

## Anomalies observed in the shallow acceptor states in GaAs

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Bound-exciton transitions have been observed from the shallow acceptors zinc and carbon in good-quality epitaxial layers of GaAs. The exciton transitions of interest are those that leave the acceptor in an excited terminal state. Three excited states were observed for carbon and six excited states for zinc. The energy positions of the higher excited states in zinc are compared with the theoretical predictions from the hydrogenic model. The carbon and germanium shallow acceptors reflect central-cell effects in the energies of their  $2P$  states. These results are contrary to the theoretical predictions that the energy levels of the  $P$  states should be independent of impurity type.

### INTRODUCTION

The shallow acceptors in GaAs have been investigated both experimentally<sup>1-4</sup> and theoretically<sup>5,6</sup> for many years. In dealing with shallow impurities in materials having single nondegenerate bands, the effective-mass theory has been used to effectively describe these impurities. The solutions to these shallow impurity problems are similar to those for the hydrogen atom and thus the nomenclature hydrogenic model for treating these impurity states. In materials that crystallize in the zinc-blende structure, such as GaAs, the valence band is degenerate at the  $\Gamma$  point, complicating the effective-mass theory for treating the acceptors in these materials. It might be expected that the higher excited states of the acceptors could be explained by the hydrogenic model. However, examination of data available for some of the higher excited states does not bear this out. Due to complications involved in the theory, it appears that understanding the acceptors in GaAs can best be approached experimentally at this time. There are a number of observations that are somewhat perplexing in that they do not conform to what one would expect from theoretical predictions. For example, one would not expect to observe central-cell effects in the excited  $P$ -state transitions of the shallow acceptors; however, it was shown by Kisker *et al.*<sup>4</sup> that the  $P$  states of the Ge acceptor are appreciably displaced in energy from the  $P$  states of C, Zn, and Si. We also show that the  $P$  states of C are displaced in energy from the  $P$  states of Mg, Zn, and Si. Here the magnitude of the displacement is less but it is still greater than can be accounted for by experimental error. It would also be expected that the central-cell effects observed in the higher excited  $S$  states would become negligibly small as the higher quantum number states are reached. The central-cell effect should fall off as  $(1/n)^3$  where  $n$  is the principal quantum number. For  $n=3$  and  $n=4$   $S$  states the central cell should not be detectable; however, we show that this is not the case.

The above observations are, for the most part, unexplained. The additional experimental data may prove helpful in understanding the overall shallow acceptor problem in GaAs.

### EXPERIMENTAL DETAILS

The crystals used in this study were undoped, high-purity, epitaxial layers of GaAs grown on semi-insulating GaAs:Cr substrates by the  $H_2:As_2Cl_3:Ga$  vapor-deposition technique. Transport measurements were used to characterize the electrical parameters of these samples. The samples were  $P$  type. The hole mobilities were  $\sim 400$   $cm^2/V$  sec with concentrations  $P \sim 10^{14}/cm^3$  at 300 K. The experimental apparatus employed in this investigation permitted high-resolution photoluminescence measurements to be performed at 2 K and in magnetic fields up to 40 kG. In the intrinsic region of GaAs a dispersion of 0.54  $\text{\AA}/mm$  was achieved using a 4-m spectrometer.

### EXPERIMENTAL RESULTS AND DISCUSSIONS

In this experiment the acceptors and their higher excited states were identified by high-resolution photoluminescence spectroscopy. The optical transitions that were used to identify the acceptors result from the collapse of neutral-acceptor bound excitons. This was one of the techniques used by Ashen *et al.*<sup>1</sup> to tabulate the energy levels of acceptors in GaAs. In the current experiment the data we obtain are for higher excited states. When an exciton bound to a neutral-acceptor state ( $A^0X$ ) decays, the terminal state will consist of the neutral acceptor in the ground state or an excited state. It can be shown from symmetry considerations that the  $2S$  state and higher excited  $S$  states are the allowed terminal states. These transitions are parity forbidden in the direct optical excitation of the hole bound to an acceptor. The excited  $S$ -state energies are the internal transition energies of the acceptor. Using these energies one would like to be able to theoretically predict the binding energy of the acceptor. The photoluminescence spectra from which six excited states of the Zn acceptor can be observed are shown in Fig. 1. In this paper emphasis will be placed on the excited states of Zn, since several more are observed and they allow comparison with predictions from the hydrogenic model. If the selection rules are obeyed, then all of these states are  $S$  states. The energies of these states for the Zn acceptor are

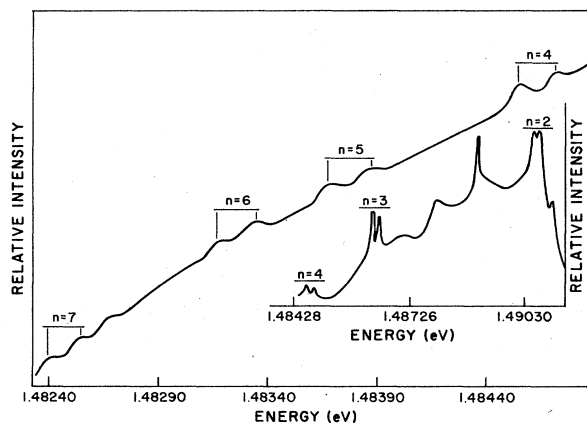


FIG. 1. Relative intensity as a function of energy showing six excited states of the Zn acceptor.

