Multiple bound excitons in GaP

R. Sauer, W. Schmid, J. Weber, and U. Rehbein
Physikalisches Institut der Universität Stuttgart,
D-7000 Stuttgart 80 Federal Republic of Germany
(Received 7 March 1978; revised manuscript received 8 February 1979)

Low-energy satellites of bound-exciton luminescence associated with the acceptors Zn, Mg, and Cd in GaP were investigated by excitation and time-dependent measurements with application of stress. The properties of the sidebands associate them with exciton satellite series in Si, Ge, and β-SiC which are currently discussed in terms of "multiple bound excitons". This multiple-bound-exciton interpretation replaces a recent explanation ascribing the lines to phonon sidebands from electronic intervalley scattering of the excitons due to the camel's-back structure of the GaP conduction band around the X point.

I. INTRODUCTION

Kaminskii *et al.*[1] in 1970 and 1971 first discovered a number of emission lines slightly below the bound-exciton lines associated with P donors or with B acceptors in Si. Since then the study of bound-exciton low-energy satellite series has attracted more and more increasing interest. Kaminskii and coworkers interpreted the extra lines as due to the radiative recombination of an electron with a hole from complexes consisting of two, three, or more excitons bound to the impurities. Subsequent papers[2,3] investigated the novel line series in more detail and supported the original idea of multiple bound excitons (MBE). Li was shown to induce a particularly extended line series.[3] These measurements were soon succeeded by the finding of analogous satellite lines in Ge, correlated with the donors P and As.[4] The early experiments up to 1974 are reviewed in Ref. 5. Studies of the Zeeman splitting of the P, Li, and B induced lines in Si called for specifically structured MBE models,[6] as were in the following period suggested by Morgan,[7] Dean *et al.*,[8] Kirczenow,[9] and Thewalt.[10] Dean *et al.* in conjunction with their version of a structured-MBE model described a bound-exciton satellite line series in cubic SiC due to the impurity N substituting for C as a shallow donor.

The most intensively discussed of these three models is the shell model of multiple bound excitons introduced by Kirczenow and experimentally advocated by Thewalt. This model is able to account for many observed features of the satellite lines[11] although on the other hand several objections were raised.[12–15] A number of discrepancies between experimental findings of different groups have yet to be elucidated.[12,15–17] The shell model arranges the electrons in Γ_1, Γ_3, and Γ_5 impurity shell states derived from degenerate multiconduction band wave functions. The assumption of multivalley bound-electron states is also basic in the MBE binding energy calculations of Wünsche *et al.*[18,19] The importance of high multiplicities via degenerate multiple electron valleys in these models suggests that MBE complexes are typical of indirect semiconductors. Recently, Almassy *et al.*[20] observed six low-energy Zn-acceptor bound-exciton satellite lines in high purity epilayers of GaAs. They ascribe the extra lines to transitions between the ground states and low-lying excited states of a bound two-exciton complex, MBE(2), and the principal single bound exciton, BE. The excited states are due to j-j coupling of electrons and holes. Since this model involves two bound electrons at maximum, it needs no multiple electron valleys. In spite of a number of difficulties, MBE complexes are at present generally believed to exist in Si, Ge, and β-SiC although there is no general agreement on a specific model. The most convincing evidence of MBE's appears to come from acceptor bound excitons in Si:Al and Si:Ga where the studies of Thewalt[21] and Lyon *et al.*[22] strongly suggest the existence of a bound two-exciton complex.

In this paper we report on low-energy satellites of the bound-exciton emission due to the acceptors Zn, Mg, and Cd in the indirect semiconductor GaP. Most of the satellite lines which we observe are not new but were already previously reported.[23–25] However, we have reanalyzed these lines and a few more satellites which were observed for the first time, by means of high-resolution excitation-dependent measurements, time resolved spectroscopy, and with application of stress to the samples. The data results in a reinterpretation of the satellite lines in terms of multiple bound excitons. This interpretation substitutes for a number of previous different explanations. Part of our present results is briefly communicated elsewhere.[26]

Low-energy sidebands of the BE emission associated with Zn in GaP were first reported by Dean *et al.*[23] but were not discussed in detail because their origin remained uncertain. Similar sidebands associated with bound-exciton luminescence due to substitutional point-defect acceptors C, Be, and Mg, and of X, an unidentified complex acceptor, were then found by Dean and coworkers.[24] The sidebands were named X_1 and X_2, and it was argued that they might originate from the decay of bound excitons strongly coupled to acoustical phonons for wavelengths comparable to the ground-state radius of the neutral acceptor. A new interpretation was advanced by Dean and Herbert[25] in terms of the camel's-back structure of the GaP conduction band. Actual experimental data on cyclotron resonance[27,28] and calculations by Lawaetz based on symmetry considerations[29] give reason to believe that the location of the minima is not exactly at the X point of the Brillouin zone resulting in a camel's-back shape of the conduction band around the zone edge X. This is confirmed by recent work on donor spectra[30] and on the fine structure of intrinsic absorption in GaP.[31] Dean and Herbert ascribed the BE satellites X_1 and X_2 to LA-phonon replicas of the exciton luminescence arising from the scattering of the BE electron between equivalent minima on the same axis in k space [g-type intervalley scattering, IVS(g)] which occurs in addition to the usual emission of momentum-conserving phonons in the electron-hole recombination of the bound exciton. They pointed out that this recombination process had not been recognized before for any semiconductor. Dean and Herbert derived characteristic camel's-back parameters $k_0 = 0.953\ k_{max}$ from the satellite displacements using the phonon dispersion relations in GaP,[32] and obtained $\Delta E \lesssim 11$ meV or $\Delta E \approx 7$ meV, respectively, from an incorrect application of Lawaetz's formula (7). They suggest that k_0 and ΔE be better set from their experimental data than would be possible from any theoretical approach. Their values differ significantly from those arrived at by Kopylov and Pikhtin[30] or by Altarelli and Sabatini[31] ($k_0 \approx 0.92\ k_{max}$ and $\Delta E \approx 3$ meV, or $\Delta E = 4$ meV, respectively). With respect to their new interpretation, Dean and Herbert labeled the X_1 and X_2 satellites IVS(g1) and IVS(g2) in Ref. 25. The exclusion of the phonon scattering interpretation of the BE satellite lines in the present work implies that no statement about the camel's-back shape in the GaP conduction band can be made at present from bound-exciton luminescence.

In Sec. II we describe some details of the experimental setup and the measurements. In Sec. III the experimental data are reported and discussed. First we give a full account of the GaP:Zn results leading to our MBE interpretation of the BE satellite lines, and then proceed with the data on Mg- and Cd-doped GaP which are analogous though less complete and detailed partly by reasons of sample quality and geometry. Our discussion of the BE low-energy lines in terms of MBE satellites will be preferentially based on a comparison with equivalent data on donor and acceptor associated MBE spectra in Si, which in this material have been investigated most thoroughly. Some qualitative differences to the Si case will be pointed out at the end.

