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Excitation spectroscopy on donor-acceptor pair luminescence in GaP

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Luminescence excitation experiments on donor-acceptor pairs in GaP are reported. Using different combinations of deep donor and shallow acceptor, we determine the unperturbed excited states of the acceptors C, Mg, Zn, and Cd as well as their dependence on the pair separation. The assignment of the states is discussed in detail. Good agreement has been found with results from ir absorption and Raman scattering.

I. INTRODUCTION

Luminescence excitation spectroscopy at high resolution has been used extensively since the availability of powerful tunable light sources (dye laser).[1-3] The method has become a valuable addition to ordinary luminescence measurements. In the latter case a multitude of electronic processes resulting from above-band-gap excitation confuses the situation and mostly the lowest excited states of the crystal or impurity are involved. However, the luminescence excitation technique opens up the possibility to selectively excite also higher electronic states. With this excitation technique tunneling of excitons between NN_i pairs in GaP,[1] and the excited exciton states in GaP,[2] were observed.

The application of luminescence excitation spectroscopy to donor-acceptor (*D-A*) pairs represents a new method to determine the excited impurity states in semiconductors. GaP is ideally suited to luminescence studies of *D-A* pairs.[4] There is no other semiconductor yet known that exhibits such a variety of *D-A* radiative recombinations as GaP with distinct spectra. GaP has the further advantage that the majority of the *D-A* luminescence lies in the visible range of the spectrum where the powerful dye lasers and sensitive detection systems are available.

We investigated various combinations of deep donors and shallow acceptors. The first results published earlier[5] indicate that in this system we can only detect the excited states of shallow acceptors. The absence of transitions involving excited donor states is understandable because the energy to excite into these states is degenerate with the energy for transitions into acceptor continuum states. In the indirect semiconductor GaP these latter processes have a much greater oscillator strength than the transition from the acceptor ground state into donor excited states. Recent publications[6,7] of excitation spectroscopy on *D-A* pairs in ZnTe have proven that in a direct semiconductor the method is capable to reveal both the donor and the acceptor excited states.

In Sec. II we explain the technique of excitation spectroscopy on *D-A* pairs and describe the apparatus used as well as the requirements for the samples. The results obtained with different *D-A* combinations are presented in Sec. III and the data for distant pair separation are compared in Sec. IV to infrared (ir) absorption and Raman scattering measurements.

In our earlier publication[5] we deduced the valence-band parameters and the band gap of GaP as well as some acceptor ionization energies by means of the effective-mass theory of Baldereschi and Lipari (BL).[8,9] All energies deduced lie about 8 meV below recently published data.[10-15] The calculation of BL have been performed under the assumption of large spin-orbit splitting ($\Delta_{so} \to \infty$). This is a crude approximation for GaP, where the spin-orbit splitting of the valence band is only twice as large as the binding energy of the shallowest acceptor. Furthermore, the screening of impurities has a strong effect on the ground-state binding energy.[16] The incorporation of both effects into the calculations might resolve the discrepancy in the acceptor binding energies, the band gap, and the free-exciton binding energy. Recent calculations for Si including both a q-dependent screening and a coupling with the split-off valence band led to a better agreement between theory and experiment.[17]

The excitation spectroscopy on *D-A* pairs supplies further information besides the isolated impurity states: By changing the pair separation in well-defined steps the binding energy of the acceptor states is established as a function of the distance to the donor. The behavior is analogous to the binding of a molecule. The experiments shown in Sec. III give an increasing binding energy for decreasing pair separation. This effect can be understood in terms of increasing Coulomb overlap of the wave functions involved. A detailed treatment is given in Ref. 18.

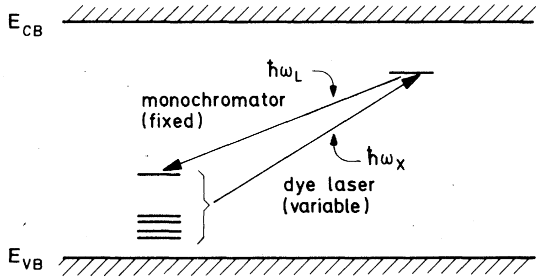

FIG. 1. Schematic representation of the technique of luminescence excitation spectroscopy on donor-acceptor pairs in semiconductors. The excitation energy is given by $\hbar\omega_X$, $\hbar\omega_L$ denotes the detection energy.

II. EXPERIMENTAL

A. Technique of excitation spectroscopy on *D-A* pair luminescence

The principle of measurement combines the properties of the *D-A* pairs with the excitation spectroscopy as shown in Fig. 1. The monochromator is tuned to transmit luminescence from a single *D-A* line of energy $\hbar\omega_L$. In this way a well-defined pair separation R is chosen corresponding to the equation[19-21]

$$\hbar\omega_L(R)=E_g-(E_D+E_A)+e^2/\epsilon R+J(R) \qquad (1)$$

where E_g denotes the band-gap energy, E_D and E_A are the ionization energies of the donor and acceptor, respectively, and ϵ is the static dielectric constant which has the value $\epsilon=11.02$.[21] The term $J(R)$ is a correction term describing the deviation of the luminescence energy $\hbar\omega_L$ from a simple Coulomb law due to the interaction of the donor and acceptor wave functions. In the case of GaP the pair spectrum below $R=30$ Å consists of discrete luminescence lines making it possible to define exactly the pair separation chosen.[4,21,22] For separations $R>30$ Å the correction term J vanishes.[21] Thus the relation between $\hbar\omega_L$ and R is a simple one taking the well-known value for $\hbar\omega_L$ $(R\rightarrow\infty)$ (Ref. 21)

