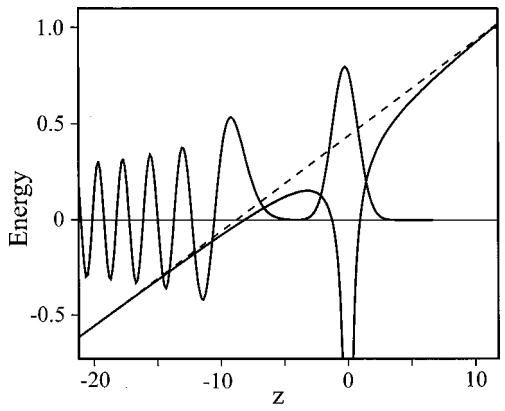

FIG. 1. Wave function of an excited electron in a strong electric field showing resonant enhancement in the Coulomb potential of the hole, a residue of the 1s bound state.

The coherent acceleration is limited by scattering which in the most simple approximation is described by the Lorentzian broadening parameter Γ. Such collisional broadening has been included into the one-electron theory by supplementing the argument of the Airy function with an imaginary part:[5]

$$\zeta = \frac{\hbar\omega - E_g + i\Gamma}{\hbar\Theta}. \tag{9}$$

Coulomb interaction modifies the electroabsorption spectra but no analytical solution has yet been found for the joint action of an external field. For small fields perturbation theory yields the quadratic Stark shift of the discrete exciton states, whereas for larger field approximate wave functions[17,18] and numerical calculations[6–8] were successfully applied.

Figure 1 shows the envelope function of the lowest excited state in a large external field. Bound and continuum states are strongly mixed to a new eigenstate. The small amplitude in the potential well of the hole indicates rapid tunneling through the Coulomb barrier and fast ionization of the exciton. Except for such resonance inside the Coulomb potential the electron wave function agrees with the Airy function, the wave function of a free particle in a constant field. Different effects prevail depending on the relative size of the exciton binding energy R and the external potential over the exciton radius a_B that defines the ionization field:

$$F_{ion} = \frac{R}{e\cdot a_B}. \tag{10}$$

For very small fields ($F \ll F_{ion}$) perturbation theory predicts a redshift of the exciton due to the quadratic Stark effect. Already at rather small-field ($F/F_{\mathrm{ion}} \sim 0.3$) perturbation theory becomes inadequate and mixing of bound and continuum states leads to the turnover of the absorption peak into a blueshift[6,8,19] as shown in Fig. 2. At high field the discrete states are strongly broadened and merge with the continuum. However, it cannot be excluded that Coulomb interaction still modifies the electroabsorption spectrum too much to be described by the Franz-Keldysh effect alone.[7]

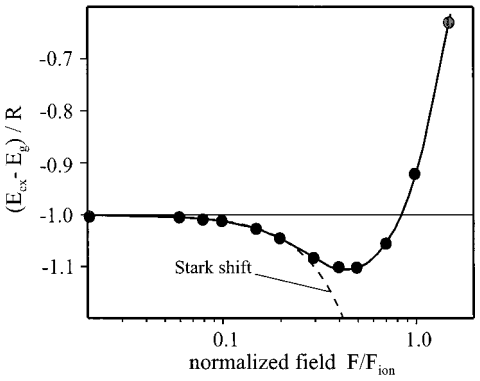

FIG. 2. Transition energy of the 1*s* exciton in a normalized electric field F/F_{ion}. Data points are from Ref. [6]. The quadratic redshift resulting from perturbation theory (dashed curve) applies only at small fields and changes at higher field to a blueshift.

III. EXPERIMENTAL DETAILS

The samples were grown by low-pressure metal organic vapor phase epitaxy as 600-nm-thick crystals lattice matched to the *n*-doped InP substrate. All samples showed at room temperature small tensile strain ($\varepsilon < 10^{-3}$) derived from narrow x-ray diffraction peaks. We found in this range of strain no indication that possible misfit dislocations affect the quality of the spectra quite in contrast to variation of composition or temperature of the samples. We present only results of the ternary alloy $In_{0.53}Ga_{0.47}As$ but equivalent spectra are obtained throughout the quaternary system (InGa) (AsP). Their evaluation reveals larger inhomogeneous broadening of excitons and smaller mean free path of free carriers.[13,14]

The sample was mounted onto the tip of a He flow cryostat. The light source was a tungsten halogen lamp filtered by a 1-m monochomator to a bandpass of 0.5 meV or less. Since the substrate was transparent below 1.4 eV all spectra could be derived from the transmitted intensity I and its field-induced change ΔI, which was measured by a nitrogen-cooled Ge detector. The doped substrate served as grounded electrode. The field in the sample was changed by a dc bias applied to a transparent Pt contact (thickness 6 nm) on top of the sample. A small superimposed voltage ΔU (square wave, $f = 1$ kHz) increased the static field and caused a transmittance change that was measured by a lock-in amplifier. The change of the absorption constant by switching from the lower field F_1 to the higher field F_2 is derived from the relative change of the transmitted intensity where d is the thickness of the crystal:

$$\Delta\alpha = \alpha(F_2) - \alpha(F_1) = -\frac{1}{d}\frac{\Delta I}{I}. \tag{11}$$