listed in Table I; also listed are the energies that would be expected from the hydrogenic model. It is seen that even the highest excited-state energies are not adequately predicted by the hydrogenic model (hydrogenic series obtained from the known binding energy). Taking the  $1S_{3/2}$  ground-state energies for the shallow acceptors in GaAs from Ashen *et al.*,<sup>1</sup> a composite plot of the available

TABLE I. Experimental energies of six excited states of the Zn acceptor in GaAs. Also included are the experimental energy differences and the energy differences predicted from the hydrogenic model.

Quantum state	Energy	$\Delta E$ (meV) Experimental	$\Delta E$ (meV) Hydrogenic model
$N=1$			
$J = \frac{3}{2}$	1.51241	21.7	23.03
$J = \frac{5}{2}$	1.51225		
$N=2$			
$J = \frac{3}{2}$	1.49067	26.0	27.2
$J = \frac{5}{2}$	1.49049		
$N=3$			
$J = \frac{3}{2}$	1.48638	27.7	28.8
$J = \frac{5}{2}$	1.48621		
$N=4$			
$J = \frac{3}{2}$	1.48468	28.6	29.5
$J = \frac{5}{2}$	1.48450		
$N=5$			
$J = \frac{3}{2}$	1.48384	29.1	29.8
$J = \frac{5}{2}$	1.48366		
$N=6$			
$J = \frac{3}{2}$	1.48332	29.87	30.1
$J = \frac{5}{2}$	1.48313		
$N=7$			
$J = \frac{3}{2}$	1.48255		
$J = \frac{5}{2}$	1.48240		

excited-state binding energies of these acceptors can be constructed as shown in Fig. 2. The plot consists of data from the literature as well as new excited-state data for C and Zn from the current experiment. In this figure the ground-state binding energies are plotted as the abscissa, with the appropriate placing of the various acceptors. The excited-state binding energies of the acceptors are plotted as the ordinate. The displaced  $2P$ -state energies of Ge taken from Kisker *et al.*<sup>4</sup> are immediately obvious. Central-cell effects would not be expected to be reflected in the  $P$ -state transitions. Less obvious, however still real, are the displaced  $2P$ -state energies associated with the C acceptor. Carbon also reflects the central-cell effect in the  $2P$  excited states.

The  $2S$  states for all of the acceptors clearly reflect the central-cell effects. A linear change in central-cell energy with acceptor binding energy is observed for all of the acceptors except Si and Cd. It is not clear what causes their departure. The  $3S$  states should reflect less of the central cell than the  $2S$  states; therefore, the transition from the  $1S$  state to the  $3S$  state should contain more of the central cell than the  $1S$  state to the  $2S$  state. The slope of the linear relationship for the  $3S$  states should be somewhat greater than it is for the  $2S$  states; in fact, the slope is somewhat less than it is for the  $2S$  states. The slope of the linear relationship for the  $4S$  states is not measurably different than that of the  $3S$  states. These measurements do not reflect the expected falloff in central-cell correction with increasing excited-state quantum number. If one analyzes Fig. 2, it becomes apparent that if the  $2P$  states of Ge did not reflect the central cell, the  $2P_{3/2}$  state would fall lower in energy than the  $2S_{3/2}$  state, and the  $2P_{5/2}(\Gamma_7)$  state would fall lower in energy than the  $3S_{3/2}$  state. This would result in a different ordering of states

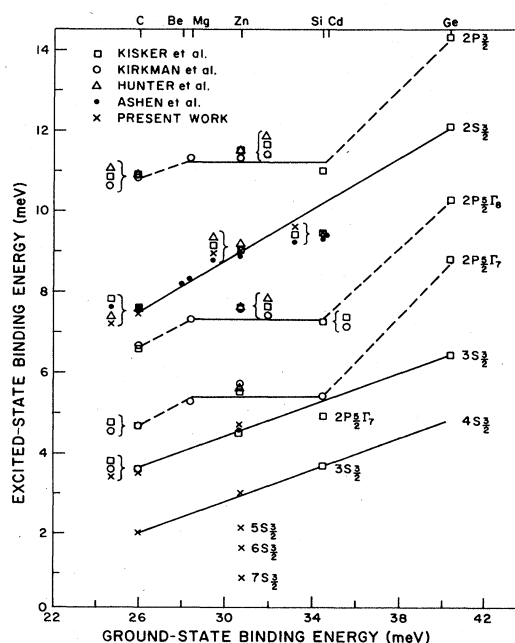


FIG. 2. Excited-state binding energy as a function of the ground-state binding energy for six different acceptors in GaAs. ●, Ref. 1; ○, Ref. 2; △, Ref. 3; □, Ref. 4; ×, Present work.