$$\hbar\omega_L(R\rightarrow\infty)=E_g-(E_D+E_A). \qquad (2)$$

The energy $\hbar\omega_X$ of the incident dye laser is tuned to energies larger than $\hbar\omega_L$. If $\hbar\omega_X$ resonantly excites a donor-acceptor pair state, an electron neutralizes the initially charged donor leaving an excited hole at the acceptor. The hole relaxes immediately into the acceptor ground state. The subsequent recombination of the electron and hole at energy $\hbar\omega_L$ is detected by the photomultiplier. If the excitation energy does not correspond to any absorption process in the material, luminescence will be absent. Similarly, if it corresponds to absorption at a *D-A* pair which has a ground-state emission energy different from $\hbar\omega_L$, then luminescence results, but is not detected. The technique has thus the selectivity to detect only those absorption processes that are specific to a chosen *D-A* pair separation. When resonance occurs, $\hbar\omega_X$ can be written[5]

$$\hbar\omega_X=\hbar\omega^*(R)=E_g-(E_D+E_A^*)+e^2/\epsilon R+J^*(R). \qquad (3)$$

E_A^* gives the energy of the excited acceptor state and $J^*(R)$ is a correction term similar to Eq. (1). Subtracting Eqs. (3) and (1) gives

$$\hbar\omega^*(R)-\hbar\omega_L(R)=E_A-E_A^*+J^*(R)-J(R). \qquad (4)$$

Monitoring the difference between excitation and detection energy thus gives directly the acceptor levels. The correction term $J^*(R)-J(R)$ vanishes, provided R is chosen large enough.[20-22] For smaller R there will be an interaction between donor and acceptor causing a shift of the binding energies. It should be noted that the excited acceptor levels are obtained directly from the measurement without any knowledge of the band gap, the donor binding energies, or the Coulomb term.

This description for excited acceptor levels is also applicable to donor levels. The method of excitation spectroscopy on *D-A* pairs has several striking advantages for the observation of excited impurity states compared to other techniques such as ir absorption. The excitation measurements (at least for GaP) are performed in the visible part of the spectrum. In this regime powerful light sources (dye laser) and sensitive detection systems (photomultiplier) are available. The excited levels of shallow impurities are often in the same order of magnitude as the optical phonons (e.g., acceptors in GaP and ZnTe). Therefore, with ir absorption spectroscopy it is extremely difficult or impossible to observe the excited states in the region of the reststrahlen band. However, with our method we can clearly resolve states within the reststrahlen band as will be seen below. In addition to the isolated impurity states we get information about $J^*(R)$ not obtainable with any other method. The selection rules for dipole transitions are altered due to the axial symmetry of the *D-A* system. Therefore our method provides simultaneously data about *s* and *p* states. The luminescence we observe is not polarized because of the large number of equivalent *D-A* sites distributed almost isotropically.

B. Apparatus

The experimental apparatus for the excitation spectroscopy is shown in Fig. 2. A dye laser pumped by a 15-W Ar$^+$ laser was operated with sodium fluorescein and coumarin-7 dyes. Thus the wavelength region from the *D-A* pair bands

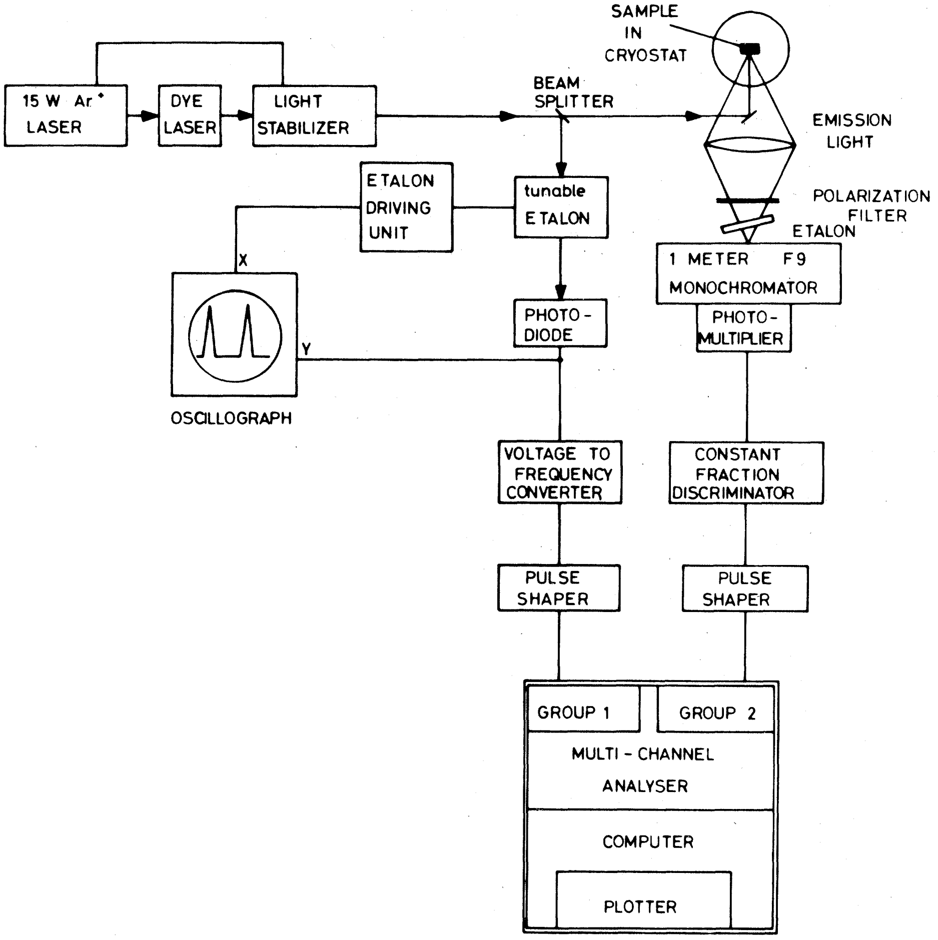

FIG. 2. Schematic diagram of the apparatus for luminescence excitation spectroscopy.