Small-field modulation thus is closely related to photomodulation spectroscopy where a built-in field is partially screened by excited carriers. However, being independent of the penetration depth of light and of the diffusion of carriers small-field electroabsorption yields more homogeneous conditions, which facilitates the quantitative analysis of the spectra. Electroabsorption spectroscopy avoids also the complex analysis of electroreflectance spectra that near the absorption edge are dominated by changes of the refractive index. Although small-field modulation provides a smaller response than the conventional electroabsorption spectroscopy that switches from low, presumably zero field to high field it has further advantages. By summing up all absorption changes along the light path the change of transmittance induced by a small voltage ΔU is not very sensitive to inhomogeneous fields resulting from residual space charge.[14] It will be demonstrated in this report that by increasing the static field in small steps a small modulating ac field separates clearly those effects which dominate in a particular range of fields.

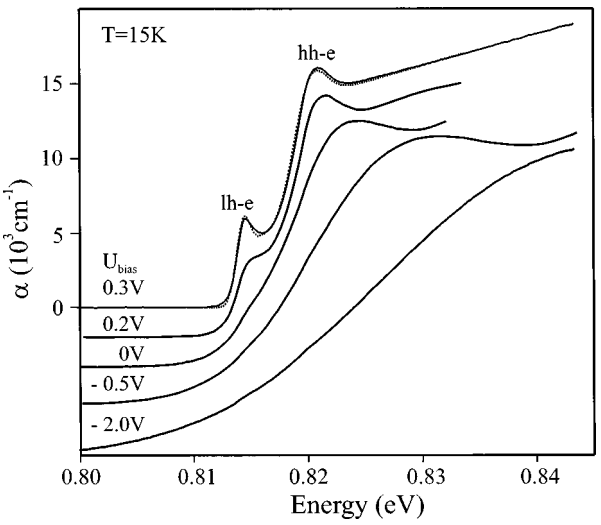

FIG. 3. Variation with dc bias of the absorption edge. Light- and heavy-hole exciton peaks, split by residual strain, appear if a built-in field is reduced by forward bias. The spectrum on top is fitted to an excitonic absorption edge with Gaussian broadening (dotted curve).

IV. EXPERIMENTAL RESULTS

A. Absorption spectra

The absorption spectrum at low temperature depends strongly on the field in the sample as shown in Fig. 3. At zero bias ($U = 0$ V) the absorption spectrum shows a long tail rising to a broad peak near 0.82 eV, which could be interpreted as a strongly broadened exciton. However, if the field is reduced by forward bias this peak shifts to lower energy and narrows. Simultaneously a weaker peak appears, with the peak below it attributed to the light-hole exciton. The splitting of heavy- and light-hole excitons by 5.7 meV is due to residual tensile strain by a small lattice mismatch ($\Delta a_\perp / a_0 = -1.21 \times 10^{-3}$) measured at the same spot by x-ray diffraction. The large width of the exciton at zero bias thus is due to an internal field set up as in a pin diode by carrier diffusion between the contact regions. Too large forward bias increased the linewidth of the excitons again probably due to screening by free carriers that diffuse from the doped substrate into the sample. Evaluation of the Franz-Keldysh effect in the next section yields a built-in field of 5.3 kV/cm, which is far above the ionization field of the exciton. Table I summarizes the relevant parameters, the binding energy and Bohr radius of heavy- and light-hole excitons derived by scaling the hydrogen model with the reduced mass[20]

TABLE I. Reduced mass μ of heavy and light holes in $In_{0.53}Ga_{0.47}As$,[20] binding energy R, and Bohr radius a_B, derived for a dielectric constant $\varepsilon = 13.9$ (Ref. 21) and the ionization fields F_{ion} of excitons.

Exciton	μ/m_0	R (meV)	a_B (nm)	F_{ion} (kV/cm)
Light hole	0.0277	1.6	32.4	0.49
Heavy hole	0.0377	2.65	19.5	1.36

and dielectric constant[21] of $In_{0.53}Ga_{0.47}As$. Experimental values of the binding energy are close to that of the heavy-hole exciton.[22,23]

If the field is sufficiently reduced the absorption edge agrees very well with an excitonic absorption edge calculated from Eq. (1). The parameters of the fit are the gap, the valence-band splitting, the exciton binding energies R, and the transition strength A, which for heavy holes is about twice as large as for light holes. The calculated spectrum was convoluted with a Gaussian to account for inhomogeneous broadening in the alloy. Under reduced forward bias, which corresponds to larger internal field, the absorption spectrum can still be matched to Eq. (1) but with larger line width and a lineshape that is better modeled by a Lorentzian reflecting increasing lifetime broadening.

