Conduction-band-to-acceptor magnetoluminescence in zinc telluride

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We report on the magnetic field behavior of free-to-bound (FB) acceptor luminescence and donor absorption in high-purity p-type ZnTe. Conduction-band Landau level states are readily seen in the acceptor FB luminescence, and yield the best current estimate of the electron effective mass in ZnTe, $m_e^*/m_0 = 0.116 \pm 0.005$, significantly different from most previous values. Spin splitting is also seen, and yields approximate hole and electron g values in agreement with recent estimates from acceptor bound-exciton (BE) luminescence, as near as can be determined. These results confirm a small negative electron g value, far from that predicted by first-order $\vec{k}\cdot\vec{p}$ theory. This discrepancy shows that interactions with higher bands are important in ZnTe. We use a five-band model together with our experimental values of m_e^* and g_e to determine the matrix elements P^2 and P'^2 of the interaction between the conduction band and, respectively, the valence and next-higher conduction bands. We find $P^2 = 32.3$ eV and $P'^2 = 7$ eV, close to values in GaAs. The polaron mass enhancement is about 5% for the electron in ZnTe. The electrons recombine with an effective temperature of ~ 14 K at a lattice temperature of ~ 5 K under typical experimental conditions. The magnetic field causes strong enhancement of "two-hole" BE luminescence satellites involving p-like acceptor excited states caused by mixing with s states for an acceptor with large central-cell contribution to its binding energy, possibly an effect of relatively long-range terms due to misfit strain. The zero-field positions of the acceptor FB band suggest that E_g is close to 2.394 eV in ZnTe at 4.2 K according to recent independent estimates of the acceptor ionization energies from these BE satellites. This, in turn, implies an internal binding energy of the free exciton close to 13 meV, significantly larger than previous values, ~ 10 meV. Large magnetic effects occurring within an absorption edge located just below the main acceptor BE line are tentatively attributed to the onset of a BE state at ionized donors, stabilized in the magnetic field.

I. INTRODUCTION

Zinc telluride is a zinc-blende (cubic) structure II-VI compound semiconductor with a forbidden gap E_g near 2.39 eV.[1] The minimum band gap is of direct type, located at the center of the Brillouin zone. Unlike all other moderate to wide-gap II-VI semiconductors, ZnTe is generally obtained p type, whether or not it is deliberately doped with potential donors or acceptors, and n-ZnTe has been obtained so far only for very high Al doping.[2] It is now possible to obtain refined p-type material with $N_A - N_D$ in the 10^{15}-cm^{-3} range and rather lightly compensated. The near bandgap low-temperature luminescence of such material is dominated by transitions due to the residual donors and acceptors. These impurities introduce bound exciton (BE) recombination with no-phonon components lying within 10 meV of the free exciton (FE) near 2.38 eV, while satellites caused by phonon emission and transitions to excited states of the spectrally dominant acceptors lie between ~25 and ~300 meV to lower energy (Fig. 1). The interpretation of these BE transitions is discussed elsewhere.[3] The residual b acceptor in Fig. 1, having $E_A^b = 61$-meV binding energy, is now recognized as $\mathrm{Li}_{\mathrm{Zn}}$, while the deeper a acceptor ($E_A^a = 148$ meV), which frequently controls the hole conductivity in refined undoped ZnTe unfortunately remains unidentified. However, it is now certain that it is due neither to the binding of a single hole at a zinc vacancy V_{Zn} nor any other double acceptor, nor a complex single acceptor such as (V_{Zn} donor) the A or self-activated center well known in the literature on II-VI compounds. Further progress with the identification of this dominant acceptor and with the reason why ZnTe cannot be made n type at moderate doping levels, at present a decisive limitation for device applications of ZnTe, requires more reliable information on the optoelectronic behavior of this key II-VI material. Valence band parameters and acceptor states have already been the subject of various investigations.[4-10]

We are concerned in the present paper with the precise measurement of the conduction-band free-electron effective mass at low impurity concentration. The electron mass can be obtained from optical spectra studying the behavior of the free electron to bound (FB) luminescence in a magnetic field. In a strong magnetic field the continuum of conduction-band states available to the

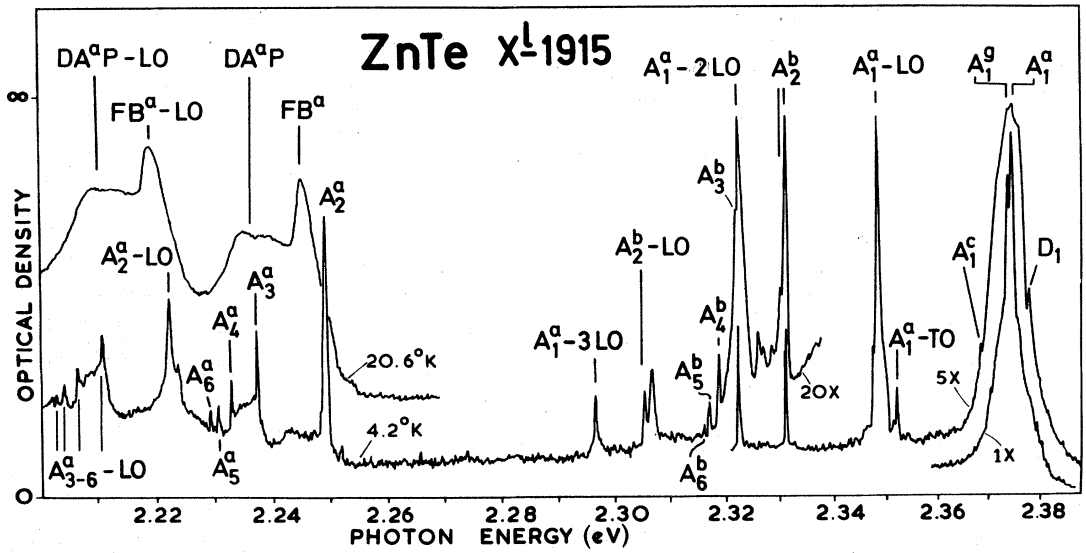

FIG. 1. Photoluminescence of refined p-ZnTe recorded photographically, relative exposure times indicated. The spectrum is overexposed even for the shortest exposure near the principal bound exciton (PBE) A_1^q due to exciton recombination at the predominant a acceptor (binding energy $E_A^a \sim 148$ meV). The subscript 1 indicates that the neutral acceptor is left in its ground electronic state after recombination. (The labeling has been slightly revised from Fig. 2 of Ref. 3 to be consistent with the note added in proof of that paper.) Satellites due to two-hole transitions in which the neutral a acceptor is left in orbital excited states are denoted A_n^a. Corresponding transitions are also seen for a shallower acceptor b identified as Li_{Zn} with $E_A^b \sim 61$ meV. Satellites of all these transitions occur due to phonon interaction mainly involving the longitudinal optical (LO) and transverse optical (TO) phonons. Weak PBE lines A_1^f and A_1^c involve further, minor acceptor species, while D_1 is the PBE transition for neutral donors (D^0,X). The spectrum at 20.6 K is dominated by recombinations at donor acceptor pairs (DAP) and of free electrons with neutral acceptors (FB).