than is theoretically predicted by Baldereschi and Lipari (BL).<sup>5</sup> In their theory<sup>5</sup> BL use an effective-mass Hamiltonian, with the Coulomb potential screened by the static dielectric constant, and calculate the binding energies of the ground state and of several low-lying excited states of acceptors in a number of semiconductors. No central-cell effects are included in their theory. Using the then-known values of the physical parameters, they calculate the binding energies of the  $1S_{3/2}$ ,  $2S_{3/2}$ ,  $2P_{3/2}(\Gamma_8)$ ,  $2P_{5/2}(\Gamma_8)$ , and  $2P_{5/2}(\Gamma_7)$  states in GaAs and find these to be 25.67, 7.63, 11.38, 7.20, and 5.33 meV, respectively. The binding energy of the ground state of carbon is very close to that calculated by BL (Ref. 5) and thus should have the least amount of central-cell correction. All the other acceptors should have positive values for this correction. In their calculation they treat the spherical part of the Hamiltonian variationally and calculate the contribution of the cubic terms using perturbation theory. In addition, they ignore the effect of the split-off valence band, as it is energetically separated from the topmost valence band by an amount much larger than the binding energy of an acceptor. They then solve for the  $4 \times 4$  Hamiltonian matrix. In a subsequent paper BL (Ref. 7) use a position-dependent dielectric function and include the effect of the split-off valence band. They solve for the  $6 \times 6$  Hamiltonian matrix variationally and calculate the binding energies of odd parity states in Ge and Si. Bernholc and Pantelides<sup>6</sup> (BP) have also calculated the binding energies of the ground states of shallow acceptors in a large number of semiconductors using a variational approach. As in Ref. 7 they include the effect of the split-off valence band and solve for the  $6 \times 6$  Hamiltonian matrix. They consider the cases in which the Coulomb potential is screened by a constant static dielectric constant and by the position-dependent dielectric function. Using the same physical parameters as those used by BL (Ref. 5), they calculate the binding energy of the ground state of an acceptor in GaAs. For the case of a constant dielectric constant the binding energy is 27.5 meV, whereas for the position-dependent dielectric function it is 32.6 meV. If one were to accept the latter value, then Zn has the smallest (slightly negative) central-cell correction with Si, Cd, and Ge having positive, and C, Be, and Mg having negative values for the central-cell correction, respectively. BP (Ref. 6) do not calculate the binding energies of the excited states. It is therefore not clear whether the use of the position-dependent dielectric function will significantly modify the excited-state energies or their ordering in GaAs. It has been suggested<sup>8</sup> that Ge, being isocoric, may have least central-cell correction, with all other shallow acceptors having negative corrections. The binding ener-

gy of the Ge acceptor (40.4 meV), however, is about 8 meV larger than that calculated by BP.<sup>6</sup> In addition, BP (Ref. 6) have also calculated the binding energies using the high-frequency dielectric constant and high-frequency position-dependent dielectric function and obtained values of 36.9 and 50.2 meV, respectively. As the shallow acceptor binding energies in GaAs are comparable to the longitudinal optical-phonon energy (36 meV), it is not clear as to what form of dielectric screening should be used. This discussion points out the problem, namely, we do not know the energy levels of an ideal acceptor (no central-cell correction), either from theoretical or from experimental studies.

As pointed out earlier, the ordering of the energy levels as calculated by BL (Ref. 5) using effective-mass theory, is obeyed by all known shallow acceptors in GaAs. For the Ge acceptor the ordering was maintained because the binding energy of the  $2P_{3/2}(\Gamma_8)$  level is considerably larger than its value for other acceptors. It is not at all clear why this happens, because the  $P$  states are not expected to show any dependence on the type of the impurity atom (no central-cell effects). In principle, it should be possible, for example, for the  $2S_{3/2}$  level to be more bound than the  $2P_{3/2}(\Gamma_8)$  level if the central-cell effects were large enough. It is apparently not the case in GaAs. In Si,<sup>7,9</sup> however, the binding energy of the  $2S_{3/2}$  level is larger than that of the  $2P_{3/2}(\Gamma_8)$  level for the In acceptor, which has a very large central-cell correction. Energy levels of acceptors in some other semiconductors such as Ge,<sup>5</sup> InSb,<sup>5</sup> InP,<sup>10</sup>  $Al_{0.47}Ga_{0.53}As$ ,<sup>11</sup> ZnSe,<sup>12</sup> and ZnTe (Ref. 13) all exhibit the same ordering as in GaAs.

## CONCLUSIONS

Several anomalies have been observed in the behavior of shallow acceptors in GaAs. Both the C and Ge acceptors reflect central-cell effects in the energies of their  $2P$  states. Theory predicts that the  $P$  states should be independent of impurity type. Six excited states are reported for the first time for the Zn acceptor. It might be expected that the higher excited states would conform to the hydrogenic model. This was not observed in the case of the Zn acceptor. The central-cell effects for higher quantum number  $S$  states should fall off as  $(1/n)^3$ . This behavior was not strictly observed for the shallow acceptors in GaAs.

A quantitative description of the excited-state acceptor energy levels in GaAs is not available at this time. It is clear that more theoretical work is required to bring about a better understanding of the shallow acceptor levels in GaAs.

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