(~5700 Å) to above-band-gap excitation of GaP (5200 Å) could be covered. A photodiode with an electrical feedback to the pump laser maintained the output power of the dye laser constant. The resolution was determined by the linewidth of the dye laser. We achieved a linewidth of 0.3 Å with an interference filter tuning element or 0.1 Å with a three-step Lyot filter inside the cavity. The laser linewidth was measured with a piezoelectrically scanned étalon. During the experiment when the laser wavelength was varied continuously, the light transmitted periodically by the untuned étalon served as the wavelength calibration for the excitation spectra. The rest of the apparatus is conventional for luminescence measurements. To reduce scattered light in the monochromator the laser light reflected from the sample was removed by a polarization filter and an interference filter tuned to the wavelength of the monochromator.

C. Samples

The samples used for excitation spectroscopy were selected under the following criteria: (i) The luminescence spectra should exhibit distinct pair lines. This means a high compensation ratio of the samples. (ii) The nitrogen concentration should be as low as possible. (iii) The samples should have about 0.5- to 1-mm thickness and should be homogeneous. Condition (iii) is necessary because of the low absorption when exciting below band gap. The excitation energy for close pairs lies in the vicinity of the *A* line (exciton bound to isolated nitrogen atom). The excitation into this electronic state is a very efficient input channel due to the large oscillator strength of the nigrogen exciton (≈ 0.1).[23] The detection of the excited states for close *D*-*A* pairs is therefore inhibited because of an energy transfer from the N exciton by interimpurity tunneling.[24]

III. RESULTS

The luminescence excitation spectroscopy on *D*-*A* pairs described in Sec. II A has been applied to different combinations of shallow acceptors and deep donors in GaP. The first results have already

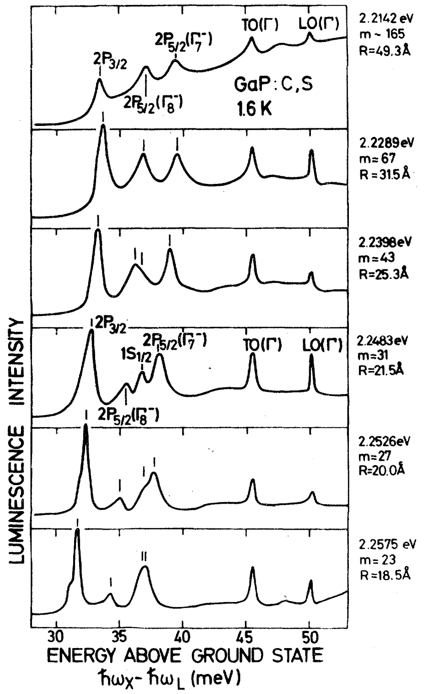

FIG. 3. GaP luminescence excitation spectra of C-S pairs for different pair separations. The detection energy $\hbar\omega_L$, the corresponding shell number m, and the pair separation R are indicated.

been published.[5] In this section we will present the detailed data for four acceptors. The discussion of the observed spectra to be due to excited acceptor states is postponed to Sec. IV A.

A. Carbon

Some spectra of the excitation of carbon-sulphur (C-S) pairs of different separation are shown in Fig. 3. Two of the peaks are identified as the TO(Γ) and LO(Γ) phonons from their energetic positions. We have not determined whether phonon-assisted absorption into the ground state, or Raman scattering is the dominant contribution to these peaks. The remaining peaks are attributed to excited acceptor states. The three lowest excited acceptor states denoted by $2P_{3/2}, 2P_{5/2}(\Gamma_8)$, and $2P_{5/2}(\Gamma_7)$ could be detected over the full range of pair separations R. In addition we could observe at small separations $R \lesssim 25$ Å a fourth peak labeled by $1S_{1/2}$. The assignment of these lines is discussed below.

In the D-A excitation spectra there is a background absorption that excites the D-A transition and overlaps the excited acceptor levels. This background is strongest when distant pairs are excited. It disappears when the D-A luminescence energy $\hbar\omega_L$ is $\gtrsim 2.24$ eV. The onset of this background lies just below the energy for the excitation of the $2P_{3/2}$ state independently of the pair separation (see spectra in Fig. 3). We believe that this background is due to transfer from closer pairs whose ground states are excited by $\hbar\omega_X$ simultaneously. This presumption is supported by the resonant excitation data (see below, Fig. 7).