The absorption spectra of discrete and continuum states connect smoothly with no particular feature indicating the onset of the gap E_g. Because only the $1s$ state of the exciton is resolved the binding energy must be determined from the scaling of the continuum absorption to the binding energy R. Such a fit, however, yields 0.8 and 1.4 meV for the light- and heavy-hole exciton, respectively, about half the energies calculated from the hydrogen model in Table I. Similar deviation has been observed on GaAs (Ref. 24) and on $In_{1-x}Ga_xAs_yP_{1-y}$.[25] Such deviation could result from the difference between the absorption spectrum α and the imaginary part $\mathrm{Im}(\varepsilon)$ of the dielectric constant to which Eq. (1) actually applies:

$$\alpha = \frac{\omega\,\mathrm{Im}(\varepsilon)}{n(\omega)c}. \tag{12}$$

Although Eq. (1) includes the factor ω it does not account for the energy dependence of the refractive index, which increases below and decreases above the sharp increase of the absorption[26] consistent with the Kramers-Kronig relations of real and imaginary part of the dielectric response function $\varepsilon(\omega)$. A decreasing refractive index beyond the exciton leads to a faster increase of the absorption spectrum of the continuum states pretending a smaller value of R.

Figure 3 confirms the extreme sensitivity of Wannier excitons to electric fields. Small reduction of the forward bias leads to rapid broadening and a shift of the heavy-hole peak to higher energy. This behavior indicates that even the small field at 0.3 V bias is still above the range where the quadratic Stark effect of perturbation theory applies. The smallest fields we achieved in any sample on n-doped substrates were always near or above the ionization field of the excitons. For larger field, i.e., at zero or reverse bias, a long absorption tail develops as predicted by theory and the peak on top shifts further into the region of band states. This absorption peak then cannot be attributed to a bound state but is one of the Franz-Keldysh oscillations.

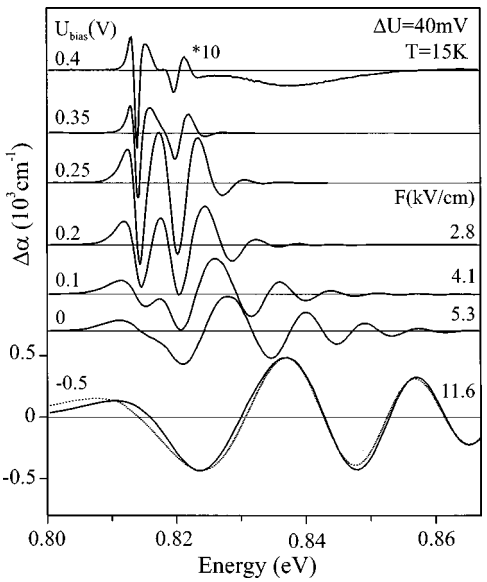

FIG. 4. Variation with dc bias of electroabsorption spectra measured with a small ac voltage. The spectra show the transition from an excitonic response to Franz-Keldysh oscillations at higher field. The dotted spectrum at the highest field is calculated from one-electron theory neglecting excitonic effects completely.

B. Electroabsorption spectra at weak fields

The modification of the absorption edge by electric fields is much better resolved in the electroabsorption spectra displayed in Fig. 4. Derived from transmittance changes due to a small ac voltage ΔU these spectra represent the difference of absorption spectra for two slightly different static fields. Most pronounced changes of the spectral line shape occur under forward bias. At the smallest field at 0.4 V forward bias we observe only a response from light- and heavy-hole excitons. The sharp negative peaks at 0.8143 and 0.8199 eV agree better than 0.5 meV with the exciton transition energies derived from the fit of the absorption spectrum and correspond to a decreasing height of the exciton peak with increasing field. Most of this loss shows up in a larger width of the exciton peak resulting in the positive peaks. The line shape of the spectrum thus is determined by lifetime broadening of the excitons. Despite its weaker oscillator strength the light-hole exciton responds more sensitively to an increasing field. Due to the larger radius and smaller binding energy the same modulating voltage ΔU causes a larger change of the effective field F/F_{ion} for the light-hole exciton.

The electroabsorption spectrum at 0.4 V bias had to be enlarged by a factor of 10 to fit into the scale of the other spectra. This small response near flatband conditions is probably due to substantial screening of the modulation voltage by injected carriers obvious also from a strongly increasing current. The peak amplitude increases rapidly as forward bias is reduced. Down to 0.25 V the electron absorption (EA) spectrum is dominated by field broadening of the excitons resulting in two negative peaks which shift slowly to higher

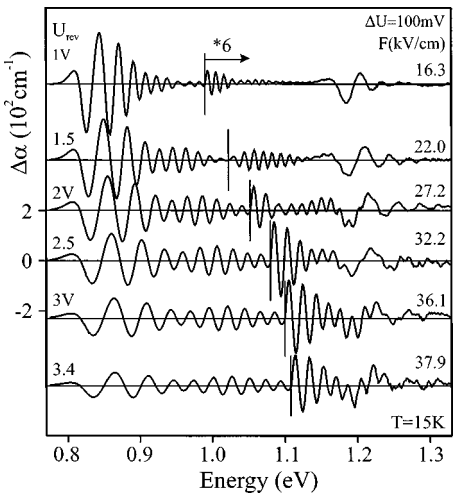

FIG. 5. Evolution of Franz-Keldysh oscillations with reverse bias. Spectra to the right of the vertical bars are enlarged by a factor of 6. Two sets of oscillations from heavy- and light-hole transitions cause the beat in the spectra. A third series develops at the gap of the split-off valence band.