II. EXPERIMENTAL

The GaP crystals used were generally tiny needles at maximum a few millimeters long and some tenth of a millimeter thick. As an exception, the best Zn-doped crystal is a comparatively large needle of $\approx$1.5 cm length and $\approx$1 mm thickness. This size enabled us to perform stress dependent measurements with this specimen, but stress was necessarily inhomogeneous because of the sample geometry. Zn- and Cd-doped crystals are grown by the water vapor transport method, Mg-doped crystals are solution grown and inadvertently doped.[24] Our luminescence spectra at medium excitation levels are quite similar to those observed by Dean *et al.*[24] For Gap:Zn we find an excellent agreement even in small details [compare, e.g., our Fig. 1(b) with Fig. 3 of Ref. 24]. From this comparison we estimate that the GaP:Zn needle contains $10^{16} - 10^{17}$ cm^{-3} Zn acceptors whereas the concentration of residual N isoelectronic traps is $\lesssim 10^{14}$ cm^{-3}. A larger amount of N traps than in GaP:Zn is contained in the Mg- and Cd-doped samples. Contaminations of S donors in various and partly considerable amounts are inadvertently present in all samples.

The crystals were immersed in liquid helium which was pumped below the λ point. The luminescence was excited by the blue 488- or 476.5-nm Ar^+-ion-laser lines. To achieve high pump levels we used either a cw laser beam of power $\leq$2 W focused to a small spot, or high power pulses ($\leq$20 W) with pulse length $\approx$12 nsec produced by a cavity dumper. The latter pulse system was also used for the time-dependent measurements and could be switched to mode-locking operation if necessary resulting in pulses of $\approx$400-psec duration. Single pulses could be selected from the mode-lock pulse chain by employing the cavity dumper. The luminescence was dispersed by a 3/4-m Spex monochromator and was detected by a S20-type cathode photomultiplier. The signals were processed by a lock-in amplifier or by a photon counting system. Details of the latter equipment are described elsewhere[33] where further reference is also given. The best spectra (i.e., revealing the highest satellite intensities in conjunction with the smallest line shapes) were generally obtained at

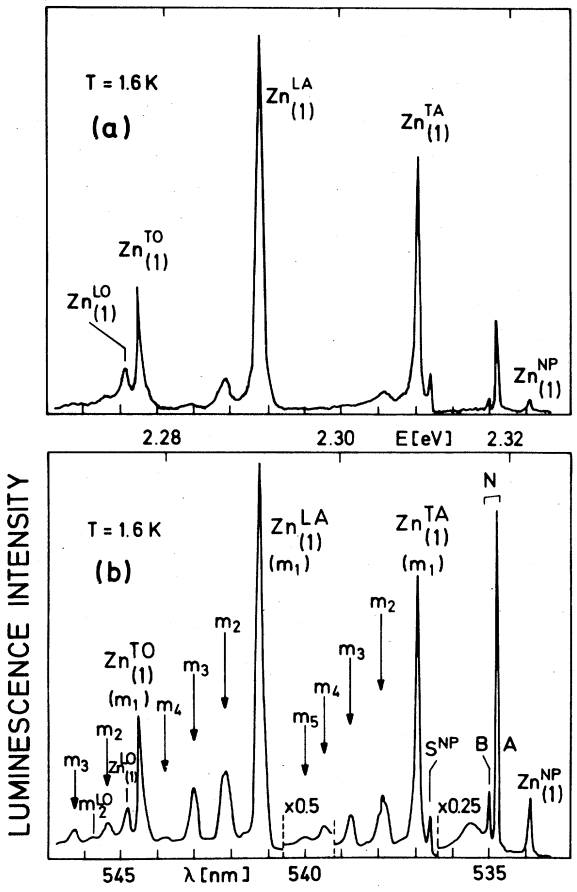

FIG. 1. Portion of the photoluminescence spectrum of GaP:Zn (a) with low excitation power, and (b) as highly excited by 12 nsec laser pulses and photoelectrically recorded. Dominant lines $Zn_{(1)}$ (m_1) are due to Zn bound excitons without (NP) or with momentum-conserving (TA, LA, TO, LO) phonons. Other lines orginate from excitons bound to residual nitrogen N (A and B lines) or to sulfur (S^{NP}). The V band (Ref. 50) is seen between the latter lines. The Zn acceptor MBE satellite lines are labeled m_2 through m_5.

pulsed excitation and quasicontinuous processing by a lock-in amplifier. For quantitative measurements such as the dependence of satellite intensities on the pump level or for the spectra under stress we employed cw excitation power.

III. RESULTS AND DISCUSSION

Figure 1 shows two low-temperature photoluminescence spectra of GaP:Zn at low and at high excitation level. The low-power spectrum is dominated by the radiation due to the decay of Zn-acceptor bound excitons labeled $Zn_{(1)}$ which is seen as no-phonon (NP) and momentum-conserving TA-, LA-, TO-, and LO-phonon assisted lines. Three more sharp lines originate from S and from N (A and B) bound excitons. Single weak satellites are observed in the TA and LA spectra below the $Zn_{(1)}$ emission. At high pump powers these satellites strongly increase relative to the $Zn_{(1)}$ lines and a number of additional satellite lines emerge from the background. These satellites are labeled m_2 through m_5 in Fig. 1, anticipating our MBE interpretation. Lines m_2 and m_3 are identical with the above-mentioned sidebands X_1 and X_2,[24] or with the lines IVS(g1) and IVS(g2),[25] respectively. Lines m_4 and m_5 are new; line m_5 can only be observed in the TA spectrum, since it is obscured in the LA spectrum by the strong dominant $Zn^{TO}_{(1)}$ emission. The new lines prove that $Zn_{(1)}$ (m_1) through m_5 form a line series with monotonically decreased intensities and regularly narrower spacings. The displacement

TABLE I. Characteristic MBE line parameters for GaP:Zn. E_{BX} (for $Zn_{(1)}$) is the excitonic binding energy to the acceptor, ΔE (for m_2 through m_5) are the line displacement energies from the BE $Zn_{(1)}$ line. Excitation exponent is the approximate exponent in the empirical power law of the intensity-to-pump relation. Decay times refer to Fig. 2, and were identically measured for m(TA) and m(LA) lines; they are discussed in the text.

Acceptor Zn $E_A = 70.1$ meV[a]	E_{BX} or ΔE (meV)	Excitation exponent	Decay time (nsec)
$Zn_{(1)}$ (m_1)	6.65[b]	1	68.3 ± 1
m_2	3.7_5[c]	1.5	37.1 ± 1
m_3	7.5	2.1	27.1 ± 1
m_4	10.4	2.7	24.5 ± 1
m_5	13.0	>2.7	···

[a]After Sturge *et al.* (Ref. 54).
[b]After Dean *et al.* (Ref. 24).
[c]For TA replica 3.9_2 meV.

TABLE II. Characteristic MBE line parameters for GaP:Mg. The notation is the same as in Table I. All data refer to the LA spectra, the decay times are identical for the TA spectra.

Acceptor Mg $E_A = 53.3$ meV[a]	E_{BX} or ΔE (meV)	Excitation exponent	Decay time (nsec)
$Mg_{(1)}$ (m_1)	6.0[a]	0.5	164 ± 2
m_2	4.1	0.6	91 ± 1
m_3	7.7	0.8	62 ± 1
m_4	10.7	>1	47 ± 1

[a]After Dean *et al.* (Ref. 24).