free electron is destroyed and transforms into the well-known Landau-level distribution. This distribution contains a series a narrow allowed bands, evenly separated by an energy which is inversely proportional to the free-electron mass. This series of lines was first reported only recently in GaAs[11,12] although the narrowing of the FB transition into the lowest $N=0$ Landau level and the appearance of spin magnetic splittings was first observed rather earlier in GaSb.[13] In contrast to the value obtainable from the analysis of donor excited states, the lattice dielectric constant does not occur in the expression for the Landau-level separation, and the experiments directly yield the electron effective mass. This mass is the "polaron" mass, which is enhanced due to the electron-phonon interaction in comparison with the "bare" electron mass as calculated by $\vec{k}\cdot\vec{p}$ or other techniques.

The breadth of the FB transition is caused by the kinetic energy available to the free electrons before recombination. Attempts to obtain very narrow FB components in a direct gap semiconductor by measurements at very low lattice temperature are limited by the density of electron states at the bottom of the conduction band and are also usually frustrated by the fact that the free electrons, like free excitons,[14] typically recombine from a population which is at an internal equilibrium with an effective temperature considerably higher than the lattice, usually at least 10 K. This effect is beneficial for the present study. The heated electron population ensures that luminescence from other than the lowest Landau level can be measured over a useful range of magnetic splittings, even at the experimentally convenient lattice temperature of 4.2 K.

II. EXPERIMENTAL

A. Crystal preparation

The single crystals used in the present investigation were grown by a modified Bridgman technique in a carbon lined quartz ampoule under Te-rich conditions at 1100 °C.[15] These as-grown crystals contain remarkably low concentrations of the luminescence activator O_{Te}, common in ZnTe,[16] as well as the very low concentrations of shallow acceptors and donors already mentioned in Sec. I.

B. Optical measurements

Most of the photoluminescence measurements reported in this paper were made using a photo-

graphic recording technique described earlier.[3] The crystals were freely suspended in the liquid refrigerant, usually He but sometimes H_2. Additional spectra were also recorded photoelectrically. In both cases luminescence was excited by above band gap light from an Ar^+ laser (4880 Å).

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Acceptor free to bound luminescence at zero magnetic field

The localization of the dominant BE, labeled A_1^a in Fig. 1, is about 6.5 meV, much larger than kT at 4.2 K. Thus the BE transitions and their satellites dominate the luminescence of lightly doped ZnTe, $N_A - N_D < 10^{16}$ cm^{-3}, for all temperatures below ~15 K. However, the no-phonon FB luminescence band for the 61-meV b acceptor Li_{Zn} can be seen in Fig. 2 weakly but clearly just above the strong luminescence line A_2^b, caused by a "two-hole" BE transition to the $n=2s$ excited state of the b acceptor. The characteristic broad asymmetric line shape of the FB transition is clearly seen by comparison with line A_1^c-LO, the LO phonon replica of a BE transition at an unidentified deep acceptor c. The A_n^b BE series is slightly broadened by a 0.2-meV splitting present in the BE (initial) state,[3] unresolved in Fig. 2. The position of the low-energy threshold of the FB band is given by

$$\hbar\omega_{FB} = E_g - E_A^b , \tag{1}$$

where E_g is the energy gap and E_A^b is the ionization energy of the b acceptor. The energy $\hbar\omega_2$ of the $n=2$ two-hole replica is

$$\hbar\omega_2 = E_{gx} - E_{bx} - (E_{1s} - E_{2s}) , \tag{2}$$

where E_{gx} is the free exciton gap, E_{bx} is the localization energy of the exciton at the neutral b acceptor and $E_{1s} - E_{2s}$ is the displacement energy of the $n=2$ two-hole satellite below the principal BE line for which the acceptor is left in the $n=1$ (ground) state. From these equations the energy difference

$$\hbar\omega_{FB} - \hbar\omega_2 = E_x + E_{bx} - E_{2s} , \tag{3}$$

where E_x is $E_g - E_{gx}$, the internal binding energy of the free exciton, thought to be ~13 meV in ZnTe[1] and $E_{2s}^b = 17.5$ meV.[9] The energy E_{bx} for the b acceptor is known to be very similar to that of the a acceptor, ~6.5 meV.[17] Thus Eq. (3) predicts that the low-energy threshold of the FB band should lie 2.0 meV *higher* than A_2^b, in good agreement with experiment, 1.5 meV. Similar considerations predict a reversal of this ordering for the much deeper a acceptor with the FB band ~3.2 meV *below* A_2^a since E_{2s}^a is larger, 22.7 meV, due to a significant central cell contribution.[9] This prediction is in good agreement with the experimental value of ~3.5 meV from Fig. 3. It should be emphasized that these comparisons provide a valid stringent test of the assignments and their quantitative interpretation, since the data in Eq. (3) are derived from the BE spectral components[3] and the recent analysis of the FE reflectivity.[1] The low-energy

