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# Spectroscopy of Excited Acceptor States in GaP

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Luminescence excitation spectroscopy of donor-acceptor pair recombination in GaP is reported. We observe $s$ and $p$ excited states of C, Mg, and Zn acceptors, and deduce acceptor binding energies and Luttinger valence-band parameters ($\gamma_1 = 4.04$, $\gamma_2 = 0.53$, and $\gamma_3 = 1.26$). Directly obtained information on the interaction between donors and acceptors characterizes the acceptor state and confirms observation of the $1S_{1/2}$ level.

This Letter reports a novel method to observe donor and acceptor excited states, and its application to C, Mg, and Zn acceptors in GaP. We evaluate valence-band parameters and ionization energies independently of other measurements, and resolve many uncertainties in the basic parameters characterizing GaP. Detailed information about the donor-acceptor (D-A) interaction is obtained more directly than with any other method.

We measure photoluminescence excitation spectra of D-A pair transition. The ground state of a D-A pair with separation $R$ decays with luminescence energy[1]

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

where $E_D$ and $E_A$ are the donor and acceptor binding energies, $E_g$ is the band gap, and $J$ is the interaction energy of a neutral-donor–neutral-acceptor pair. Luminescence from D-A pairs of a selected $R$ is observed by choosing an appropriate $\hbar\omega_L$, and the emission intensity is recorded as a function of excitation energy $\hbar\omega_x$. A dye laser with linewidth 0.3 meV is used as excitation source.
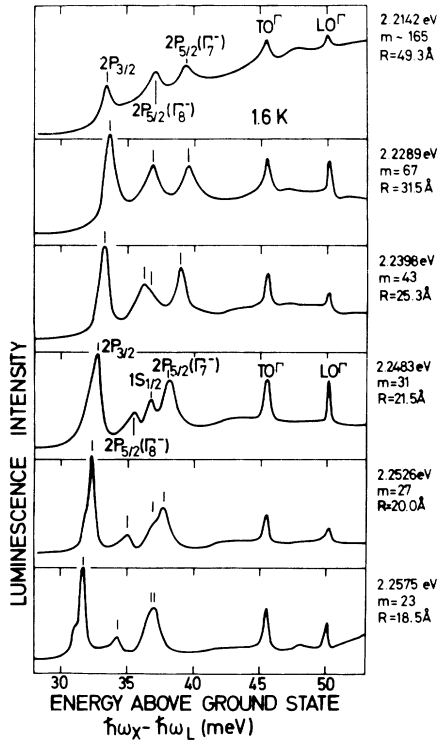
A peak in the excitation spectrum corresponds

FIG. 1. GaP luminescence excitation spectra of C–S donor-acceptor recombination at the indicated luminescence energies (right-hand side). Pair separation $R$, and shell number $m$ (for definition, see Ref. 1), and identification of acceptor states are shown.



FIG. 2. $R$ dependence of carbon acceptor levels from GaP luminescence excitation spectra as in Fig. 1.

to absorption electively exciting the observed D-A pair. For a transition between an excited acceptor level and the donor ground state, a peak occurs when

$$\hbar\omega_x = \hbar\omega^*(R)$$
$$= E_g - (E_D + E_A{}^*) + e^2/\epsilon R + J^*(R), \qquad (2)$$

where the starred terms refer to excited acceptor states. From Eqs. (1) and (2),

$$\hbar\omega^*(R) - \hbar\omega_L(R) = (E_A - E_A{}^*) + J^*(R) - J(R). \qquad (3)$$

Therefore, the acceptor levels are obtained directly from the excitation spectrum, provided $R$ is chosen large enough so that both $J$ and $J^*$ are negligible. No knowledge of $E_g$, $E_D$, or the Coulomb term is required.

Advantages of this method are that the measurements (at least for GaP) are in the visible part of the spectrum where the most sensitive spectroscopic techniques can be used. The selection rules allow both $s$ and $p$ acceptor states to be observed, in contrast to electronic Raman scattering or infrared absorption. Donor levels may al-
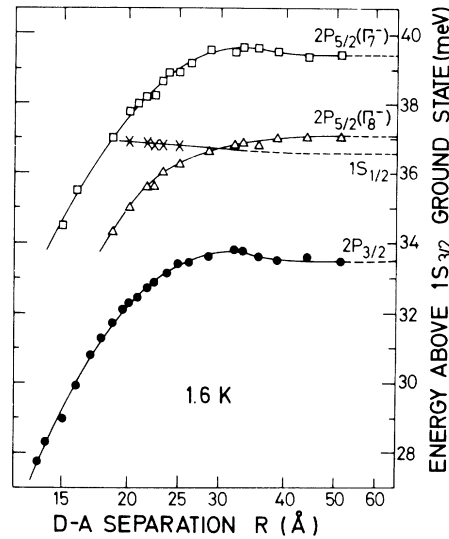
so be obtained in the same way, and direct information is obtained about the $R$ dependence of $J$ and $J^*$.

Examples of excitation spectra for carbon acceptors (and sulfur donors) in GaP are shown in Fig. 1. Two of the peaks are $TO^\Gamma$ and $LO^\Gamma$ phonon replicas of absorption into the D-A ground state, while the remainder are attributed to acceptor excitation. When $R$ is 30 to 50 Å, we observe three acceptor levels which disappear at larger $R$ because of decreasing D-A overlap. At smaller $R$, the levels shift in energy, and a fourth peak is resolved (Fig. 1).