TABLE III. Characteristic MBE line parameters for GaP:Cd. The notation is the same as in Table I. All data refer to the LA spectra, differences to the TA spectra are denoted.

Acceptor Cd $E_A = 102.5$ meV[a]	E_{BX} or ΔE (meV)	Excitation exponent	Decay times (nsec)
$Cd_{(1)}$ (m_1)	8.4[b]	increasing	12.2 ± 0.1
m_2	3.0[c]	↓	7.4 ± 0.2
m_3	6.8[d]	(see Fig. 6)	5.3 ± 0.2

[a]After Sturge *et al.* (Ref. 54).
[b]After Dean *et al.* (Ref. 24).
[c]For TA replica 3.2 meV.
[d]For TA replica 7.0 meV.

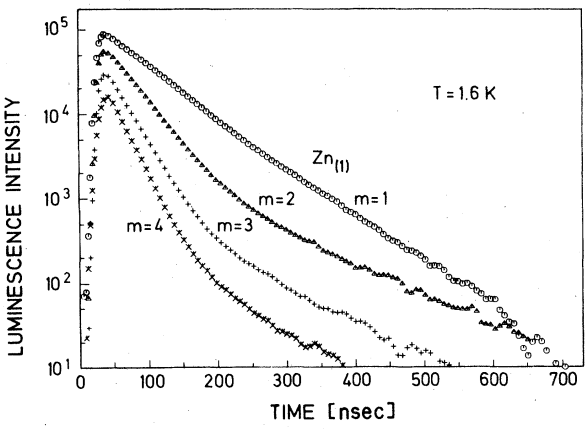

FIG. 2. Luminescence decay of the m lines in GaP:Zn after pulsed excitation (pulse width 12 nsec) as measured in the TA-phonon-assisted series. Corresponding line decays are equal for the LA series within the experimental error of <5%. For decay times see Table I.

energies of the m lines from the BE line $Zn_{(1)}$ are listed in Table I. To enable a comparison between Zn, Mg, and Cd acceptors, we refer in Tables I–III for all parameters to the LA spectra. Slight discrepancies in the TA spectra are specified there. For GaP:Zn the center-of-gravity of the lines has been used for the determination of the displacements. This leads to small but distinct differences between the TA and LA displacements for some lines, e.g., for m_2 in GaP:Zn. In this case the discrepancy is due to fine structure in the m_2 component which is clearly resolved in the TA and LA spectra and differs from one to the other spectrum. The fine structure is discussed below. The reason for equivalent displacement discrepancies in GaP:Cd should be similar although in this case the m_2 and m_3 satellites are broader and do not show resolved fine structure. Taking the TA displacement energies of the m_2 and m_3 lines in GaP:Zn, 3.9_2 or 7.5 meV, respectively, we find an approximate agreement with Dean *et al.*[24] who reported values of 4.1 or 7.6 meV, respectively. Dean and Herbert obtained *acceptor–independent* displacements of 4.2_3 and 7.8_3 meV in their reanalysis of the previous experimental data[25] which compare less well with our present values.

Lines m_4 and m_5 can only be observed under hard laser pumping, and they vanish rapidly when the pump power is decreased as do lines m_2 and m_3. At pump levels slightly higher than in Fig. 1(b) we obtained spectra where the intensities of lines m_2 (LA) and m_3 (LA) were equal, and upon further increase in optical pump power became even reversed. However, an intensity reversal of m_2 and m_3 lines could not be reached in the TA spectrum. This corroborates our experience that some features of the m lines ($m > 1$) in the TA and LA spectra are not identical though similar. Qualitatively, the stronger dependence of the m lines, $m > 1$, than of the BE line on pump power is obvious from Fig. 1. We investigated the excitation dependence also quantitatively. For this purpose we defined line intensities by baselines which were constructed by straightly connecting the minima between the m lines. It was found that the m line intensities approximately follow power laws up to medium excitation levels and tend to saturate at the highest levels. Except for the latter regime, the exponents in the luminescence-to-pump relations are nearly one for the bound excitons $Zn_{(1)}^{TA}$ and $Zn_{(1)}^{LA}$, and increase monotonically for the lines of higher indices. Values are compiled in Table I.

In Fig. 2 we plot the decay of luminescence intensities after excitation by short light pulses. In these experiments, the monochromator was set to the peak wavelengths of the lines and the integral luminescence passing through the spectrometer was recorded; thus, the intensities in Fig. 2 include the background. The decay is exponential for all m lines investigated and is different in a first regime extending over one to two orders of magntiude. This fast initial decay is followed by a second range of comparably slow but also exponential decay. All decay curves were independently measured in the corresponding TA and LA components where they are identical within the experimental error (<5%) except for small differences in the long-lived tails at $t \gtrsim 500$ nsec. This shows evidence that if there is substantial background radiation it should be correlated with TA- and LA-phonon-assisted radiation as is the case for the bound-exciton lines under discussion. In the initial decay regime the bound-exciton lines clearly dominate the spectra in the excitation mode employed and hence the corresponding decay times should be due to the impurity associated lines. Time constants of this initial luminescence decay are compiled in Table I. They were obtained from least-squares fits

to the data points using a sum of two exponentials for each line. A special computer program was employed granting sufficient accuracy to the fits of the long-lived tails. The decay times τ_m in Table I are thus corrected for contributions of the long-lived decay. The values arrived at are well distinguished and monotonically reduced in the line series. They support the interpretation that all m lines originate from independent acceptor-exciton complexes. Our value $\tau_1 = 68.3$ nsec is considerably different from that contained in Fig. 19 of the work of Dean *et al.*[24] ($\approx$110 nsec). We found a similar discrepancy in the case of Mg bound excitons ($\tau_1 = 164$ nsec, Table II, and $\approx$190 nsec,[24] respectively), but there is fair agreement for Cd bound excitons ($\tau_1 = 12.2$ nsec, Table III, and $\approx$14 nsec,[24] respectively). The reason for the disagreements is not clear.

We believe that also the long-lived tails in Fig. 2 are not substantially influenced by underground radiation and are due to the m lines. The major part of the background is probably due to electron-hole-drop (EHD) luminescence which was shown to exist in GaP.[34,35] This is confirmed by the observation that the NP region of the spectrum is practically free from broad background radiation. Shah *et al.*,[35] for a nominal temperature of 2 K at high optical excitation similar to our experimental situation, measured an initial EHD luminescence decrease with 35 nsec time constant tending to a much faster decay above $\approx$100 nsec. We shall assume that this luminescence decay is characteristic of the *whole* broad EHD recombination band. Since this decay absolutely differs from our decay curves in Fig. 2 it may be argued that an underlying EHD radiation does not substantially disturb the measured kinetics. This is supported by comparison with the well-investigated decay curves of B-induced satellite lines in Si,[36] which are surprisingly similar to those in Fig. 2. Besides the same typical overall decay characteristic, a common detail is, e.g., the approximately equal long-lived decay of the m_2, m_3, and m_4 lines which is slower than for the m_1 line. Schmid[36] in Si:B measured the difference of m line peak intensities and minima between the lines in a time-resolved experiment. He found that the long-lived tails were still present and did not greatly differ from those obtained when only the peak intensities were recorded. By virtue of the conspicuous analogy we assume the same to be true for the Zn-associated lines in GaP.