energy. At 0.25 V the excitonic features merge to a single response while at higher energy additional peaks appear that indicate the onset of the Franz-Keldysh effect of the band states. At 0.2 V where in the absorption spectrum the excitons are still resolved (Fig. 3) the electroabsorption spectrum consists of a set of oscillations with the first negative peaks coinciding with the excitonic absorption peaks. Except for some enhancement of the leading peaks the spectrum attains already the line shape of the Franz-Keldysh effect. The peak positions line up according to Eq. (8) and yield a static field of 2.8 kV/cm based on the reduced mass of the heavy-hole transition. Above 4 kV/cm the light-hole exciton response vanishes under the first positive peak and at 5 kV/cm only a small distortion of the spectral line shape near the first zero remains from the light-hole excitons while the response of the heavy-hole excitons is part of the first negative peak of a series of oscillations. Excitons are no longer apparent in the absorption or in the electroabsorption spectrum, which is dominated by an increasing number of Franz-Keldysh oscillations. For fields of 11.6 kV/cm at 0.5 V reverse bias the electroabsorption spectrum agrees almost perfectly with a calculated spectrum based on the Franz-Keldysh effect with energy dependent lifetime broadening. Coulomb interaction seems negligible now since the deviation between experiment and one-electron model remains very small even at the onset of the spectrum.

C. Spectra of the Franz-Keldysh effect

A large number of Franz-Keldysh oscillations develops under reverse bias as shown in Fig. 5. The peak positions shift with increasing field in perfect agreement to the scaling of the excess energy $E-E_g$ to the electro-optic energy $\hbar\Theta$ of the heavy hole. At higher fields more than 40 peaks are observed that obey strictly Eq. (8) as demonstrated before.[14] Closer inspection reveals two sets of oscillations related to heavy- and light-hole transitions. The stronger heavy-hole transitions dominate the general shape of the spectrum and the position of the peaks while light-hole transitions cause the beat of the peak amplitudes first observed at the gap of Ge.[27] Because of their smaller reduced mass light holes scale to a larger electro-optic energy and yield an independent set of smaller amplitude and different period. At fields above 20 kV/cm the oscillations from the band gap reach the gap of the split-off valence band where another set of oscillations is observed and above 35 kV/cm oscillations stretch over 0.5 eV up to the gap of the InP substrate.

The Franz-Keldysh oscillations result from coherent acceleration of free electrons and holes by the field that modifies the excited states. Because coherent motion is terminated by scattering, the range of oscillations is limited by the collision rate. A detailed study revealed that δE the range of observable oscillations increases linearly with field both for the ternary and the quaternary alloys.[14] Such linear increase is incompatible with a constant collision time τ commonly invoked to explain the damping of Franz-Keldysh oscillations. Because electron and hole acquire between collisions a maximum momentum $k(\tau)=eF\tau$ the corresponding energy range should increase quadratically with field if the collision time is constant:

$$\delta E=\frac{(eF\tau)^2}{2\mu}. \tag{13}$$

A linear increase with field follows from the quite general assumption of a collision rate $1/\tau$ that is proportional to the carrier velocity v. This assumption results in a mean free path $L=v\tau$ that is independent of the carrier energy and leads to the observed linear relationship of δE and field F that determines the gain of the energy carriers over the mean free path:

$$\delta E=eF\cdot L. \tag{14}$$

The ternary sample presented here has a mean free path of 160 nm at low temperature which decreases to about half this value at room temperature. This value is confirmed for 400 meV excess energy up to the gap of the split-off band. Quaternary alloys show a smaller mean free path, varying with composition down to 60 nm at low temperature in good agreement with the variation of the excitonic linewidth obtained from absorption and electroabsorption spectra.[13]

In view of such a large mean free path Franz-Keldysh oscillations may be limited in thin samples by the external boundaries. In recent photomodulation spectra of GaAs an improved quality of Franz-Keldysh oscillations has been attributed to an enhanced lifetime of carriers by passivation of an interface.[28] However, the thickness of the reference samples was only 100 nm while the improved spectrum was taken from a 150-nm-thick crystal. Because the mean free path in the binary compound GaAs is probably larger than in the ternary alloy $In_{0.53}Ga_{0.47}As$ it is likely that the Franz-Keldysh oscillations were limited in either case by the thickness of the sample.

The validity of Eq. (8) for the peak positions enables the measurement of the field in the sample and its variation with bias voltage. The field at zero bias is 5.3 kV/cm which by multiplication with the thickness d of undoped layers yields a diffusion potential of 0.3 V between the Pt contact and the substrate. For small bias the field increases linearly with the external voltage as shown in Fig. 6. The increase $\Delta F/\Delta U$

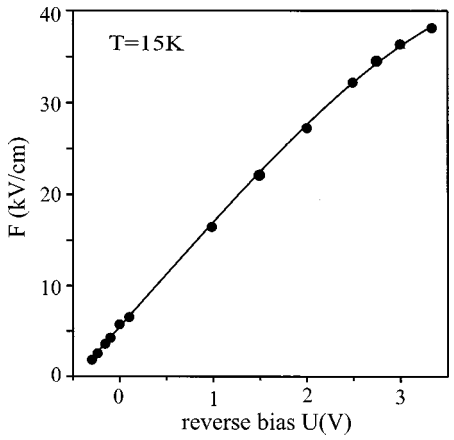

FIG. 6. Variation with bias voltage of the field in the sample as derived from the peak positions of Franz-Keldysh oscillations.