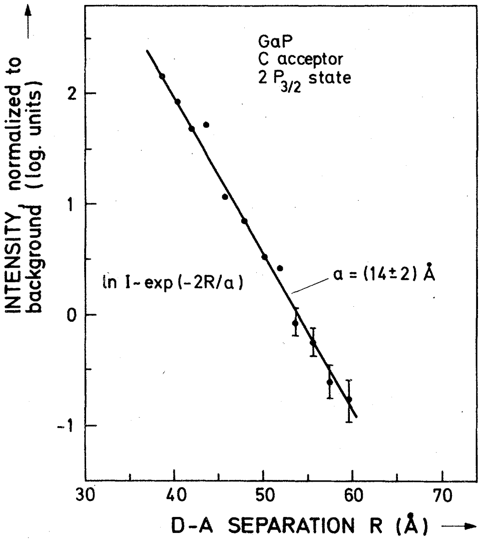

FIG. 4. R dependence of the intensity of the $2P_{3/2}$ excited state of the carbon acceptor in GaP as observed with luminescence excitation spectroscopy.

For pair separations $R \gtrsim 50$ Å the excited acceptor states are no longer detectable. The reason is that decreasing overlap of the electron and hole wave functions yields a decreasing transition probability that varies as $e^{-2R/a}$. This R dependence of the intensity of the $2P_{3/2}$ state is given in Fig. 4. The parameter a is found to be 14 ± 2 Å. This result gives a measure of the acceptor Bohr radius, and is reasonably close to the value of ~18 Å found from direct observations of the decay lifetime of C-S pairs.[25]

The detailed relationship between the energies of the excited acceptor levels and the separation R is shown in Fig. 5. At large pair separations $R > 40$ Å the observed energy differences $\hbar\omega_X - \hbar\omega_L$ [see Eq. (4)] for the three p states tend to a constant value. At these pair separations the pertubation of the excited states due to the donor is negligible yielding the excited acceptor states for the isolated C acceptor. The energy differences are listed in Table I. The energy differences decrease with decreasing R. This effect can be explained by the increasing pertubation of the p states due to the donor. The decreasing energy differences mean an increase in the magnitude of the correction term $J^*(R)$ of Eq. (4) (both correction terms are negative). A behavior completely

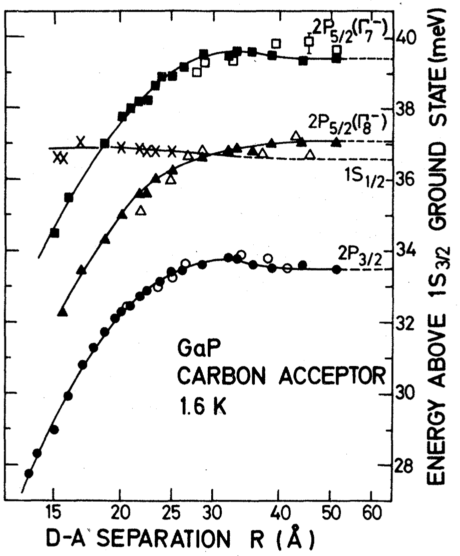

FIG. 5. R dependence of the energies of excited carbon acceptor levels from excitation spectroscopy on C–S pairs in GaP. Full points, excitation spectroscopy; open points, resonant excitation (see text).

different from that of the p states is shown by the state $1S_{1/2}$: Its energy difference to the $1S_{3/2}$ state remains nearly constant down to the smallest pair separations measured.

Information about the influence of the donor on the R dependence of the acceptor levels is obtained by investigations of the C-Te pair spectra. The Te donor has a smaller ionization energy than S (Te: 92.6 meV; S: 107 meV).[11,26] The result of the excitation spectroscopy is displayed in Fig. 6. The essential behavior of the excited acceptor states is the same as in the C-S case. In detail the unperturbed levels at large R agree exactly with those of Fig. 5. Thus the donor has *no* influence on the isolated acceptor states at pair separations $R > 40$ Å. For decreasing pair separation the energy differences $\hbar\omega_X - \hbar\omega_L$ for the C-Te combination decrease more rapidly than those for the C-S case (Fig. 5). This is obvious for the $2P_{3/2}$ state at the pair separation of, e.g., 15 Å. In a simple model the Te donor has a larger Bohr radius than the S donor. Thus the perturbation of the acceptor levels is larger than that for S and starts at larger R. The decrease of the $2P_{5/2}(\Gamma_7)$ state begins for $R \lesssim 35$ Å in Fig. 6 whereas the starting point is $R \approx 30$ Å in Fig. 5.

A method complementary to the excitation spectroscopy is the resonant excitation with fixed laser energy and tuned monochromator. The incident laser energy is chosen to be smaller than the band gap of GaP in contrast to ordinary luminescence measurements. Three typical spectra for different excitation energies are shown in Fig. 7. The data are taken with the same sample as used for Fig. 3. The incident laser energy is in resonance with a transition (excited acceptor state to donor ground state) for specific pair separations. The hole relaxes into the ground state. The recombination of the electron and the hole in the impurity ground states produces an enhancement of the luminescence. As there have been observed three p states the enhancement occurs three times giving the three peaks in the spectrum. The energy difference of the exciting laser light to each of these peaks again gives the energy above the $1S_{3/2}$ acceptor ground state. By tuning the dye laser to larger energies the luminescence of pairs with smaller separations is enhanced. The results of this type of measurements are plotted in Fig. 3 (open points). The agreement between the excitation spectroscopy and the resonant excitation is excellent.

TABLE I. Experimental data for the energy differences of the $1S_{3/2}$ ground state and excited states of different acceptors in GaP. Energies are given in meV; the experimental uncertainty is 0.1 meV.