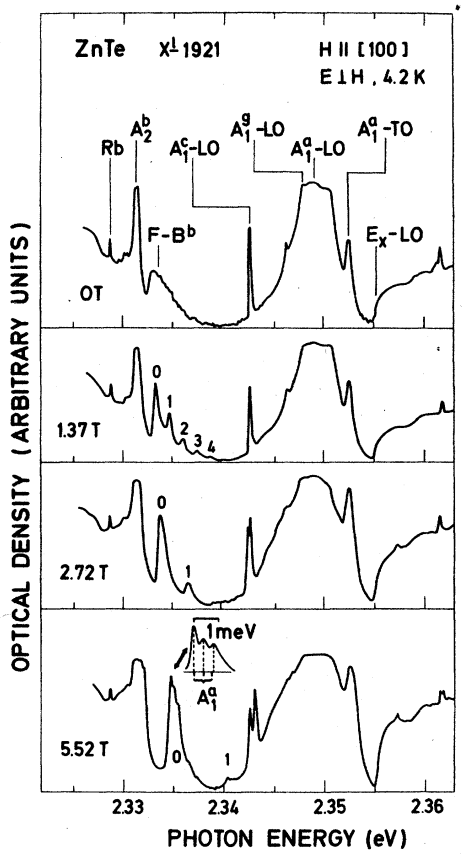

FIG. 2. Photoluminescence of refined p-ZnTe recorded photographically for the indicated magnetic fields. As in Fig. 1 the spectrum is dominated by bound-exciton transitions, in this region mainly the satellites of the a- and g-acceptor PBE due to phonon emission and the two-hole satellite A_2^b for the b acceptor. The low-energy threshold of the LO satellite of the free-exciton luminescence band, broad at the high optical excitation rates used here, is denoted E_x-LO. A rubidium calibration line is denoted Rb. The single asymmmetric band F-B^b observed at $B=0$, caused by radiative recombination of free electrons with the neutral b acceptor is transformed by a magnetic field into a series of evenly spaced narrow lines labeled 0, 1, 2, ···. These lines appear because the free electron is confined within the Landau levels of the conduction band at finite fields. Further structure can be seen in each component at sufficiently high fields because of spin splittings of the electron and hole, shown in the insert for the $N=0$ Landau component at 5.52 T. The strong component A_1^a-LO appears anomalously broad due to considerable photographic overexposure in these spectra.

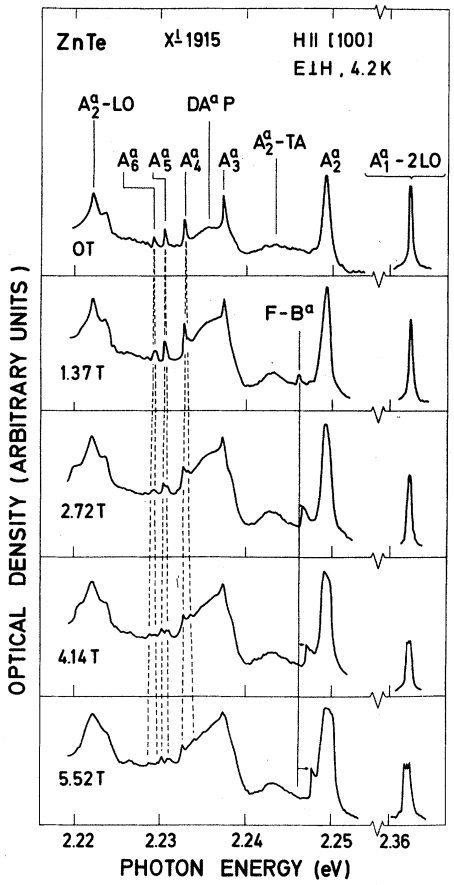

FIG. 3. Photoluminescence of refined p-ZnTe recorded photographically at the indicated magnetic fields. The spectrum is similar to Fig. 2 except that here we show the magnetic splittings of two-hole and free-to-bound components for the dominant a acceptor of larger ionization energy. Central cell shifts conspire to set the $N=0$ FB Landau level just below the strong PBE two-hole satellite A_2^a, here overexposed, which obscures luminescence from higher Landau levels. Insets at the right show that the magnetic splittings of A_2^a, not well resolved because of an anomalously large linewidth, is qualitatively similar to the 2LO phonon replica A_1^a-2LO, as is also true for the two-hole satellite A_3^a. The large apparent splittings of two-hole satellites of higher orbital states, indicated by the dashed lines, are discussed in the text.

thresholds of the FB luminescence together with the values of E_A recently computed from the observed s and p acceptor excited-state energies may provide the best current estimate of E_g for ZnTe. We obtain $E_g = 2.394_0$ and 2.393_5 eV at 4.2 K using the data in Figs. 2 and 3 together with $E_A^a = 148.1$ eV and $E_A^b = 60.9$ meV.[9]

B. Electron Landau-level phenomena in acceptor free-to-bound luminescence

The striking feature of Fig. 2 is the appearance of sharp subcomponents within the original broad Maxwell-Boltzmann line shape in the presence of a magnetic field. The magnetic field also produces small splittings in the BE lines best seen in Fig. 2 for the sharp component A_1^c-LO. These splittings are due to the Zeeman effect in the paramagnetic initial and final states of the recombination of excitons bound to neutral acceptors previously fully described and interpreted for the dominant a acceptor.[3] These BE splittings are much more complicated for the shallower b acceptor because of the 0.2-meV zero-field splitting in the initial (BE) state and will not be considered here. We simply note that the Zeeman behavior of the A_1^c line is also significantly different from A_1^a and has the form expected for recombination at an axial center with [111] symmetry. The magnetic splittings within the FB transitions are much larger and correspond to transitions from different Landau levels to the acceptor states. The energy E_N of the Nth Landau level is given by[18,19]

$$E_N = (N+\tfrac{1}{2})\hbar\omega_c - [(N+\tfrac{1}{2})\hbar\omega_c]^2/2E_g , \qquad (4)$$

where $\omega_c = eH/m_e^*c$, H is the magnetic field, E_g is the energy gap, m_e^* is the free-electron mass near the bottom of the conduction band, and $\hbar, c$ have their usual meanings. The first term in Eq. (4) is the well-known expression for parabolic bands and the second term represents a correction for nonparabolicity of the conduction band. Even when $\hbar\omega_c \sim 10$ meV, corresponding to $B \sim 10$ T and already well beyond the range of Fig. 4,

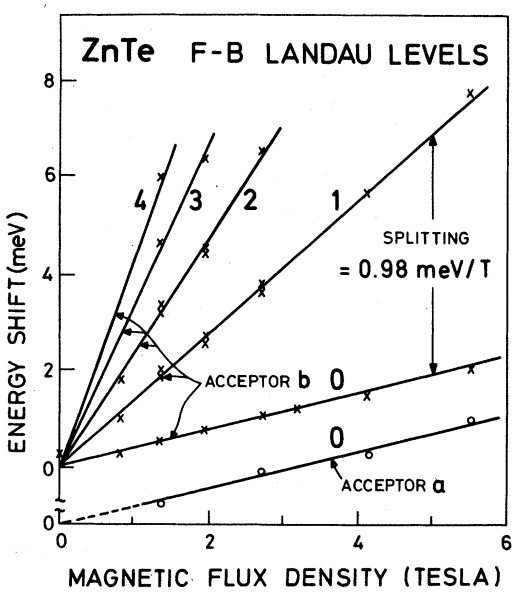

FIG. 4. Magnetic field dependence of the peak energy of the Landau-level structure in the FB luminescence of the a and b acceptors in ZnTe. Only the lowest $N=0$ state is clearly seen for the deeper a acceptor (Fig. 3). The Landau-level separations yield the free-electron effective mass m_e^*.

the mass increase due to the second term is only 0.4% and accordingly this correction has been neglected. Using the data in Fig. 4 we derive

$$m_e^*/m_0 = 0.116 \pm 0.005 \quad (5)$$

according to Eq. (4) from the energy separation between the 0th and 1st Landau level. The diamagnetic shift of the acceptor states is eliminated from the analysis when this difference is used. The same result as given in Eq. (5) was obtained from photoelectrically recorded data measured on two other crystals and not shown in Fig. 4. Problems with the spin splittings discussed further in Sec. IIID were avoided by taking an average of data for π ($E \| B$) polarization in Voigt configuration. The inset in Fig. 5 shows that no correction is then needed for the spin splitting.