An interpretation of the decay curves—in terms of MBE models or alternative conceptions—is difficult. In either case numerous possible strongly coupled formation and decay processes of the independent exciton complexes have to be considered. This makes a model description on the basis of rate equations an absolutely impracticable way. In view of these obstacles to a complete understanding of the reaction kinetics, Schmid[36] and Munz[37] in the case of Si looked for *invariable* decay constants neither depending on the doping level of the samples nor on the excitation pulse power. They associate such invariables with the lifetimes of the complexes containing physical information on the electronic structure of these states. For Si:B and for Si:Al, Si:Ga and Si:Li, Si:As,[36] whose MBE lines all show decay characteristics like in Fig. 2, Schmid and Munz could show that the initial decay times have to be associated with the lifetimes. In the present GaP:Zn case, we could not vary the Zn concentration of the samples; however, it was made sure that the development of line intensities in the very first time interval ($\lesssim$100 nsec) after excitation depends on the pulse power but that the following exponential curves are invariable. Hence, the values τ_m in Table I are interpreted as the lifetimes of the exciton complexes. Similar experiments were performed on GaP:Mg and GaP:Cd samples with similar results. This is why we chose for the representation of the luminescence decay in Figs. 2 and 7 measurements at excitation levels as low as possible where the initial exponentials are prominent in a larger time interval than for higher excitation levels.

The series character of the satellites in GaP, their intensity-to-pump relations, and their lifetime systematics are highly analogous to the bound-exciton low-energy line series in Si, Ge, and β-SiC. They suggest that the GaP luminescence likewise has to be associated with "multiple bound excitons". The new experimental data rule out former interpretations of the satellites. In particular, the phonon scattering explanation would require identical excitation dependencies and decay curves for all m lines since the same initial BE state is employed. This interpretation could also hardly explain the spectral positions in the line set which are far from being equidistant. Furthermore, anticipating the results on Mg- and Cd-doped GaP our line displacements show a marked dependence on the acceptor species (Tables I–III) which cannot be understood by this recent model. Species dependencies were also reported in the original work on acceptor-bound-exciton luminescence by Dean *et al.*[24] but the recent reanalysis of the previous data[25] yielded acceptor-independent line displacements.

Further analogies can be drawn between the present m lines and the MBE lines in the above mentioned indirect semiconductors. Dean and coworkers[24] pointed out that the m_2 and m_3 lines in GaP:Zn exhibit no striking behavior in a magnetic field additional to that exhibited by the principal exciton $Zn_{(1)}$ components. The same evidence was given by Sauer and Weber[6] in the case of Si:P, Si:Li, and Si:B MBE satellites where all lines investigated split almost identically except for thermalization features.[38] In the present study we applied stress to the large GaP:Zn needle by pressing a small leaf spring on the

cylindric periphery of the needle. This stress was inhomogeneous and often produced diffuse lines. Beyond this, the leaf forces were different from experiment to experiment and could not be varied between single runs as long as the sample was immersed in liquid helium, making the measurements rather tedious. Better results were obtained when only luminescence from a small sample spot was recorded by suitably adjusting the optical imaging system. In these cases we observed relatively sharp line spectra (Fig. 3). The S- and N-associated BE lines split into doublets which were familiar to us from independent uniaxial stress measurements on GaP:S and GaP:N samples cut into parallelpipeds, and which for low stress were found to split isotropically to a very good approximation.[39] The m lines split into nearly equally spaced doublets. The doublet spacings are within experimental accuracy equal to the splitting of the S^{NP} line and are therefore attributed to the holes in the Zn bound-exciton complexes. The $Zn_{(1)}$ (m_1) doublet components thermalize but the m_2 components do less, and the m_3 components show very small or no thermalization at all. Note that the m_2 component intensities behave slightly different in the TA and LA spectra. The center-of-gravity shifts are identical for all m lines. These principal features were observed in all serviceable spectra irrespective of the stress magnitudes. Again, we find a close analogy to stress-dependent measurements on MBE Si lines[15,17] whose dominant doublet splitting is for all lines in a series identical but shows a successive reduction of the components thermalization from m_1 (fully thermalizing) toward the low-energy lines. An explanation of this peculiar behavior was first given by Herbert *et al.*[40] and later in more detail by Thewalt[16] in terms of MBE models. The thermalization behavior is so characteristic of the MBE satellite lines in Si that spectra like that in Fig. 3 give further evidence to our MBE interpretation of the GaP:Zn lines.

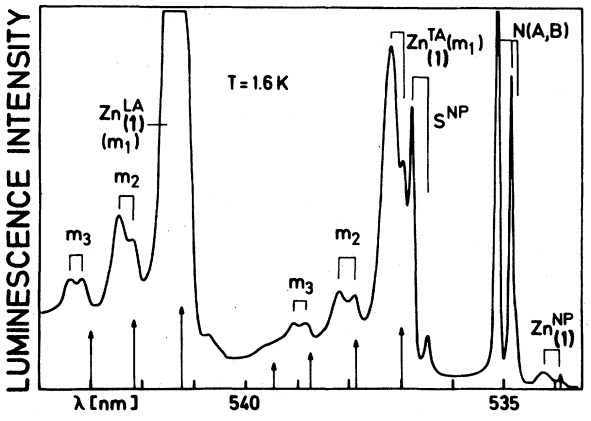

FIG. 3. High excitation photoluminescence spectrum of GaP:Zn under stress. Stress split line components are marked by brackets, and the zero stress positions of the m lines are indicated by vertical arrows.

Dean and Herbert[25] emphasized that the satellites are seen more strongly when the excitonic binding energy E_{BX} is small. This tendency also applies to the Si MBE lines, e.g., to the donor associated series: The satellites at comparable doping levels of the samples are relatively strong for Li (Ref. 3, see also the spectrum of Lyon *et al.*[41] showing m_2 through m_4 lines in a >60% intensity range of the BE Li line at medium excitation power), but are dramatically cut off in the As series (typical reduction from m_1 to m_4 on order 1 to 50 at 10^{14}-cm^{-3} As concentration and at medium excitation[42]), and P being in between. The associated binding energies are