Acceptor	$1S_{1/2}$	$2P_{3/2}$	$2P_{5/2}(\Gamma_8)$	$2P_{5/2}(\Gamma_7)$	$2P_{1/2}$
C	36.6	33.5	37.1	39.4	···
Mg	35.5	39.7	43.4	···	···
Zn	33.4	48.4	51.7	54.5	57.2
Cd	···	82.8	88.6	···	···

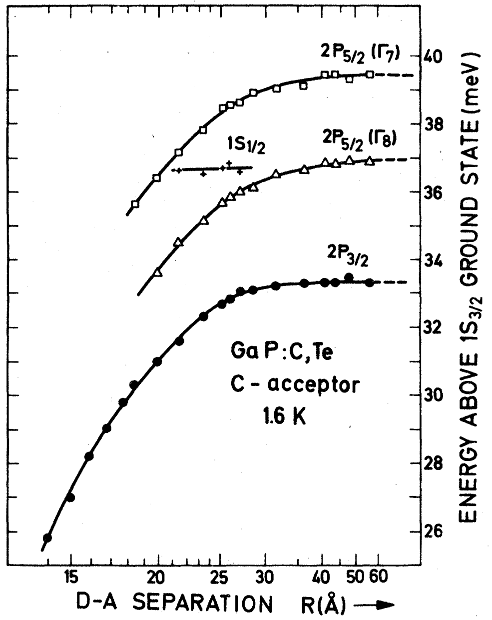

FIG. 6. R dependence of the energies of excited carbon acceptor levels from excitation spectroscopy on C–Te pairs in GaP.

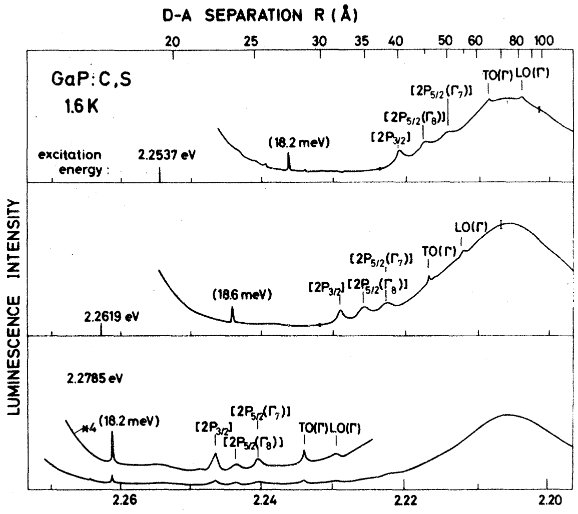

FIG. 7. Resonant luminescence spectra for different excitation energies as marked on the left-hand side of the energy scale. The spectra were recorded with GaP doped with C and S. The peaks denoted in brackets with the p levels are the ground-state transitions to which the exciting laser light is resonant with a transition (excited acceptor state to donor ground state).

The peaks named TO(Γ) and LO(Γ) in Fig. 7 occur because of the creation of phonons as in the excitation spectra. The origin of the peaks having an energy difference of 18.2 or 18.6 meV with respect to the excitation energy is unknown. The broad band at about 2.205 eV is the luminescence from distant pairs. This feature is related to the background in the excitation spectra (see Fig. 3) and is presumed to arise from transfer between the resonantly excited *D-A* pair, and other neighboring pairs.

B. Magnesium

The R dependence of the excited states of the Mg acceptor is shown in Fig. 8. The measurements were performed with a sample doped in addition with the Te donor. The energy differences to the ground state for the p states are larger than those for the C acceptor (see Fig. 5) because of the larger binding energy of Mg yielding a larger value for $\hbar\omega_X - \hbar\omega_L$ in Eq. (4). The $2P_{5/2}(\Gamma_7)$ state could not be observed because the energy for exciting this transition is equal to the excitation of the ground-state transition with creation of a TO(Γ) phonon.

The R dependence of the two states is similar to that observed for C. The term $J^* - J$ [Eq. (4)] affects the energy differences already at $R \cong 35$ Å due to the larger Bohr radius of the Te donor. However, the energy differences of the $1S_{1/2}$ state increase slightly with decreasing pair separation. The energetic separation of the two p states at large R is exactly the same as reported for the C state (see Table I). These observations confirm the identification shown.

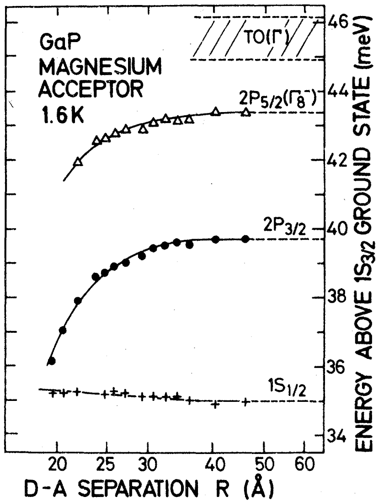

FIG. 8. R dependence of the energy of excited magnesium acceptor levels from excitation spectroscopy on Mg-Te pairs in GaP. The excitation into the TO(Γ) phonon masks the $2P_{5/2}(\Gamma_7)$ level.

C. Zinc

Figure 9 shows five spectra of excitation measurements on Zn-S pairs of different separations R. The spectrum at $R = 30.4$ Å is characteristic for distant pairs. In addition to the two phonons and the three already identified $2P$ states, we could detect the theoretically predicted $2P_{1/2}$ state. The $1S_{1/2}$ peak is present again at 33.4 meV. The lines named C (?) have the right position and energetic separation to be the C excited states. Carbon is an acceptor which can be accidentically incorporated into the crystal very easily. The crystals used were grown without taking specific care of C. Thus there is always a small doping of C in our crystals leading to the peaks in the spectra although the observation energy $\hbar\omega_L$ is not resonant with a C-S pair transition.