Only data for the $N=0$ Landau level appear for the a acceptor in Fig. 4 because the higher-order components became obscured by the strong two-hole BE satellite almost as soon as they became clearly resolved from the FB component associated with the $N=0$ Landau level (Fig. 3). However, there is very good agreement between the magnetic shift rate of the $N=0$ component for both a and b acceptors, confirming that these magnetic effects are dominated by the behavior of the free electron and are quite insensitive to the degree of localization of the hole in the final state of the transition. This agreement extends to the deviation from linearity below 1 T, mainly caused by the method of analysis employed in Fig. 4. The main effect of taking the peak energy rather than the low-energy threshold of a fit to the Maxwell-Boltzmann profile is an underestimate of the shift rate at low magnetic fields as the line shape rapid-

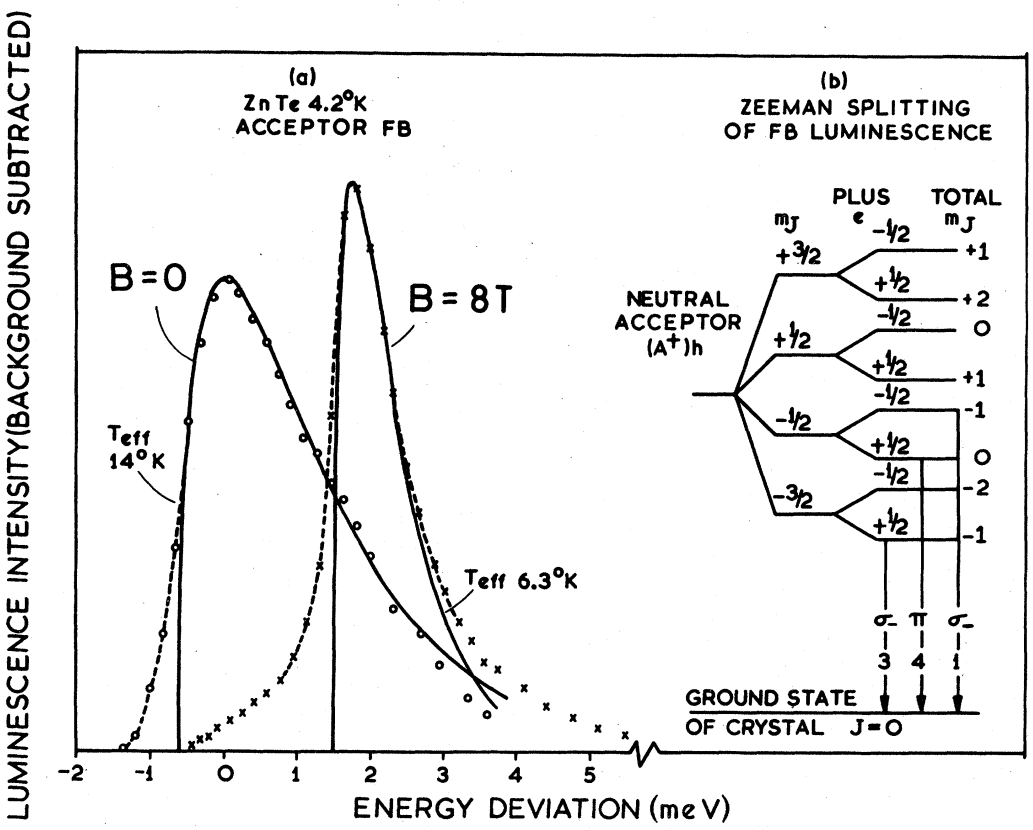

FIG. 5. (a) The FB luminescence for the 61-meV b acceptor recorded photoelectrically at zero magnetic field and for σ^- circular polarization ($E \perp B$) at 8 T, where only luminescence from the $N=0$ Landau level is significant because of thermalization. Points are experimental, the dashed curves are an empirical smooth fit to those points. The solid curve for $B=0$ is a Maxwell-Boltzmann function for an effective electron temperature of 14 K, a good fit to the experimental data except at the low-energy tail most sensitive to additional line broadening. (b) Zeeman splittings of the free electron and bound hole relevant for the FB recombination. Electron ($J=\frac{1}{2}$) and hole ($J=\frac{3}{2}$) split as independent particles in the Paschen-Back limit since there is no bound electron state before recombination. The total m_J is given by combination of the independent splittings of the electron and hole as shown. The final state of the transition corresponds to an ionized acceptor and is nonmagnetic. The polarizations of three of the six electric dipole-allowed transitions and their relative intensities in the absence of thermalization are indicated, σ corresponds to $E \perp B$, π to $E \| B$.

ly becomes dominated by the magnetic field and very much narrower as described in Sec. III C. This method of analysis was used for Fig. 4 since it is difficult to make quantitative line-shape analyses from photographic data and is not expected to introduce problems except at the lowest fields as indicated. This point has been fully discussed with reference to very similar phenomena recently observed in p-GaAs.[11,12]

The mass m_e^* entering Eq. (4) is the "polaron" mass related to the "bare" mass $(m_e^*)_0$ as calculated by $\vec{k}\cdot\vec{p}$ or other techniques by[20]

$$m_e^* = (1+\alpha/6)(m_e^*)_0 , \tag{6}$$

where $\alpha = (e^2/\hbar)(1/\epsilon_\infty - 1/\epsilon_0)(m_e^*/2\hbar\omega_{LO})^{1/2}$ is the polaron coupling constant, ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants, and $\hbar\omega_{LO}$ is the LO phonon energy of the ZnTe lattice. The constant α is ~0.3 for electrons in ZnTe, and thus we obtain a bare mass $(m_e^*)_0$ of only $\sim 0.11 m_0$, much lower than the theoretical estimates given in Refs. 21 and 22, $(m_e^*)_0/m_0 \sim 0.17$–0.18.