$$E_{BX}(\mathrm{Li}) \approx 3.3 \text{ meV} ,$$

$$E_{BX}(\mathrm{As}) \approx 5.5 \text{ meV} ,$$

and

$$E_{BX}(\mathrm{P}) \approx 4.9 \text{ meV} .$$

We disregard in this comparison the reversed ordering of the valley-orbit states of the Li bound electron altering the multiplicity of the exciton states. In accord with the above formulated "rule", Dean *et al.* in their previous investigation[24] did not observe satellites for the deeper acceptor Cd ($E_{BX}=8.4$ meV) in GaP, but clearly resolved up to three extra lines in the TA- and LA-phonon assisted spectra for the shallower acceptor Mg ($E_{BX}=6.0$ meV). These lines are labeled "?" or are unlabeled in Fig. 7 of Ref. 24. We could also resolve these lines in our experiments on Mg-doped GaP. A high-excitation photoluminescence spectrum is shown in Fig. 4. In our sample the BE satellites are in the TA spectra not as clearly seen as by Dean *et al.* because the m_2 line is on the low-energy side superposed by luminescence due to Si contamination, and because the m_4 line lies as a weak shoulder on luminescence whose origin is not clear. The satellites are, however, without disturbance resolved in the LA spectra. They are positioned such that the line interspacings successively decrease (Table II) as is common of MBE series. In contrast to GaP:Zn (Table I) and GaP:Cd (Table III) we did not find a difference in the m line displacements ΔE_m from the BE line between the TA and LA spectra. Keeping our explanation of this effect for GaP:Zn in mind, we may conclude that the fine structure of the m lines is negligibly small for Mg as the shallowest acceptor among Zn, Mg, and Cd. This is consistent with data of Dean *et al.*[24] who pointed out that the bound-exciton zero-field splittings producing the multicomponent BE lines increase with the localization energy E_{BX} of the exciton. We note in particular that the Mg line displacements from the principal

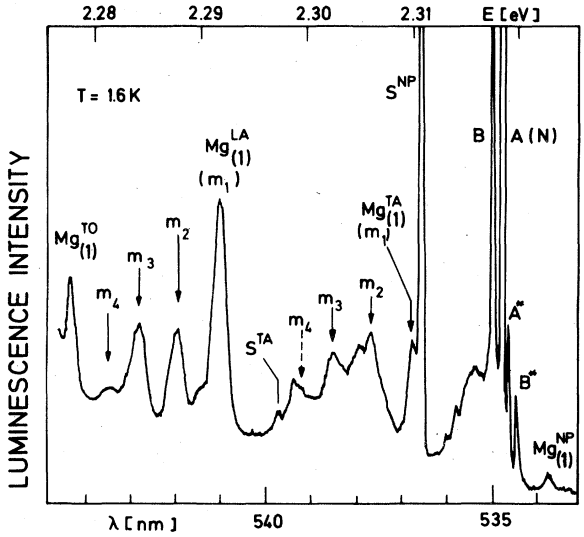

FIG. 4. Portion of the high-excitation photoluminescence spectrum of GaP:Mg as recorded photoelectrically. The MBE lines are labeled m_2 through m_4. Lines A^* and B^* originate from the radiative decay of electron-hole pairs from nitrogen bound-exciton molecules (Ref. 51).

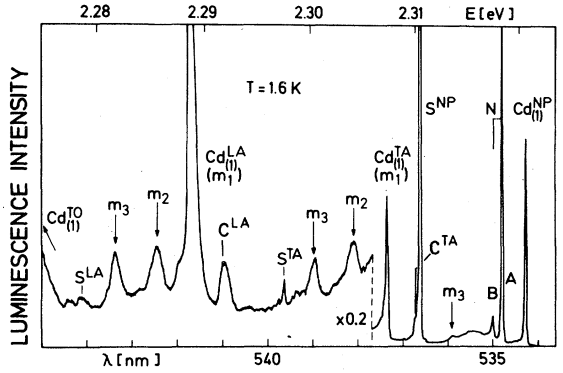

FIG. 5. Portion of the high-excitation photoluminescence spectrum of GaP:Cd. Cd induced MBE satellites m_2 and m_3 which were very weakly seen in Ref. 25, are well resolved. Lines C^{TA} and C^{LA} are due to excitons bound to residual C.

bound-exciton line $Mg_{(1)}$ are definitely different from the corresponding ones in Zn-doped GaP. We investigated the excitation dependence of the luminescence intensities and found essentially power laws whose exponents are also compiled in Table II. For low pump levels we observe in the spectra merely the BE $Mg_{(1)}$ lines with the participation of various momentum-conserving phonons along with the luminescence from residual S and N bound excitons. Decay curves of the lines were measured after 12 nsec excitation pulses and showed principally the same characteristic behavior as the GaP:Zn curves in Fig. 2. Under pulse excitation conditions the m_4 (LA) line was also strong enough to be investigated. Lifetimes of the exciton complexes (Table II) were obtained by least-squares fits as described for GaP:Zn. They are again invariables of the decay kinetics. In conclusion, the data on GaP:Mg sum up to be a certain proof that the sidebands are Mg induced MBE satellites.

Dean *et al.*[24] in their basic investigation of acceptor-exciton luminescence could not detect BE satellites in GaP:Cd. This is consistent with the "rule" connecting satellite intensities and the exciton binding energy E_{BX}, since Cd is by far the deepest of all shallow acceptors in GaP. Refined analysis in the more recent work of Dean and Herbert[25] eventually yielded two weak broad satellites for Cd doping considerably obscured by luminescence from contaminants. In the present study we could observe two well resolved Cd-associated satellites in GaP:Cd labeled m_2 and m_3 (Fig. 5). Their displacements from the BE $Cd_{(1)}$ line are as in the GaP:Zn case slightly different in the TA and LA spectra. Neither of these values coincides with corresponding displacements of Zn or Mg induced m_2 or m_3 satellites. Lines m_2 and m_3 need highest optical excitation in order to be clearly seen, at mediate pump levels they are absent from the spectra normalized to equal BE $Cd_{(1)}$ intensities. The measured intensity-to-pump relations of lines m_1 through m_3 are plotted in Fig. 6. They coincide (except for constant factors) for various replicas of the $Cd_{(1)}$ lines, and show higher-order dependencies on laser excitation for the m_2 and m_3 lines. It is most probable that due to the applied high laser powers we are already outside the excitation range, where in the logarithmic scales of Fig. 6 the expected power laws would give straight lines. Unlike the case of Si,[2,3] but similar to the case of SiC,[8] all intensities decrease above a certain high pump level. This effect is due to sample heating under the intense excitation. Decay curves which could be measured for all three lines in the TA as well as in the LA spectral range are shown in Fig. 7. They resemble principally those of GaP:Mg or GaP:Zn (Fig. 2) but exhibit much less pronounced long-lived tails. The decay times derived from Fig. 7 are substantially shorter because the excitonic binding energies are larger for Cd than for Zn and Mg. Dean *et al.*[23,24] for the principal bound-exciton lines associated with different acceptors demonstrated that a relation $\tau_1 \sim E_A^{-4}$ exists between the exciton lifetimes τ_1 and the acceptor ionization energy E_A. This relationship can be understood in terms of a localized Auger recombination by the effects of hole wave function overlap at the acceptor site and the probability of momentum transfer which are both determined by the depth of the impurity. A similar relationship holds for shallow donor and acceptor bound excitons in Si as was recently experi-