The excitation spectra for Zn exhibit a variety of additional peaks named $Y1$-$Y6$. The first four of these peaks lie below the excited p states and behave similarly to the p states with decreasing R: Their energy differences to the ground state become smaller (explicitly shown in Fig. 10). Line $Y3$ can only be separated from the TO(Γ) phonon at $R \cong 20$ Å. $Y5$ appears clearly for separations $R \lesssim 35$ Å. Similar structures have been seen in Si doped with In or the isocoric Al lying below the excited states of these impurities.[27] The lines la-

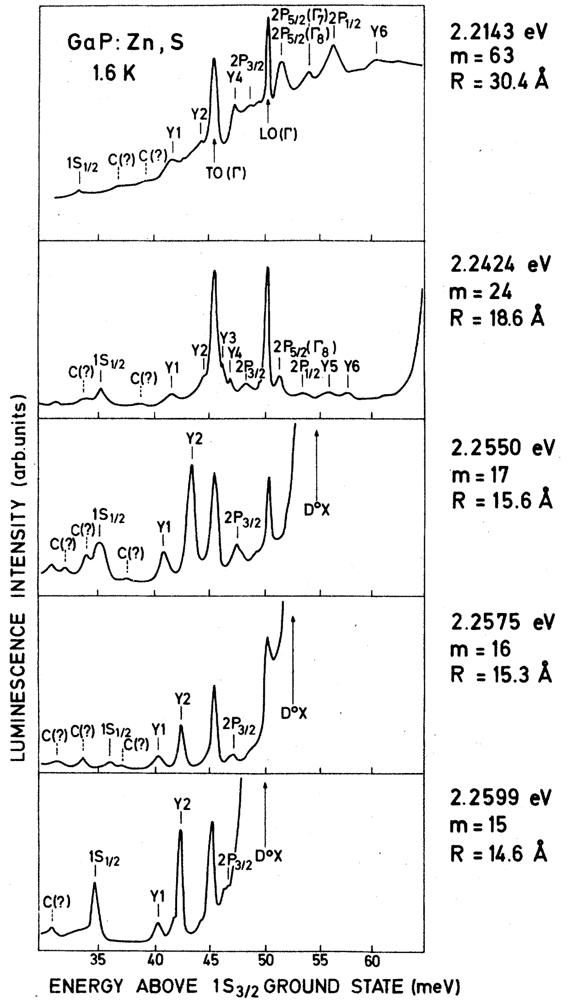

FIG. 9. Luminescence excitation spectra of Zn-S pairs in GaP for different pair separations. The detection wavelength $\hbar\omega_L$, the corresponding shell number, and the pair separation are indicated on the right-hand side.

beled $X1$ to $X4$ in Ref. 27 have recently been attributed to defects of unknown nature behaving like an acceptor.[27]

Peak $Y2$ of the isocoric Zn acceptor in GaP exhibits a resonance still unexplained at pair distances of $R = 15.6$ Å and $R = 14.6$ Å. At these separations the intensity of $Y2$ exceeds that of the phonons. The peak $1S_{1/2}$ has a similar but less pronounced behavior: These resonances are marked by arrows in Fig. 10. This figure gives the detailed R dependence of all peaks. On the right-hand side the lines observed in Raman scattering[28,29] are indicated by the notation R. The details will be discussed in Sec. IV B. The position of the unperturbed $2P$ states at large separations R are displayed in Table I. With decreasing R the $2P_{5/2}(\Gamma_8)$ state shows an interesting behavior. Instead of crossing the LO(Γ) phonon the $2P_{5/2}(\Gamma_8)$ state joins closely to it. This behavior can be explained by an interaction between phonon and hole. Similar observations are reported for an excited state of Si:Ga.[30] There the measurements had to be performed with ir absorption under uniaxial stress.

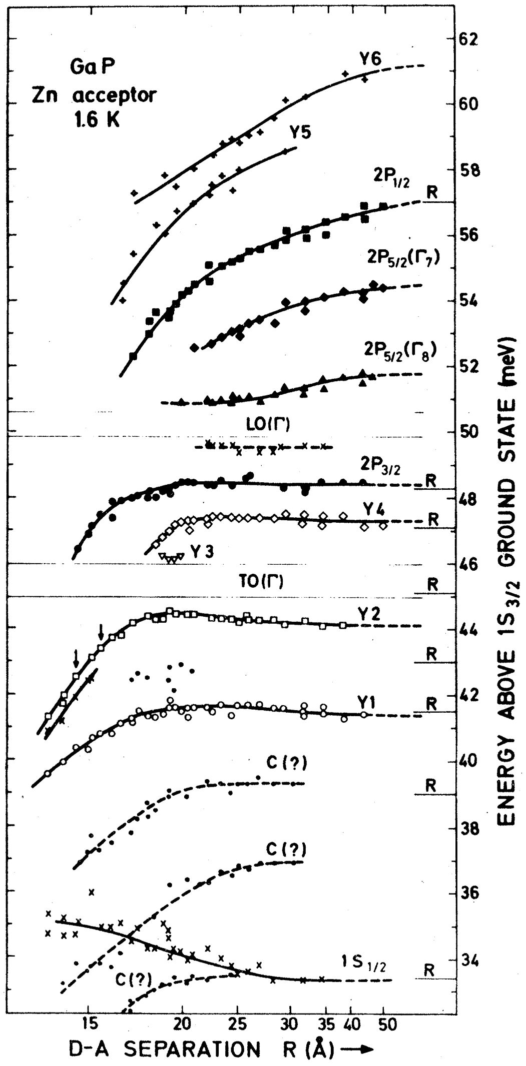

FIG. 10. Detailed R dependence of the energy of the levels observed with excitation spectroscopy on Zn-S-doped GaP samples. The levels indicated by C (?) are presumably carbon excited states. On the right-hand side the results of Raman scattering experiments (Ref. 29) are shown by levels marked with R.