Since Eq. (6) represents a simple mass renormalization, Eq. (4) predicts a linear splitting of the Landau levels as a function of magnetic field. However, taking into account the electron-phonon interaction to next higher order than deriving Eq. (6), there is a correction to the Landau-level energy E_N depending on N. For the difference $E_1 - E_0 = \hbar\omega_c + \Delta E_{1,0}$ the correction $\Delta E_{1,0}$ is given by[23]

$$\Delta E_{1,0} = -\tfrac{3}{20}\alpha(\hbar\omega_c)^2/\hbar\omega_{LO} . \tag{7}$$

The apparent mass enhancement due to Eq. (7) amounts to 1% only at 6 T, the maximum field shown in Fig. 4, and has been neglected.

The discrepancy between $(m_e^*)_0 \sim 0.11 m_0$ and the larger $\vec{k}\cdot\vec{p}$ results is what one might have expected after similar discrepancies have been found for the electron g factor g_e, namely, $g_e(\text{exp}) = -0.38$ (Ref. 3) in contrast to $g_e(\text{theor}) = +0.44$ (Ref. 22). In a five-band model g_e and $(m_e^*)_0$ are given by[24]

$$\frac{m_0}{(m_e^*)_0} - 1 = \frac{P^2}{3}\left(\frac{2}{E_g} + \frac{1}{E_g+\Delta_0}\right) - \frac{P'^2}{3}\left(\frac{2}{E(\Gamma_8^c)-E_g} + \frac{1}{E(\Gamma_7^c)-E_g}\right) + C , \tag{8}$$

$$\frac{g_e}{g_0} - 1 = \frac{-P^2}{3}\left(\frac{1}{E_g} - \frac{1}{E_g+\Delta_0}\right) - \frac{P'^2}{3}\left(\frac{-1}{E(\Gamma_8^c)-E_g} + \frac{1}{E(\Gamma_7^c)-E_g}\right) + C' , \tag{9}$$

where P^2 and P'^2 are the matrix elements representing the interaction of the conduction band with the valence band and the next higher conduction band, respectively, while the coupling of the conduction band to all other bands is lumped into C and C'. $E(\Gamma_7^c)$ and $E(\Gamma_8^c)$ are the energies of the second lowest conduction bands and Δ_0 is the spin-orbit splitting. $(m_e^*)_0$ and g_e both depend mainly on the same two matrix elements P^2 and P'^2, and thus P^2 and P'^2 can be deduced from the experimentally determined values of $(m_e^*)_0$ and g_e. Assuming $C = -2$ and $C' = -0.02$ according to Ref. 24 and taking the other energies as given in Ref. 24 we derive $P^2 = 32.3$ eV and $P'^2 = 7$ eV, close to the values given for GaAs.[24] P^2 is essentially insensitive to the value taken for C, but P'^2 increases as C becomes closer to zero and $P'^2 = 12$ eV for $C = 0$.

Our value of the electron effective mass [Eq. (4)] is in perfect agreement with the considerably less accurate value $m_e^* = 0.12 m_0$ derived from the electron to hole mobility ratio determined by Hall measurements on heavily doped n-ZnTe : Al.[2] It is also consistent with a shallow donor ionization energy $E_D = 18.3$ meV derived from donor acceptor pair excitation spectra,[10] which correspond to $m_e^* \sim 0.13 m_0$ for a dielectric constant $\epsilon \sim 10$. El Akkad[25] established a somewhat larger upper limit of $E_D \sim 22$ meV for ZnTe from the analysis of donor and acceptor FB transitions in p-type material appreciably more heavily doped than used in the present work, while Baker *et al.*,[26] estimated $E_D \sim 30$ meV from an analysis of DAP spectra, which would suggest $m_e^* \sim 0.22 m_0$. Particularly *low* values have been obtained from some experimental analyses of free-exciton reflectivity. For example, the reduced electron-hole mass ratio of only $0.07 m_0$ reported by Kase[27] is more than 10% less than the value obtained by Venghaus *et al.*[1] and corresponds to a polaron electron mass of only $\sim 0.10 m_0$, too small according to the present work. The approximate estimate obtained by Nahory and Fan[28] from the periodicity of intrinsic oscillatory photoconductivity is $\sim 0.10 m_0$, if the value of the heavy hole mass obtained later by Stradling[5] is used, once again much too small. By contrast a *large* experimental value of $m_e^* \sim 0.22 m_0$ has also been reported from the diamagnetic shift rate of the weakly bound excitons in ZnTe,[29] assuming the shifts to be dominated by the electron and using a hydrogenic model. Our own measurements[3] give a lower diamagnetic shift rate than the hydrogenic model with $m_e^* = 0.12 m_0$. However, the reduction is only about 20% and does not correspond to an electron mass as large as 0.22. We believe the hydrogenic donor model is not quantitatively accurate for these bound exciton transitions since m_e^* is not negligible compared with m_h^* in ZnTe. Large quenching effects can be observed in the

diamagnetic shift rate when $m_e^* \sim m_h^*$,[30] and some reduction can be detected even when m_e^*/m_h^* is about half the value in ZnTe, for example in GaAs.[31]

C. Line shape of free-to-bound luminescence components

The pronounced change in line shape and width of the FB transition is very clearly seen in Fig. 5. These FB components were measured at ~5 K in a crystal for which this luminescence was particularly significant at this temperature. At zero or very low magnetic fields the shape function $I(E)$ is given by[32]

$$I(E) = (\text{const})N(E)\exp(-E/kT)\,, \tag{10}$$

where $N(E)$ is the conduction-band density of states, $dN(E)/dE$ being proportional to $(m_e^*)^{3/2}E^{1/2}$, T is the effective electron temperature, and k is Boltzmann's constant. The fit of this expression to the experimental data in Fig. 5(a) gives $T_{\text{eff}} \sim 14$ K, substantially in excess of the lattice temperature as discussed in Sec. I. The deviation between experiment and theory most noticeable on the much steeper low-energy side of the FB band is probably caused by collisional induced broadening, a lifetime effect for the free electrons. Assuming Gaussian broadening, we estimate a broadening parameter Γ of about 0.31 meV from the fit of the zero-field spectrum in Fig. 5(a).