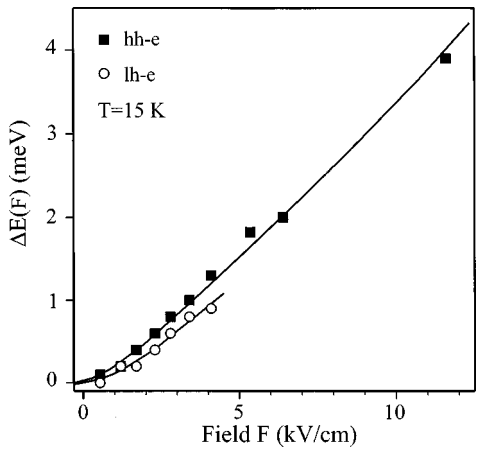

FIG. 7. Field-induced shift ΔE of light- and heavy-hole excitons derived from the shift of the respective negative peaks in the electroabsorption spectra. The point at the highest field is the first negative peak of the Franz-Keldysh oscillations. Lines are guides to the eye.

$\approx$12 (kV/cm)/V, however, is only 70% of the value anticipated if the applied voltage drops off over the undoped region. A substantial fraction of the applied voltage is lost by serial resistance and variation of the space charge in the doped region, which accounts for part of the built-in field. For larger reverse bias the field increases sublinearly with the external voltage. A constant modulation voltage ΔU therefore produces modulation fields ΔF that vary with bias. For the excitonic spectra in Fig. 4 the modulation field was about 0.5 kV/cm which is sufficient to produce absorption changes of the order 10^2 cm^{-1}. Between 1 and 3.4 V reverse bias the modulation voltage of 0.1 V corresponds to a modulation field that decreases from 1.2 to 0.7 kV/cm. The flat-band position is extrapolated to 0.45 V forward bias but no electroabsorption spectrum could be measured under such condition. Carrier diffusion, probably electrons from the doped substrate, caused screening of the modulation voltage, which is already apparent from the small signal height of the spectrum obtained for 0.4 V bias.

V. DISCUSSION

A. Excitonic spectra

The spectra show three distinct field regions where different effects dominate the response to a small modulating field: a purely excitonic signal at very low field, a transition range where excitons are present and Franz-Keldysh oscillations evolve that finally determine the spectrum in the high-field region. Excitonic electroreflectance spectra are common in the case of large exciton binding energy, such as PbI_2, where Franz-Keldysh oscillations are absent even for fields as large as 2×10^5 V/cm.[11] In case of CdS where the exciton binding energy is 30 meV (Ref. 29) a weak redshift is observed at low field but field broadening dominates the electroabsorption spectra, which again show no oscillations above the gap.[10] To our knowledge no Franz-Keldysh oscillations are reported for samples with pronounced excitons. This is not surprising because large exciton binding energy is related to a larger reduced mass which is unfavorable for Franz-Keldysh oscillations by two reasons: (i) the field required for a certain value of $\hbar\Theta$ increases quadratically with the mass and (ii) the smaller mobility resulting from a larger mass reduces the mean free path for coherent acceleration. Few data exist for field effects on excitons of large radius and small binding energy. Field broadening of the 1*s* exciton state is observed in case of highly purified Ge single crystals at low temperature but no Stark shift is reported.[30,31] A small initial redshift of the exciton has been observed in low-temperature reflectance spectra of GaAs, which turns into a blueshift at larger field.[32] These experiments were limited to small fields and Franz-Keldysh oscillations were not observed.

We expect from Fig. 2 that a quadratic Stark shift of the weakly bound excitons of $In_{0.53}Ga_{0.47}As$ can be observed only for fields below 0.5 kV/cm, a range that was not accessible to our experiments. Consequently, the plot of the exciton transition energy, taken from the negative EA peaks, reveals only a blueshift (Fig. 7). The negative peak coincides at small field with the exciton transition energy and with increasing field gradually into the first negative peak of the Franz-Keldysh effect, which dominates above 10 kV/cm. In the transition range at fields a few times the ionization field discrete and continuum states are strongly mixed and can no longer be distinguished. Residual strain in our samples causes splitting of the valence band resulting in two closely neighbored excitons. Although strain alters the hole masses we expect little influence on the reduced mass and binding energy of the heavy-hole exciton, which is determined by the electron mass. Due to the small splitting the excitons may be coupled by the field but such coupling has apparently little influence on the line shape of their electroabsorption response. We find good agreement with spectra calculated by Blossey with a theory for a single exciton and nondegenerate bands.[8,9]