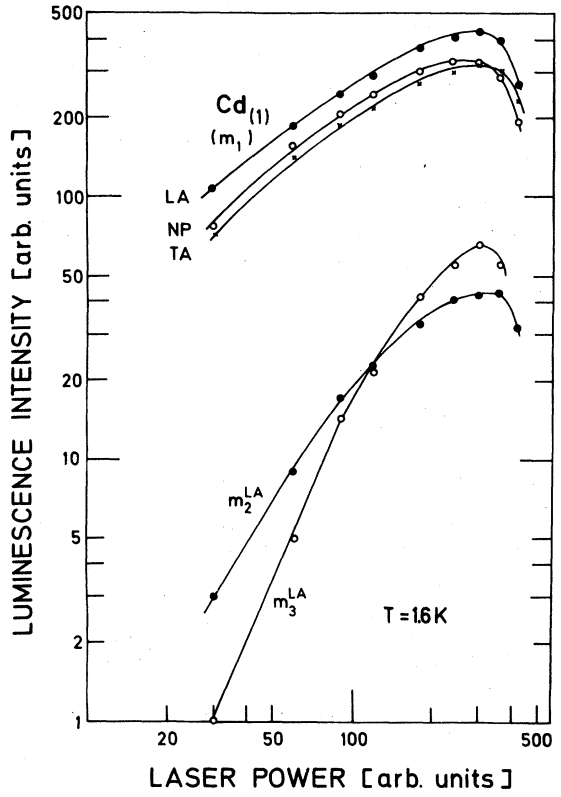

FIG. 6. Intensity-to-pump relations for the m_1 through m_3 Cd-associated bound-exciton lines in GaP.

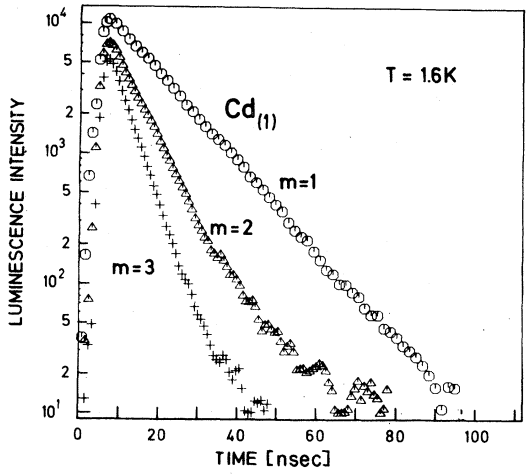

FIG. 7. Luminescence decay of the m lines in GaP:Cd after ≈400 psec pulse excitation as measured in the TA and LA spectra. For decay times see Table III.

mentally observed and theoretically confirmed in independent papers[33,43,44] supporting the basic conception of Dean *et al.* in GaP. As for the lifetimes of the m_2 lines we meet the situation which is familiar from all Si MBE series[36]: τ_2 is in each case $\tau_2 \approx 0.5\tau_1$ or slightly larger. A full discussion of this point and of the lifetime systematics in Si will be given elsewhere.[36] To summarize, like the Zn and Mg acceptors all investigated properties of the Cd-associated lines meet to suggest the MBE interpretation of the satellites. Low-energy satellites were reported to exist also in Be- and C-doped GaP and for doping with the axial complex center X.[24] We feel that these satellites should be interpreted in terms of MBE lines.

After conclusive evidence has been given in the foregoing for the existence of MBE line series in GaP it is interesting to compare typical relative energetic positions of the m lines in this material with those in Si, Ge, and β-SiC. The m line positions depend on the impurity ionization energy (see Tables I through III for GaP, or Refs. 4 and 15 for Ge and Si, respectively). By virtue of the Haynes rule, they depend as well on the excitonic binding energy to the impurity, E_{BX}. The species characteristic shifts are much smaller than the associated line displacements δE_m from the excitonic gap E_{GX} which in a MBE model assuming ground state-to-ground state transitions correspond to the binding energy of the mth exciton to the complex. Thus, in several cases the species dependence partially cancels when the line displacements δE_m are related to E_{BX}. For a survey it may be justified to bring up those moderately shallow impurities as representative for each material which induce extended line series. Four examples are compiled in Table IV. Except for comparably insignificant variations the relative displacement energies δE_m are surprisingly similar. This behavior may stress the generically identical origin of the satellite line series in all four semiconductors.

In the discussion on the existence of multiple bound excitons the observation of fine structure in the m lines plays an important role. Fine structure of the acceptor BE lines in Si was detected in luminescence by Vouk and Lightowlers[45,46] after it had first been seen in absorption by Dean *et al.*[47] The fine structure is believed to originate from hole-hole and hole-electron j-j coupling in the bound-exciton complex although these experiments could not decide in favor of one among three possible models. Bound-exciton absorption in Si:Al, Si:Ga, and Si:In was recently studied by Elliot *et al.*[48] giving preference to one particular model. Dean *et al.*[8] when discussing their version of a MBE model suggested that fine structure should also be seen in the acceptor m_2 satellite lines. According to their conception it should mirror the BE fine structure without thermalization of the components since it is due to the splitting of the principal single bound exciton as the m_2 transition final state. Thewalt[21] reported doublet splittings of BE low-energy sidebands in Si:Al and Si:Ga which he ascribed to m_2 satellites following the prediction of

TABLE IV. MBE satellite displacement energies δE_m from the excitonic gap, E_{GX}, normalized to the associated excitonic binding energy E_{BX} for typical shallow impurities in four indirect semiconductors. Last digits of δE_m values are approximate.

Material	E_{BX} (meV)	$\delta E_m/E_{BX}$ m_1	m_2	m_3	m_4	m_5	m_6	m_7
Si:P[a]	4.9[a]	1	1.73	2.29	2.67	2.94	3.20	3.47
Ge:As[b]	1.33[b]	1	1.65	2.15	2.46	2.84	3.09	···
SiC:N_C[c]	10.9[d]	1	1.74	2.29	2.74	3.13	3.58[g]	···
GaP:Zn[e]	6.65	1	1.56[f]	2.13	2.56	2.95	···	···

[a]Unpublished data of the authors.
[b]Evaluated from Fig. 3 of Martin (Ref. 4).
[c]Evaluated from Fig. 1 of Dean *et al.* (Ref. 8).
[d]From $E_{GX}=2.390$ eV after Choyke *et al.* (Ref. 55) and $h\nu$(BE) $=2.3791$ eV after Hartmann and Dean (Ref. 56).
[e]Present work, see Table I.
[f]For TA replica 1.59.
[g]The m_6 line is not certain.

Dean *et al.* This interpretation was supported by Lyon *et al.*[22] who showed that in Si:Ga the m_2 satellite is a nonthermalizing triplet which energetically precisely mirrors the BE line triplet. This is regarded to be the most direct evidence of the existence of acceptor bound two-exciton complexes.