The density of states function $dN(E)/dE$ is strongly modified in a magnetic field[18]

$$\frac{dN(E)}{dE} = \frac{\omega_c}{(2\pi\hbar)^2}(m_e^*)^{3/2}\sum_{N=0}^{\infty}\left(\frac{E-(N+\frac{1}{2})\hbar\omega_c+\{[E-(N+\frac{1}{2})\hbar\omega_c]^2+\Gamma^2\}^{1/2}}{[E-(N+\frac{1}{2})\hbar\omega_c]^2+\Gamma^2}\right)^{1/2} \tag{11}$$

neglecting spin-splitting effects. As before, the energy-dependent expression Eq. (11) must be multiplied by the Maxwell-Boltzmann factor $\exp(-E/kT)$ to obtain the overall FB line shape $I(E)$. We now obtain a series of narrow lines with thresholds at the Landau energies E_N ($N = 0, 1, 2, \ldots$) whose widths are now totally determined by Γ but whose relative intensities are determined by the Maxwell-Boltzmann envelope function. The fit in Fig. 5(a) of the 8-T spectrum, where $\hbar\omega_c \gg \Gamma$, shows clearly that the experimental data are now very badly described by the simple Maxwell-Boltzmann function, just as expected from Eq. (11). The halfwidth of the low-energy side of the now very narrow experimental spectrum, dominated by collisional lifetime broadening, gives $\Gamma = 0.32$ meV, close to the value derived from the zero-field spectrum.

D. Spin splittings of $N=0$ Landau level in acceptor free-to-bound luminescence

Rühle and Göbel[11] and earlier Bimberg and Rühle[13] noted that the shift rate of the experimentally observed $N = 0$ FB luminescence peak must be less than that of the $N = 0$ Landau level, $\frac{1}{2}\hbar\omega_c$ [Eq. (4)] because of the spin (Zeeman) splittings of the free electron and bound hole indicated in Fig. 5(b). As in GaAs, the reduction for ZnTe is dominated by the hole, where thermalization will ensure that the effective g value g_{eff} is that of the $m_J = -\frac{3}{2}$ state, close to 0.9.[3] This shift rate is further slightly reduced by the spin splitting of the free electron (Fig. 5). However, this effect will be small because of the small relevent g value $\frac{1}{2}g_e = -0.19$,[3] and because electron thermalization will be much less complete.

A small tendency for the Landau levels 0 and 2 to be relatively strong compared with 1 and 3, allowing for the effect of thermalization which is a monotonic function of N, can be seen from Fig. 2. Rühle and Göbel[11] point out that this is a consequence of the selection rule $\Delta N = 0, 2$ for electron-hole recombinations between Landau levels.

This discussion of the effect of Zeeman splitting on the shift rate of the $N = 0$ Landau level requires closer examination because we have used a hole g value reported by Dean *et al.*[3] from BE measurements on the deep a acceptor for both the a- and b-acceptor FB magnetoluminescence. Experience with acceptors in GaP[33] suggests that the isotropic component of the hole g value will be *relatively* insensitive to the state of binding, perhaps decreasing slightly with increasing localization. Direct confirmation of this insensitivity is obtained from the magnitude of the Zeeman splittings clearly apparent *within* the $N = 0$ Landau level at the highest field shown in Fig. 2. Three magnetic subcomponents clearly appear for polarization $E \perp B$ within the narrowed line shape whose quantitative

form was discussed in Sec. III C. Rühle and Göbel[11] also reported spin splittings, rather less well resolved than in Fig. 2, while Bimberg very recently observed the completely resolved six-component Zeeman spectrum in GaAs.[12] We have observed qualitatively the same splitting pattern for the FB and BE luminescence at 3.2 T, where our experimental geometry with an iron magnet permits examination in the Voigt configuration. We find two components for $E \| B$ with about half the overall splitting of the three shown for $E \perp B$, consistent with the inset in Fig. 5. The degree of thermalization in the $E \perp B$ FB luminescence at 4.2 K is appreciably greater than in the BE luminescence even at 1.5 K. This is consistent with expectation since the large hole g value which dominates the thermalization process occurs in the *initial* state of the FB transition (Fig. 5) but in the *final* state of the BE transition.

The breadth of the FB magnetic subcomponents does not permit very precise estimates of the g values. However, we find the splittings to be isotropic, as near as can be determined, with the hole g value $K = 0.7 \pm 0.15$ and $g_e = -0.15 \pm 0.15$. These approximate values are consistent with those obtained from the a-acceptor BE.[3] The electron g value is more accurately determined as -0.38 ± 0.05 from the BE data. The large extent of the disagreement from the lowest order $\vec{k} \cdot \vec{p}$ theoretical value of +0.47 has been discussed previously.[3] However, we note from the inset in Fig. 2 that the overall splitting for $E \perp B$, equal to $3K - g_e$ [Fig. 5(b)] is slightly but distinctly larger (about 15%) for the b-acceptor FB than for the a-acceptor BE luminescence. We interpret this to mean that K is slightly smaller for hole binding to the 148-meV compared with the 61-meV acceptor, in agreement with the general trend expected from the theory for increasing localization energy.[30] Zeeman splitting of the FB transition associated with the 148-meV acceptor can also be seen at 4.14 T in Fig. 3. Unfortunately, the structure is not sufficiently clear at this field to establish whether the hole g value is slightly less than in the FB component of the 61-meV acceptor, while the $N = 0$ FB component of the 148-meV acceptor is already starting to merge with the strong A_2^a satellite at 5.52 T.

E. Magnetic effects on bound exciton two-hole satellites of the a acceptor

Zeeman splittings of the two-hole bound-exciton satellites for the a acceptor can also be seen in Fig. 3. These splittings are clearest for the strongest components A_2^a and A_3^a, though unfortunately the magnetic substructure is still not very striking in the densitometer trace at the highest field available, 5.5 T. The problem is that component A_2^a has an excessive linewidth at zero field, apparently because the energy interval $A_1^a - A_2^a$ is 125.6 meV, close to the 4th overtone of the LO vibrational energy of the ZnTe lattice. The halfheight width of A_2^a is close to 0.5 meV (Figs. 1 and 3), ~2.2 times greater than that of A_3^a, and several of the transitions to higher acceptor excited states. We presume this excess broadening is caused by a limitation of the lifetime of the 2s excited state produced by strong electron-phonon coupling, an effect extensively examined for photoexcitations of the donor Bi and acceptor Ga in Si which obey a similar relationship with the lattice vibrational energy.[34] This effect occurs for the fundamental of the lattice energy in Si, but may still be significant at a high-order overtone for the polar ZnTe lattice, where electron-phonon coupling is much stronger than in the covalent Si lattice. This is particularly true for the relatively deep a acceptor, where a FB or BE transition which removes the hole from the ground state exhibits Poisson coupling[35] with a mean number of emitted LO phonons of ~1.4 compared with ~0.23 for the b acceptor. The broadening for the two-hole transition to the $n = 2$ acceptor state is also very significant for the shallow g acceptor, identified with Ag_{Zn}, where the near resonance occurs with the third overtone of the LO energy. Exact resonance can occur for both acceptors since the phonons can be selected at some finite wave vector, where the LO energy is appropriately reduced from the zone center, zero-wave-vector value of 26.1 meV.[10,36] However, one can see from the right-hand side of Fig. 3 that the overall broadening of A_2^a and $A_1^a - 2\,\mathrm{LO}$ are very similar and a qualitatively similar splitting pattern can be discerned in the original photographic data. The Zeeman splitting pattern of A_3^a can also be seen to be qualitatively very similar to A_1^a. However, the effect is somewhat obscured and the intensity distribution is distorted by a dramatic weakening of the discrete two-hole satellites in favor of a broad component underlying A_3^a and A_4^a which is also present at zero field. This broad component is also more prominent in crystals with relatively strong donor BE luminescence and is due to distant DAP transitions. The broad component labeled $A_2^a - \mathrm{TA}$ in Fig. 3 some 6.5 meV below A_2^a is probably a transverse acoustic phonon replica of this strong no-phonon component.[36]