At the energy of 49.5 meV a weak peak occurs below the phonon LO(Γ) which is also observed in electronic Raman scattering.[28] As explained in Ref. 28 this peak is due to a local perturbation of the crystal in the vicinity of the donor.

Again the background in the spectra for large pair separation (cf. Fig. 9) is present as was observed for the C acceptor (see Fig. 3).

D. Cadmium

The results for excitation measurements on Cd–S-doped samples are shown in Fig. 11. The excited acceptor states observed by ir absorption[31,32] are indicated at the right-hand side by ir. With excitation spectroscopy we could only resolve the lowest two states $2P_{3/2}$ and $2P_{5/2}(\Gamma_8)$. Their energies at large separations R are in excellent agreement with the ir data. The higher excited states are masked by the structures $Z1$–$Z3$. These three lines are not related to the pair lines. They remain at fixed absorption energies. This can be seen by adding the energies for $\hbar\omega_L(R)$ and the energy above ground state for a specific point of the Z lines.

$Z1$: 2.2792 eV ,

$Z2$: 2.2862 eV ,

$Z3$: 2.2963 eV .

The luminescence spectra display only peak $Z1$. Peaks $Z2$ and $Z3$ are related to $Z1$ because their energetic differences and their intensity ratios are always equal. A possible explanation for $Z1$ might be a zero phonon transition of an exciton bound to a deep impurity.

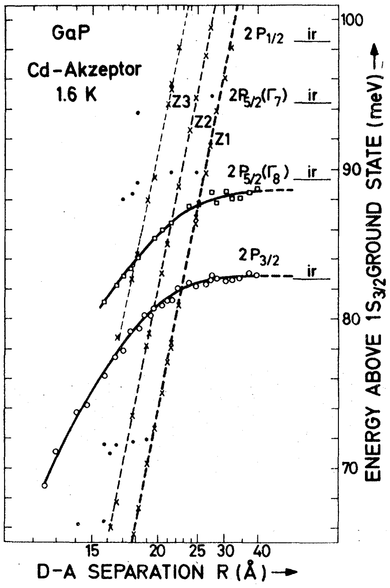

FIG. 11. Detailed R dependence of the energy levels observed with excitation spectroscopy on Cd–S-doped GaP samples. The levels on the right-hand side marked by ir are ir absorption data (Ref. 31). The peaks $Z1$, $Z2$, $Z3$ are not related to the pair states (see text).

Cd is the deepest acceptor examined in this paper (ionization energy $E_A = 102.6$ meV)[10]. For calculating the excited Cd states some contributions to the wave functions from the Γ_7 valence band have to be taken into account due to the small spin-orbit splitting Δ_{so}. This splitting amounts to 82 meV,[33] and thus is smaller than the binding energy of Cd. Therefore the energetic difference between the $2P_{3/2}$ and $2P_{5/2}(\Gamma_8)$ state is larger than those for the shallower acceptors. This effect is known in Si where the value Δ_{so} is also comparable to the acceptor binding energy.[9] Recent calculations have shown that for Si the theoretical description of the excited acceptor states is improved very much by taking into account the Γ_7 contributions.[17,34]

IV. DISCUSSION

A. Identification of excited acceptor states in excitation spectra of *D-A* pairs

The identification of the peaks observed in the excitation spectra shown in Sec. III is based on the following arguments: (i) The observed structures do not depend on the choice of the donor for large pair separations (cf. Figs. 5 and 6). (ii) The relative energy differences between the peaks at large R are nearly the same for all acceptors except Cd. (iii) ir absorption measurements for Cd (Ref. 31) and C (see below) yield the same position of the states at large R. (iv) The donor excited states are known from two-electron transitions[26,35] and ir absorption.[36] These states lie at much higher energies (S: 60 meV) than the peaks reported here. Therefore donor states can be excluded in this context.

The assignment of the excited acceptor states was adopted from the theory of Baldereschi and Lipari.[8,9] In the previous publication we used this theory to deduce valence-band parameters as well as acceptor binding energies and the band gap of GaP.[5] These latter energies were only about 8 meV below the latest data for GaP,[10] giving a strong argument for the right identification of the excited acceptor states. However, the discrepancy of 8 meV shows that the present theory can be used for qualitative treatments only.