These findings directly concern the GaP:Zn MBE lines since these also show fine structure. The BE fine structure for acceptors in GaP was previously discussed[24] in terms of electron and hole *j-j* coupling and of crystal-field splittings, and for the particular acceptor Cd was experimentally studied in detail. In GaP:Zn, besides the BE line, the m_2 line exhibits pronounced fine structure (Fig. 8) which is similarly contained in the spectra of Dean *et al.*,[24] though not discussed. Fine structure is also existent in the m_3 satellite but is not distinct enough for a detailed investigation. The $Zn_{(1)}$ (m_1) fine structure in Fig. 8 is almost identical to the previously reported spectra.[24] The high-energy components rapidly vanish due to thermalization at elevated temperature. In our experiments the sample temperature was varied by changing the power I_0 of the exciting laser beam which was constantly focused to a small spot on the sample surface. The m_2 line fine structure also depends on the temperature though to a reduced degree. This is different from the situation in Si.[22] Another difference from the Si case is that we cannot find a correlation between the fine-structure components in the m_1 and m_2 lines, since the m_2 satellite does not mirror the BE line. It may be argued that some fine-structure components in the m_1 and m_2 transitions are not seen, possibly because they are not sufficiently well resolved or are too weak. Even in this case it would be hard to claim an energetically reversed component structure between the m_1 and m_2 lines from Fig. 8. Since the m_3 transition is also weakly split it is conceivable that the MBE(2) state (the m_2 transition initial state) consists of two or more closely spaced levels, appending thermalizing components to the m_2 line spectrum . Such MBE(2) state splitting was explicitly not expected in the former discussion of the acceptor MBE model,[8,21] and in GaP:Zn decidedly *fewer* components are seen in the m_2 line than in the $Zn_{(1)}$ (m_1) emission. In view of the importance of the fine structure to the understanding or the validity of MBE models in the present case, future studies are highly desirable.

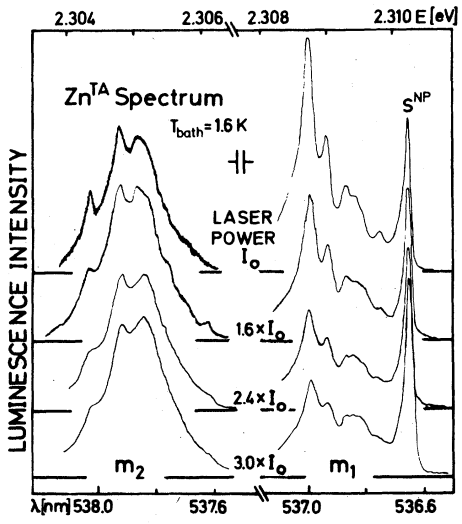

FIG. 8. Fine structure of $Zn_{(1)}$ (m_1) and m_2 lines in GaP:Zn at different temperatures. These were produced by sample heating under intense increasing optical excitation power I_0.

In this context we point out a third difference between acceptor induced satellite lines in Si and in

GaP. The only acceptor in Si associated with an extended, regularly spaced set of satellites is B. The BE boron line shows a very small fine structure in the form of unresolved shoulders.[10,49] Likewise, an unresolvable fine structure is seen in the m_2 B satellite[49] from which no conclusion on a MBE model can be drawn. The m_2 satellites in Si:Al and Si:Ga however, which led to the above discussed MBE model belong to sets of satellites which are less extended and nonuniformly positioned. In these cases the fine structure is large causing the interpenetration of m_2 and m_1 components in the spectra. From the positions of those line components which are assumed to connect MBE ground states the binding energy of the second exciton is found to be almost equal to the binding energy of the first in Si:Al or to be even smaller in Si:Ga.[22] In GaP:Zn, applying the same MBE conception as for Si:Al and Si:Ga, the spectroscopic shift

$$\delta E_2 = E_{BX} + \Delta E_2 = 10.4 \text{ meV}$$

as the approximate binding energy of the second exciton markedly exceeds that of the first, $E_{BX} = 6.65$ meV. For GaP:Cd, a single BE high-energy component was reported spaced $\approx$1 meV from the main $Cd_{(1)}$ line.[24] Corresponding fine-structure components in the m_2 transition should be observable possibly with incomplete resolution. In the present study, however, we did not find reliable indications of a substructure in the m_2 and m_3 transitions. On this experimental basis we conclude that even for the relatively deep acceptor Cd in GaP the second exciton binds with a substantially larger binding energy to the impurity than the first. This is qualitatively different from Al or Ga bound excitons in Si. As for the deeper acceptor In in Si, it was recently shown that the line 4 meV below the BE emission is not a MBE satellite but has to be attributed to an exciton recombination into an excited In acceptor state.[50]

It is striking that in all acceptor induced spectra which we observed lines m_2 and m_3 are much stronger than lines m_4 and m_5 if the latter are seen at all. This abrupt break in the satellite line intensities is also prominent in Si:B for $m > 3$ and is obvious for the Li-, P-, and As-associated line series in Si for $m > 4$. This behavior can be understood in a MBE shell model (which need not necessarily by the Kirczenow-Thewalt model) since the fourfold degenerate Γ_8 hole states are filled for acceptor bound excitons from MBE(3) on and for donor bound excitons from MBE(4) on.

With a multiple bound-exciton interpretation of the satellite lines we meet an extremely interesting situation in GaP since in this material excitonic molecules bound to N isoelectronic traps are already believed to exist.[51] This explanation applies to extra lines labeled A^* and B^* showing up energetically above the A and B lines (which are due to N bound excitons), and was derived from excitation-dependent measurements and Zeeman splittings. The A^* and B^* lines were in our measurements also seen in a GaP:Mg sample (Fig. 4) which contains appreciable amounts of N. Referring to the data of Merz *et al.*,[51] the second exciton binds to the nitrogen center less strongly ($\approx$9 meV) than the first exciton which has a binding energy of $\approx$11.5 meV. This tendency of binding energies is contrary to that for the acceptor bound excitons.

Very recently, one of the authors (U.R.[52]) performed photoluminescence experiments in GaP:S on low-energy sidebands of the radiation due to the decay of sulfur bound excitons. These sidebands were likewise previously reported but not investigated since they are very weak.[53] They are the lines labeled S_α and S_γ which appear in the no-phonon region of the spectrum below lines S^0 (S^{NP} in our notation). Reaction kinetics such as pump power dependence and luminescence decay make plausible to associate them with S bound m_2 and m_3 MBE satellite lines.

In conclusion, we have shown that multiple bound-exciton lines exist in GaP. The lines are prominent for acceptors as binding centers and are most intense for small acceptor ionization energies. Sulfur may introduce weak donor bound MBE lines. The data presented manifest that the occurrence of MBE line series is not a matter peculiar to a few specific cases but appears to be a *typical* high-excitation effect common to numerous impurities in numerous indirect cubic semiconductors.

ACKNOWLEDGMENTS

It is a pleasure to express our gratitude to M. D. Sturge (Bell Laboratories, Murray Hill) and to W. Senske (Max-Planck-Institut für Festkörperforschung, Stuttgart) for the loan of the GaP samples, and D. Munz for his help with a number of experiments. We are grateful for the steady interest in this work and the stimulation by M. H. Pilkuhn. The financial support of the Deutsche Forschungsgemeinschaft (SFB 67) is gratefully acknowledged.