The most dramatic magnetic field effect for the two-hole satellites A_4^a-A_6^a, associated with the higher acceptor excited states is an apparent splitting indicated by the dashed lines in Fig. 3, much larger than the spin splittings just described. Such an effect is unexpected, since the holes in these

s-like states should not exhibit any orbital magnetic moment. However, closer examination of the magnetic data and the zero-field spectrum (Fig. 3) shows that no splitting of the strong zero-field two-hole satellites occurs. Instead, the weak additional satellites visible on the high-transition-energy tails of each strong component for $n < 5$ in the high quality zero-field spectrum of Fig. 1 become stronger and are repelled away from the initially dominant components as the magnetic field is increased. The s-p splitting is clearly revealed in a strong magnetic field, also for those states like $n = 6$ where the zero-field splitting is too small to be detected even in the original photographic data. These weak components have been associated with transitions to the $np_{3/2}$ hole excited states,[9] using the nomenclature of Baldereschi and Lipari[37] in which the dominant two-hole satellites involve $ns_{3/2}$ hole states. No such dramatic effects can be noticed in the magnetic behavior of two-hole satellites of much shallower acceptors such as Li_{Zn}, where the zero-field intensities of transitions to p states are very much weaker (Fig. 2). This suggests that the s-p mixing apparent for two-hole satellites A_4^q-A_6^q in Fig. 3 is an effect of the central cell of the acceptor impurity which becomes greatly enhanced as the wave functions of the excited hole states become compressed and distorted in the strong magnetic field. Breakdown of the parity selection rule is usually attributed to interimpurity interactions, expressed in terms of a background electric field from the quasiuniform distribution of ionized donors and acceptors.[38] For a purely electric field effect, the s states become mixed mainly with the p_0 magnetic substates. The rapid increase in strength of transitions to the p_0 substates compared with the s states with increasing magnetic field is a characteristic feature of the Stark electric field coupling model.[38] However, the greater prominence of the parity-forbidden transitions for impurities with large ionization energies[34] suggests that relatively long-range contributions to the central cell binding potential due to misfit strain may play a key role. Related effects have been noticed for donor states in GaAs.[39]

F. Magnetic effects on the donor free-to-bound absorption

The relationship of the localization energies at typical donors and acceptors, the donor ionization energy, and the free-exciton energy in ZnTe is such that the donor FB (or BE) luminescence in ZnTe occurs at *lower* energy than the luminescence of excitons at neutral donors or possibly even neutral acceptors. Using the nomenclature introduced for CdS,[40] the I_3 line lies below I_2 and is in the vicinity of I_1. The A_1^q (I_1) generally marks the onset of strong near gap absorption in p-type ZnTe. We notice just below the A_1^q resonance line a weak absorption continuum (Fig. 6) whose threshold energy, correcting for broadening, lies about 22 meV below E_g according to the most reliable recent estimates for ZnTe.[1] This is about 3.5 meV larger than the accurate estimate of E_D for the dominant donor as determined from the two-electron transitions observed in photoluminescence under resonant excitation at the donor principal BE line D_1 (I_2), and from excitation spectra for DAP luminescence.[8,10] This energy shift might suggest that there is an appreciable binding energy for the hole at a neutral donor as in CdS.[40] However, the featureless form of the absorption edge at $B = 0$ is not consistent with this idea and suggests that there is no BE state at an ionized donor in ZnTe, like GaAs.[41] If there is no bound state, the absorption represents the inverse of the donor FB luminescence. We have also seen a luminescence band near 2.372 eV under appropriate conditions of selective excitation by a tuneable

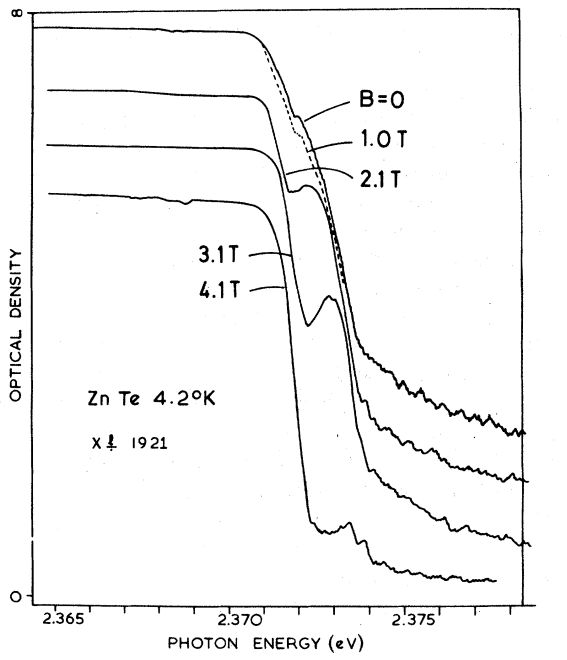

FIG. 6. A small portion of the near-gap optical absorption spectrum for a refined p-ZnTe crystal of ~0.5 mm thickness. No significant transmission occurs above ~2.374 eV because of strong absorption caused by acceptor PBE transitions A_1^f and particularly A_1^q (Fig. 1). The absorption notch appearing near 2.372 eV at low fields and shifting to higher energies approximately quadratically with magnetic field is attributed to a BE state at ionized donors becoming stabilized by the magnetic field.

dye laser at $B = 0$ and notice that this band is much broader than A_1^q or D_1, as expected for FB luminescence even at 2 K. Both this luminescence and the absorption continuum is stronger in crystals containing higher donor concentrations as judged from the relative strength of the D_1 and DAP luminescence compared with the dominant, purely acceptor related BE luminescence. No special two-electron or two-hole satellites appear under resonant laser excitation near 2.372 eV, consistent with the view that only two electronic particles are involved in the relevant transitions.