At very low field where the redshift of the exciton dominates the electroabsorption spectrum should resemble the derivative of the absorption spectrum, i.e., a positive peak followed by a negative one. When lifetime broadening becomes significant the positive peak at low energy decreases in height, the negative peak shifts to the exciton transition energy, and a positive peak appears at higher energy. In this case perturbation theory is no longer applicable because bound and continuum states are too strongly mixed. The

relative size of the two positive peak changes with increasing field in favor of the high-energy peak. The EA spectrum of the light-hole exciton for the smallest field in Fig. 4 shows a slightly larger positive peak below the exciton as predicted for a field close to half the ionization field. Such a small field near 0.5 kV/cm is consistent with an extrapolation of the field from Fig. 6. At slightly larger field, at 0.35 V forward bias, the first positive peak becomes smaller than the second one indicating a field above half the ionization field. This trend has been observed by matching the excitonic spectra of PbI_2 measured at the large field of 80 and 285 kV/cm.[9] These strong fields are still below the ionization field because of the much larger binding energy of 70 meV and no Franz-Keldysh oscillations from continuum states are observed.[11] The scaling to the ionization field used in this theory thus is applicable over a large range of binding energies and provides a consistent description of low-field electroabsorption spectra, which are dominated by lifetime broadening of excitons.

B. Electroabsorption spectra above the ionization threshold

At 10 kV/cm, about an order of magnitude above the ionization field, the electroabsorption spectrum agrees with a calculated spectrum based solely on free carriers and ignoring electron hole interaction (Fig. 4). This seems surprising because the absorption spectrum measured under the corresponding reverse bias of 0.5 V shows significant Coulomb enhancement of the interband absorption. A crucial test for the applicability of the one-electron theory is a quantitative description not only of the field-induced shift of oscillations but also of the amplitudes which has not succeeded before for a significant number of oscillations. Part of this failure may arise from experimental conditions. In most cases electroreflectance spectra were analyzed but they are sensitive to the inhomogeneous field near the surface. A more important reason is that by switching from low to high field in favor of a better signal-to-noise ratio some response of the exciton states is involved.

Part of the failure lies in the treatment of collisional broadening. For data of Ge it has been noticed quite early that Airy functions with constant broadening parameter yield no satisfactory description of modulated spectra even over a rather limited range.[33,34] An exponential decay of the amplitudes with increasing energy has been proposed to match a relatively small number of oscillations in several materials, including $In_{0.53}Ga_{0.47}As$ but no justification for such dependence is given.[35] Classical scattering theory, on the other hand, assuming scattering rates proportional to the carrier velocity, results in a mean free path between collisions that is independent of the carrier velocity. The mean free path, which is incompatible with a constant collision time determines the energy that free carriers pick up between collisions. This view of a constant mean free path is confirmed by the observation that the range of Franz-Keldysh oscillations increases linearly with the electric field over 400 meV.[14] We replace therefore the imaginary part in the argument of the Airy functions [Eq. (9)] by a broadening parameter that increases with the square root of the kinetic energy $E-E_g$ to account for a collision rate $1/\tau$ that increases with the carrier velocity:

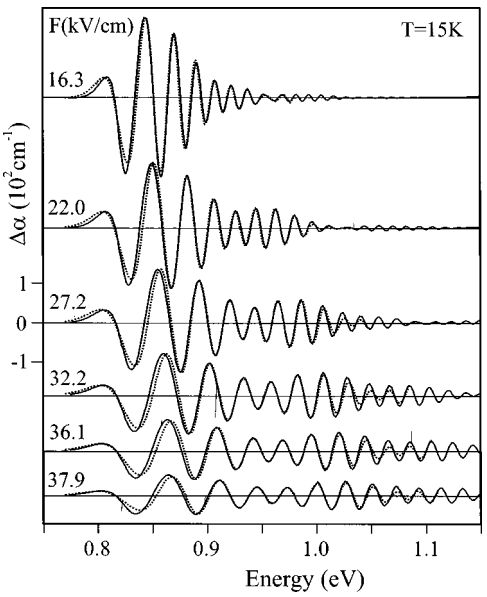

FIG. 8. Comparison of a set of electroabsorption spectra with spectra calculated by one-electron theory (dotted lines) using for all spectra the same energy dependence for collisional broadening.

$$\Gamma = \frac{\hbar}{\tau} = \gamma\sqrt{E-E_g}. \tag{15}$$

Both the static and the modulating fields are taken from Fig. 6. We made in each case small adjustments of the transition strength A to match the calculated peak height near the gap to the experimental spectrum. Another parameter is the gap E_g in the Franz-Keldysh theory that turns out to be slightly below the exciton transition energy and very close to the first zero crossing. This gap marks the onset of the density of excited states with no distinction of bound and free states. The prefactor γ of the energy-dependent broadening thus is the only parameter to describe the decay of oscillations for all spectra far beyond the fundamental gap.

The fit of a whole set of experimental spectra in Fig. 8 to a model based on a single set of parameters yields over a wide energy range almost perfect agreement and confirms the validity of the one-electron theory. The electro-optic energy of the heavy-hole transition varied from 14 to 25 meV for reverse bias between 1 and 3.4 V and is much larger than the exciton binding energy. All spectra use the same broadening parameter $\gamma = 0.38\sqrt{\text{meV}}$ for heavy- and light-hole transitions. The collision rate corresponds to a broadening parameter Γ which increases from 2.7 to 6.6 meV as the excess energy increases from 50 to 300 meV. The broadening parameters thus are much smaller than $\hbar\Theta$, consistent with the large number of observable oscillations. Such broadening parameters correspond to scattering times between 240 and 100 fs, which is in the range of coherent lifetimes observed in ultrafast spectroscopy of excitons.