B. Results of other methods

The ir transmission of p-type GaP doped with C and S has been measured by Fourier spectroscopy at 20 K. The C concentration was not known exactly. Therefore we examined several crystals with different hole concentrations in the 10^{16}-cm^{-3} range. Figure 12 gives a characteristic spectrum which is in good agreement with a recent publica-

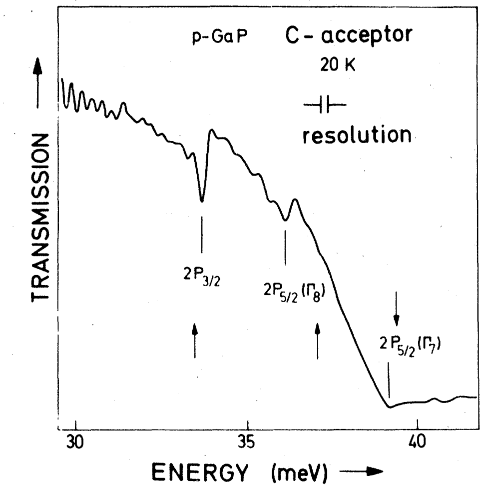

FIG. 12. ir transmission spectrum for a *p*-GaP sample doped with C and S. The arrows indicate the results of the excitation measurements (see Figs. 3 and 4).

tion.[37] The transmission decreases to higher energies due to the reststrahlen band between the TO and LO phonons. The three lowest excited states are indicated; in particular the $2P_{3/2}$ state being the lowest of all excited acceptor states is clearly seen. The arrows mark the position of the peaks observed with excitation spectroscopy (see Figs. 5 and 6). The agreement between both methods is excellent except for the $2P_{5/2}(\Gamma_8)$.

The ir absorption for a series of shallow acceptors in GaP has recently been published.[32] The results for Cd (Refs. 31, 32) have already been included in Fig. 11. The agreement there was excellent too (see Table II). In Ref. 32, only the $2P_{3/2}$ state was observed for C at the same energy as we did. For Mg and Zn there is a disagreement (see Tables I and II). The reason might be that the ir absorption is complicated due to the reststrahlen band. Therefore a wrong identification of the excited states is possible. In the case of Zn our state at 57.2 meV has been found in the ir absorption too but named there as $2P_{5/2}(\Gamma_8)$.[32] However, we identified it as $2P_{1/2}$ because its energetic position lies close to that which can be theoretically calculated with our published valence-band parameters.[5]

The comparison with Raman scattering experiments[28,29] shows that *s*-like states are apparent too in our spectra (compare Tables I and II). The line called B in the Raman spectra[29] is identical to our $1S_{1/2}$ peak. The identification of this peak as $2S_{3/2}$ can be excluded definitely. When changing from the shallow C acceptor to the deeper Zn a $2S_{3/2}$ state should shift to *larger* energy differences by about 2 meV due to the central-cell correction. This value can be estimated using a simple hydrogenic model. However, a shift of the peak of 3.1 meV to *lower* energy differences is observed. Careful examination of the Zn Raman spectra[29] also revealed the structure which we called *Y*1. The behavior of the Raman peak in a magnetic field implies that B is not purely *s*-like.[29] In Si:B a similar line below the excited *p* states[38] has been unexplained for a long time. Recent calculations[17] interpret this state as a mixture of *d*-like states of the upper valence band ($J=\frac{3}{2}$) with *s*-like states of the split-off valence band ($J=\frac{1}{2}$). The energetic position of this state is strongly determined by the magnitude of the spin-orbit splitting. The *Y* structures in Figs. 9 and 10 might be due to a similar effect since the spin-orbit splitting affects all excited states. However, theoretical calculations are not yet available. Under uniaxial stress the B peak shifts to higher energies.[21] This same behavior is observed with $1S_{1/2}$ when decreasing the pair separation indicating an analogy between uniaxial stress and perturbation of acceptor states by the donor.

This discussion demonstrates that luminescence excitation spectroscopy on distant *D*-*A* pairs reveals the unperturbed excited *s* and *p* states. The excitation measurements on excitons bound to NN pairs only yield *s* states.[2] The reason is that the selection rules for dipole transitions allow *p* state transitions in the case of *D*-*A* pairs due to the axial symmetry of the system.

Recently the infrared photoconductivity of GaP:C

TABLE II. Result of other methods for the enery differences of the $1S_{3/2}$ ground state and excited states of different acceptors in GaP. Energies are given in meV.

Acceptor	Raman[a] B	ir absorption $2P_{3/2}$	$2P_{5/2}(\Gamma_8)$	$2P_{5/2}(\Gamma_7)$	$2P_{1/2}$	Raman[a] C
C	36.5 ± 0.5	33.8	36.3	39.2	···	···
Mg[b]	34.7 ± 0.5	···		52.3	···	47.2
Zn[b]	33.4	···	57.1 ± 0.2	61.6 ± 0.2	64.8 ± 0.5	57.0
Cd[b]	···	82.7	89.3	94.4	98.5	···

[a] References 28 and 29.

[b] ir absorption data from Refs. 31 and 32.

and GaP:Zn was published[37] and some of the observed structures were identified as excited acceptor states by means of our data.[5]

V. SUMMARY

We report a new method to measure excited impurity states in semiconductors: the luminescence excitation spectroscopy on D-A pairs. This method is applied to GaP containing shallow acceptors and deep donors with the following results: For distant D-A pairs ($R > 40$ Å), the unperturbed electronical excited states of the acceptor, including both s and p states were observed. The donor excited states could not be detected because the excitation energy necessary to excite these transitions is degenerate with continuum states of the acceptor. The reported acceptor states exhibit an energetic splitting into the states $2P_{3/2}, 2P_{5/2}(\Gamma_8)$, $2P_{5/2}(\Gamma_7)$, and $2P_{1/2}$ as predicted qualitatively by the effective-mass theory of Baldereschi and Lipari. The excited states obtained with the new method are in good agreement with Raman scattering as well as ir absorption-data. The advantage of the method is that in contrast to ir absorption the energetic regime of the reststrahlen band is accessable.

Decrease of the D-A pair separation increases the binding energies of the excited states. In a further publication we have shown that the increasing overlap of the impurity wave functions is responsible for this effect.[18]

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