The donor-related absorption edge near 2.372 eV becomes rapidly sharper and develops a well-defined absorption notch in a magnetic field of a few Tesla (Fig. 6). This notch is still rather broad compared with the BE lines, however. We tentatively suggest that it may mark the onset of a field-induced BE state at the ionized donor. The magnetic shift rate of this broad absorption notch is hard to measure accurately because of a large change in shape. However, it appears to be predominantly quadratic with a shift rate of about 7×10^{-2} meV/T^2, roughly 8 times larger than the BE diamagnetic shift rate[3] and about 6 times the value for an effective mass donor in ZnTe with $m_e^* = 0.12m_0$. We presume that this large diamagnetic shift rate is evidence for the very diffuse nature of this field-induced BE state.

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[1]H. Venghaus, P. E. Simmonds, J. Lagois, P. J. Dean, and D. Bimberg, Solid State Commun. 24, 5 (1977). There is more recent evidence that the precise value of E_g may be slightly larger than 2.392 eV as reported in this paper. Current estimates from dye-laser excitation spectroscopy suggest that the free-exciton binding energy E_x may be close to 13 meV, which implies $E_g = 2.394$ eV since the exciton gap is close to 2.381 eV. H. Rodot, P. Lederc, and N. Hammond, J. Electron. Mater. 1, 2 (1972) report $E_g = 2.395$ eV derived from free-exciton luminescence using $E_x = 10$ meV.

[2]F. T. J. Smith, Solid State Commun. 9, 957 (1971).

[3]P. J. Dean, H. Venghaus, J. C. Pfister, B. Schaub, and J. Marine, J. Lumin. 16, 363 (1978).

[4]T. L. Larsen and D. A. Stevenson, J. Appl. Phys. 44, 843 (1973); D. B. Chesnokova, B. F. Ormont, S. L. Miloslavov, and T. V. Saunina, Fiz. Tekh. Poluprovodn. 10, 2204 (1976) [Sov. Phys. Semicond. 10, 1311 (1976)].

[5]R. A. Stradling, Solid State Commun. 6, 665 (1968).

[6]J. F. Scott, R. L. Hollis, S. Nakashima, H. Kojima, and T. Hattori, Solid State Commun. 20, 1121 (1976); R. L. Hollis, Phys. Rev. B 15, 932 (1977); R. L. Hollis and J. F. Scott, Phys. Rev. B 15, 942 (1977).

[7]T. Hattori, S. Nakashima, and A. Mitsuishi, in *Proceedings of the 13th International Conference on the Physics of Semiconductors, Rome, Italy*, 1976, edited by F. G. Fumi (North-Holland, Amsterdam, 1976), p. 635.

[8]S. Nakashima, T. Hattori, and Y. Yamaguchi, Solid State Commun. 25, 137 (1978).

[9]D. C. Herbert, P. J. Dean, H. Venghaus, and J. C. Pfister, J. Phys. C 11, 3641 (1978).

[10]H. Venghaus, P. J. Dean, P. E. Simmonds, and J. C. Pfister, Z. Phys. B 30, 125 (1978).

[11]W. Rühle and E. Göbel, Phys. Status Solidi B 78, 311 (1976).

[12]D. Bimberg, Phys. Rev. B 18, 1794 (1978).

[13]D. Bimberg and W. Rühle, in *Proceedings of the 12th International Conference on the Physics of Semiconductors, Stuttgart, Germany*, 1974, edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 561. The narrowing of the FB band was first observed in GaAs by J. A. Rossi, C. M. Wolfe, and J. O. Dimmock, Phys. Rev. Lett. 25, 1614 (1970).

[14]R. Ulbrich, Phys. Rev. B 8, 5719 (1973).

[15]B. Katircioglu, J. L. Pautrat, D. Bensahel, and N. Magnea, Radiat. Eff. 37, 183 (1978).

[16]D. I. Kennedy and M. J. Russ, J. Phys. Chem. Solids 32, 847 (1971).

[17]Determined from dye-laser excitation spectra, taking the value for the upper polariton branch, H. Venghaus (unpublished).

[18]L. M. Roth and P. N. Argyres, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 1, p. 159.

[19]E. J. Johnson, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3, p. 153.

[20]H. Fröhlich, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1963), p. 1.

[21]M. Cardona, J. Phys. Chem. Solids 24, 1543 (1963); 26, 1351 (1965).

[22]P. Lawaetz, Phys. Rev. B 4, 3460 (1972).

[23]D. M. Larsen, Phys. Rev. 135, A419 (1964).

[24]C. Hermann and C. Weisbuch, Phys. Rev. B 15, 823 (1977).

[25]F. El Akkad, Phys. Status Solidi B 76, 85 (1976).

[26]A. T. J. Baker, F. J. Bryant, and W. E. Hagston, J. Phys. C 6, 1299 (1973).

[27]K. Kase, Jpn. J. Appl. Phys. 12, 1098 (1973).

[28]R. E. Nahory and H. Y. Fan, Phys. Rev. Lett. 17, 251 (1966).

[29]Quoted by J. F. Scott and R. L. Hollis, Solid State Commun. 20, 1125 (1976).

[30]P. J. Dean, D. Bimberg, and F. Mansfield, Phys. Rev. B 15, 3906 (1977); D. Bimberg and P. J. Dean, Phys. Rev. B 15, 3917 (1977).

[31]A. M. White, I. Hinchliffe, P. J. Dean, and P. D. Greene, Solid State Commun. 10, 497 (1972).

[32]D. M. Eagles, J. Phys. Chem. Solids 16, 76 (1960).

[33]P. J. Dean, R. A. Faulkner, S. Kimura, and M. Ilegems, Phys. Rev. B 4, 1926 (1971).
[34]See, for example, N. R. Butler, P. Fisher, and A. K. Ramdas, Phys. Rev. B 12, 3200 (1975).
[35]J. J. Hopfield, J. Phys. Chem. Solids 10, 110 (1959).
[36]J. C. Irwin and J. LaCombe, J. Appl. Phys. 41, 1444 (1970).
[37]A. Baldereschi and N. O. Lipari, Phys. Rev. B 8, 2697 (1973).
[38]D. M. Larsen, Phys. Rev. B 8, 535 (1973).
[39]Enhanced interaction with donor central cell potentials has been reported by R. F. Kirkman and R. A. Stradling, described in *Electroluminescence, Topics in Applied Physics*, edited by J. I. Pankove (Springer-Verlag, Berlin, 1976), p. 72.
[40]D. G. Thomas and J. J. Hopfield, Phys. Rev. 128, 2135 (1962).
[41]R. Ulbrich and B. Moreth, Solid State Commun. 14, 331 (1974).