The very small deviations of the calculated from the experimental spectra even near the gap confirm that Coulomb interaction is negligible in weak-field modulation spectra at fields above the ionization field of the exciton. This is quite different from spectra obtained by switching from low to high field. Such spectra show on top of Franz-Keldysh oscillations a very narrow negative peak due quenching of the

discrete exciton state if low-field conditions are really achieved. Corresponding electroreflectance spectra have been published for GaAs.[36] If the static field has ionized the bound states as under reverse a small increase of the field has no further effect on the bound states and little effect on the Coulomb enhancement of the exciton continuum.

The calculated spectrum is a superposition of two sets of Franz-Keldysh oscillations for light and heavy holes. Their different mass results in slightly different periods causing beat of the amplitude in perfect agreement with the experiment. Fourier transform of the experimental oscillations yields ratios of 3:1 and 1:0.8 for the amplitudes A and the electro-optic energy $\hbar\Theta$ for heavy and light holes, respectively. These values are consistent with the reduced masses and the theoretical transition probability. It is not possible to fit the spectrum with a common mass of heavy and light transitions,[35] which would eliminate the beat in the spectra. Numerical noise limited the calculation of Franz-Keldysh oscillations to a range shorter than that actually observed. Near the end of the calculated spectra where, due to the beat of heavy- and light-hole response, the signal should decrease again the experimental spectrum shows larger amplitudes than calculated. We attribute this deviation to the vanishing beat of the spectra for two possible reasons: a faster collision rate of light holes that could scatter into the heavy-hole band and the increase of the light-hole mass for larger k values leading to a similar reduced mass and a period of light- and heavy-hole oscillations.

Based on data over a relatively small range it had been noticed that the period of the oscillations is quite insensitive to broadening and nonparabolicity of the bands.[37] Our data confirm this finding, however, to keep the calculated peak positions in step with the experimental data over the whole energy range we had to increase the electron mass slowly with energy to account for the nonparabolic conduction band. This increase by about 20% over 0.4 eV leads to minor corrections of the field strength derived from Eq. (8) alone. Details of this analysis, including the evaluation of the oscillations of the split-off valence band, will be published in a forthcoming paper. The reproduction of the spectra by superposition of two independent series of Franz-Keldysh oscillations points to negligible coupling of heavy- and light-hole bands by the electric field. Such influence has recently been proposed[38] but is certainly not confirmed by our data. However, the reduced mass of the dominant heavy-hole transitions is determined by the small electron mass. Changes in the valence-band structure therefore must be large to modify the Franz-Keldysh oscillations.

VI. CONCLUSION

Electroabsorption spectra measured by small modulation of a static field resolve two limiting cases for the interaction of field and electronic states in a semiconductor. At low field below their ionization threshold narrow exciton transitions dominate the spectrum. The weakly bound Wannier excitons are extremely sensitive and the diffusion potential across a heterostructure may be sufficient to cause severe broadening. Field broadening thus determines the line shape of the excitonic spectra. A quadratic Stark shift of the exciton as expected from perturbation theory may occur at even lower field but has not been observed because of insufficient compensation of the built-in field. In a small transition range where fields are of the order of the ionization field the discrete states become part of the continuum and their absorption peaks disappear in a broad absorption tail. Simultaneously, Franz-Keldysh oscillations develop and overlap with the excitonic features.

At fields a few times the ionization field excitonic features have vanished completely and the electroabsorption spectrum consists of a large number of Franz-Keldysh oscillations. These oscillation stretch with increasing field with the peculiar $F^{2/3}$ power dependence related to the envelope function of accelerated particles. The oscillations include bound and unbound states, which in such a field can no longer be distinguished. The band gap derived from the oscillations is slightly below the exciton transition energy and marks the onset of the density of states rather than the gap of band-structure theory. For small fields the first negative peak of these oscillations is very close to the energy of the exciton ground state. In this range one-electron theory describes the electroabsorption spectrum quantitatively, which greatly facilitates the evaluation of the spectra. Excellent agreement over a large energy range is achieved by assuming a collision rate that increases with $\sqrt{E-E_g}$. Such a collision rate is proportional to the carriers velocity and corresponds to a mean free path that is independent of the field and can be derived from the spectral range of Franz-Keldysh oscillations. For $In_{0.53}Ga_{0.47}As$ crystals of high quality we find at low temperature a mean free path of 160 nm that decreases at room temperature by a factor of 2. We emphasize that satisfactory agreement of calculated and experimental spectra is not achieved for an energy-independent collision rate.