[1]A. S. Kaminskii and Ya.E. Pokrovskii, JETP Lett. 11, 255 (1970); A. S. Kaminskii, Ya.E. Kokrovskii, and N. V. Alkeev, Zh. Eksp. Teor. Fiz. 59, 1937 (1970) [Sov. Phys. JETP 32, 1048 (1971)].
[2]R. Sauer, Phys. Rev. Lett. 31, 376 (1973).
[3]K. Kosai and M. Gershenzon, Phys. Rev. B 9, 723 (1974).
[4]R. W. Martin, Solid State Commun. 14, 369 (1974).
[5]R. Sauer, *Proceedings of the 12th International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. Pilkuhn (Teubner, Stuttgart, 1974), p. 42.
[6]R. Sauer and J. Weber, Phys. Rev. Lett. 36, 48 (1976).
[7]T. N. Morgan, *Proceedings of the 13th International Conference on the Physics of Semiconductors, Rome, 1976,* edited by F. G. Fumi (Tipografia Marves, Rome, 1976), p. 825.
[8]P. J. Dean, D. C. Herbert, D. Bimberg, and W. J. Choyke, Phys. Rev. Lett. 37, 1635 (1976).
[9]G. Kirczenow, Solid State Commun. 21, 713 (1977) and Can. J. Phys. 55, 1787 (1977).
[10]M. L. W. Thewalt, Solid State Commun. 21, 937 (1977) and Can. J. Phys. 55, 1463 (1977).
[11]M. L. W. Thewalt, in *Physics of Semiconductors, 1978,* edited by B. L. H. Wilson, IPPS Conf. Ser. No. 43 (Institute of Physics and Physical Society, London, 1979), p. 605.
[12]R. Sauer, W. Schmid, and J. Weber, Solid State Commun. 24, 507 (1977).
[13]S. A. Lyon, D. L. Smith, and T. C. McGill, Phys. Rev. Lett. 41, 56 (1978).
[14]K. R. Elliott and T. C. McGill, Solid State Commun. 28, 491 (1978).
[15]R. Sauer and J. Weber, Phys. Rev. Lett. 39, 770 (1977).
[16]M. L. W. Thewalt, Solid State Commun. 25, 513 (1978).
[17]M. L. W. Thewalt and J. A. Rostworowski, Phys. Rev. Lett. 41, 808 (1978).
[18]H. J. Wünsche, V. E. Khartsiev, and K. Henneberger, Phys. Status Solidi B 85, K 53 (1978).
[19]H. J. Wünsche, K. Henneberger, and V. E. Khartsiev, Phys. Status Solidi B 86, 505 (1978).
[20]R. J. Almassy, D. C. Reynolds, C. W. Litton, K. K. Bajaj, and G. L. McCoy (private communication).
[21]M. L. W. Thewalt, Phys. Rev. Lett. 38, 521 (1977).
[22]S. A. Lyon, D. L. Smith, and T. C. McGill, Phys. Rev. B 17, 2620 (1978).
[23]P. J. Dean, R. A. Faulkner, and S. Kimura, Solid State Commun. 8, 929 (1970).
[24]P. J. Dean, R. A. Faulkner, S. Kimura, and M. Ilegems, Phys. Rev. B 4, 1926 (1971).
[25]P. J. Dean and D. C. Herbert, J. Lumin. 14, 55 (1976).
[26]R. Sauer, W. Schmid, J. Weber, and U. Rehbein, *Physics of Semiconductors, 1978,* edited by B. L. H. Wilson, IPPS Conf. Ser. No. 43 (Institute of Physics and Physical Society, London, 1979), p. 623.
[27]J. Leotin, J. C. Ousset, R. Barbastre, S. Askenazy, M. S. Skolnik, R. A. Stradling, and G. Poiblaud, Solid State Commun. 16, 363 (1975).
[28]K. Suzuki and N. Miura, Solid State Commun. 18, 233 (1976).
[29]P. Lawaetz, Solid State Commun. 16, 65 (1975).
[30]A. A. Kopylov and A. N. Pikhtin, Fiz. Tekh. Poluprovodn. 11, 867 (1977) [Sov. Phys. Semicond. 11, 510 (1977)].
[31]M. Altarelli and R. A. Sabatini, Solid State Commun. 25, 1101 (1978).
[32]J. L. Yarnell, J. L. Warren, R. G. Wenzel, and P. J. Dean, in *IAEA Symposium on Neutron Inelastic Scattering, Copenhagen-1968* (IAEA, Vienna, 1968), p. 301.
[33]W. Schmid, Phys. Status Solidi B 84, 529 (1977); and thesis (Stuttgart, 1977) (unpublished).
[34]H. Maaref, J. Barrau, M. Brousseau, J. Collet, and J. Mazzaschi, Solid State Commun. 22, 593 (1977).
[35]J. Shah, R. F. Leheny, W. R. Harding, and D. R. Wight, Phys. Rev. Lett. 38, 1164 (1977).
[36]These data are in detail described and discussed in Ref. 33 (thesis) and are to be published. Preliminary results on B- and P-doped Si are contained in Ref. 5, recent more accurate data on Si:P are given in Ref. 12. For Al and Ga, the data refer to the m_2 doublet lines as, e.g., reported in Ref. 21.
[37]D. Munz, Diplomarbeit (Stuttgart, 1977) (unpublished).
[38]"Thermalization" refers here and in the discussion of the piezospectra to the empirical intensity ratios of the split-line components.
[39]Unpublished results of one of the authors (J. W.). For stress parallel to [111] see. e.g., J. L. Merz, A. Baldereschi, and A. M. Sergent, Phys. Rev. B 6, 3082 (1972).
[40]D. C Herbert, P. J. Dean, and W. J. Choyke, Solid State Commun. 24, 383 (1977).
[41]S. A. Lyon, D. L. Smith, and T. C. McGill, Solid State Commun. 28, 317 (1978).
[42]Unpublished data of the authors; a survey of spectra is contained in Ref. 33 (thesis).
[43]S. A. Lyon, G. C. Osbourn, D. L. Smith, and T. C. McGill, Solid State Commun. 23, 425 (1977).
[44]G. C. Osbourn and D. L. Smith, Phys. Rev. B 16, 5426 (1977).
[45]M. A. Vouk and E. C. Lightowlers, *Proceedings of the 13th International Conference on Physics of Semiconductors, Rome, 1976,* edited by F. G. Fumi (Tipografia Marves, Rome, 1976), p. 1098.
[46]M. A. Vouk and E. C. Lightowlers, J. Lumin. 15, 357 (1977).
[47]P. J. Dean, W. F. Flood, and G. Kaminsky, Phys. Rev. 163, 721 (1967).
[48]K. R. Elliott, G. C. Osbourn, D. L. Smith, and T. C. McGill, Phys. Rev. B 17, 1808 (1978).
[49]W. Keiper, Zulassungsarbeit zum höheren Lehramt (Stuttgart, 1978) (unpublished).
[50]R. Sauer, W. Schmid, and J. Weber, Solid State Commun. 27, 705 (1978).
[51]J. Merz, R. L. Faulkner, and P. J. Dean, Phys. Rev. 188, 1228 (1969).
[52]U. Rehbein, Diplomarbeit (Stuttgart, 1979) (unpublished).
[53]P. J. Dean, Phys. Rev. 157, 655 (1967).
[54]M. D. Sturge, A. T. Vink, and F. P. J. Kuijpers, Appl. Phys. Lett. 32, 49 (1978).
[55]W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. 133, A1163 (1964).
[56]R. L. Hartmann and P. J. Dean, Phys. Rev. B 2, 951 (1970).