The key to the good agreement of one-electron theory and experiment is the elimination of bound exciton states by a static field, leaving only the Coulomb enhancement of the interband absorption, which obviously is not sensitive to small variation of the field. Weak modulation spectroscopy provides access to quantitative information on many sample properties. The narrow excitonic spectra at low-field resolve strain-induced splitting of the valence band and inhomogeneous broadening. The Franz-Keldysh oscillations at higher field measure the internal field based only on the reduced mass while their variation with dc bias gives access to the distribution of the field in the sample. The beat of the amplitudes shows furthermore that two independent series of oscillations of heavy- and light-hole transitions coexist pointing to negligible coupling of the valence bands by the field. The range of oscillations yields the mean free path and reveals an energy-dependent scattering rate. The mean free path is quite large, 160 nm in a ternary alloy at low temperature. Spectra obtained on thin samples therefore may be modified by the external boundaries.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft. We wish to thank P. Wiedemann, I. Gyuro, and E. Zielinski, from the research center of Alcatel-SEL at Stuttgart, who provided the samples for this study.

[1] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
[2] W. Franz, Z. Naturforsch. A **13**, 484 (1958).
[3] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **34**, 1138 (1958) [Sov. Phys. JETP **7**, 788 (1958)].
[4] D. E. Aspnes, Phys. Rev. **147**, 554 (1966).
[5] D. E. Aspnes, Phys. Rev. **153**, 972 (1967).
[6] H. I. Ralph, J. Phys. C **2**, 378 (1968).
[7] J. D. Dow and D. Redfield, Phys. Rev. B **1**, 3358 (1970).
[8] D. F. Blossey, Phys. Rev. B **2**, 3976 (1970).
[9] D. F. Blossey, Phys. Rev. B **3**, 1382 (1971).
[10] H. Lange and E. Gutsche, Phys. Status Solidi **32**, 293 (1969).
[11] P. I. Perov, L. A. Avdeeva, and M. I. Elison, Fiz. Tverd. Tela **11**, 541 (1969) [Sov. Phys. Solid State **11**, 438 (1969)].
[12] G. Weiser and J. Stuke, Phys. Status Solidi **45**, 691 (1971).
[13] A. Jaeger, G. Weiser, P. Wiedemann, I. Gyuro, and E. Zielinski, IEEE J. Sel. Top. Quantum Electron **1**, 1113 (1995).
[14] A. Jaeger, G. Weiser, P. Wiedemann, I. Gyuro, and E. Zielinski, J. Phys.: Condens. Matter **8**, 6779 (1996).
[15] F. Pollak, in *Semiconductors and Semimetals*, edited by T. P. Pearsall (Academic, New York, 1990), Vol. 32.
[16] D. E. Aspnes, Phys. Rev. Lett. **31**, 230 (1973).
[17] I. A. Merkulov and V. Perel, Phys. Lett. **45A**, 83 (1973).
[18] I. A. Merkulov, Zh. Eksp. Teor. Fiz **66**, 2314 (1974) [Sov. Phys. JETP **39**, 1140 (1974)].
[19] G. Czajkowski, Nuovo Cimento D **9**, 781 (1987).
[20] K. Alavi, R. L. Aggarwal, and S. H. Groves, Phys. Rev. B **21**, 1311 (1980).
[21] R. Blachnik and O. Madelung, in *Semiconductors*, edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982); O. Madelung, in *Semiconductors*, edited by O. Madelung and M. Schulz, Landolt-Börnstein, New Series, Group III, Vol. 22, Pt. a (Springer-Verlag, Berlin, 1987).
[22] K. H. Goetz, D. Bimberg, H. Jurgensen, J. Selders, A. V. Solomonov, G. F. Glinskii, and M. Razeghi, J. Appl. Phys. **54**, 4543 (1983).
[23] D. K. Gaskill, N. Bottka, L. Aina, and M. Mattingly, Appl. Phys. Lett. **56**, 1269 (1990).
[24] M. D. Sturge, Phys. Rev. **127**, 768 (1962).
[25] K. Satzke, G. Weiser, R. Höger, and W. Thulke, J. Appl. Phys. **63**, 5485 (1988).
[26] C. Tanguy, Phys. Rev. Lett. **75**, 4090 (1995).
[27] P. Handler, S. Jasperson, and S. Koeppen, Phys. Rev. Lett. **23**, 1387 (1969).
[28] B. T. Jonker, O. J. Glembocki, R. T. Holm, and R. J. Wagner, Phys. Rev. Lett. **79**, 4886 (1997).
[29] J. Voigt, F. Spiegelberg, and M. Senoner, Phys. Status Solidi B **91**, 189 (1979).
[30] Q. H. F. Vrehen, Phys. Rev. **145**, 675 (1966).
[31] T. Nishino, T. Yanagida, and Y. Hamakawa, J. Phys. Soc. Jpn. **30**, 579 (1971).
[32] L. Schultheis, K. Köhler, and C. W. Tu, Phys. Rev. B **36**, 6609 (1987).
[33] D. E. Aspnes and A. A. Studna, Surf. Sci. **37**, 631 (1973).
[34] A. M. Joullie, S. Gaillard, and C. Alibert, Solid State Commun. **13**, 665 (1973).
[35] J. P. Estrera, W. M. Duncan, and R. Glosser, Phys. Rev. B **49**, 7281 (1994).
[36] D. E. Aspnes and A. A. Studna, Phys. Rev. B **7**, 4605 (1973).
[37] D. E. Aspnes, Phys. Rev. B **10**, 4228 (1974).
[38] J. Hader, N. Linder, and G. H. Döhler, Phys. Rev. B **55**, 6960 (1997).