The detailed $R$ dependence of C and Mg acceptor levels is shown in Figs. 2 and 3. The peak energies tend to constant values at large $R$, where $J$ and $J^*$ are negligible, therefore giving the true acceptor energies without perturbation by the donor. These energies and similar data for Zn are given in Table I.

Our identification of the excited states is shown in Figs. 1, 2, and 3 using the notation of Baldereschi and Lipari (BL).[2] The $1S_{1/2}$ levels agree with the Raman scattering data[3] for all three acceptors. We return to the discussion of these levels below. The remaining three peaks have the same relative sparation for all three acceptors. Thus none of them can be the $2S_{3/2}$ level whose central-cell correction will change by ~2 meV between C and Zn. The only feasible identification is therefore the one shown. The absence of the $2S_{3/2}$ level is not understood but we note that it is also not seen in Raman scattering.[3]
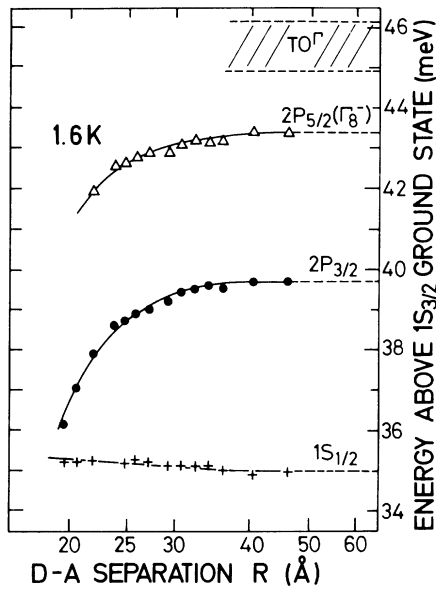
FIG. 3. $R$ dependence of magnesium acceptor levels from GaP luminescence excitation spectra of Mg-Te pairs. The $2P_{5/2}(\Gamma_7^-)$ level is obscured by the $TO^\Gamma$ replica of the ground-state transition (compare Fig. 2).

The energy differences of the $2P$ acceptor levels were fitted to the variational calculation by BL.[2] The resulting values of $\mu$ and $\delta$ (band parameters used by BL) as well as the deduced values of $E_A$ and the effective-mass binding energy $E_A^{EM}$ are shown in Tables I and II. The fit assumes a large spin-orbit splitting of the valence bands, which introduces a small error. We estimate this error using the interpolation procedure suggested by BL and obtain corrections to $E_A$ of 0.3 meV, and to $E_A^{EM}$ of 2 meV, included in Table I. The effective masses for light and heavy holes along (111) were calculated to be $0.16\,m_e$ and $0.56\,m_e$, which agrees with cyclotron resonance results[5] [$(0.16 \pm 0.02)\,m_e$ and $(0.54 \pm 0.05)\,m_e$], if the Luttinger parameters given in Table II are

TABLE I. Observed energy level of C, Mg, and Zn acceptors in GaP relative to the $1S_{3/2}$ ground state. Also shown are derived ionization energies $E_A$, central-cell corrections $E_{CC}$, and calculated effective-mass binding energies $(E_A^{EM})$. Energies in meV; errors are 0.1 meV for C and Mg, 0.2 for Zn.

|  | $1S_{1/2}$ | $2P_{3/2}$ | $2P_{5/2}(\Gamma_8^-)$ | $2P_{5/2}(\Gamma_7^-)$ | $E_A$ | $E_{CC}$ |
|---|---|---|---|---|---|---|
| C | 36.6 | 33.5 | 37.1 | 39.4 | 46.9 | 9.3 |
| $M_g$ | 35.0 | 39.7 | 43.4 | ? | 53.1 | 15.5 |
| Zn | 33.8 | 47.5 | 51.4 | 53.3 | 61.0 | 23.4 |
| $E_A^{EM}$ | 100 | 24.2 | 27.9 | 30.3 | 37.6 | 0 |

TABLE II. Valence-band parameters of GaP obtained from the present work (SS) compared with Lawaetz's (L) theoretical values (Ref. 4). Errors for $\mu$ and $\delta$ are 0.02.

|  | $\mu$ | $\delta$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|
| SS | 0.48 | 0.18 | 4.04 | 0.53 | 1.26 |
| L | 0.66 | 0.162 | 4.20 | 0.98 | 1.66 |

used. Note that if $\mu$ is changed by more than 10% from 0.48, it is no longer possible to obtain agreement.

Several important conclusions result from the above data. $E_A(\text{Zn})$ agrees with the value of 60 $\pm$ 2 meV obtained from the Hall effect,[6] confirming our identification of the acceptor states. The relative values of $E_A$ are also close to those found from D-A luminescence spectra.[7] The valence-band parameters are near to the range of values given by the various calculations,[4] but are not very close to any one set. For example, $\mu$ is 30% lower than was calculated by Lawaetz.[4,2] The effective-mass binding energy is about 10 meV less than previously supposed[2] and therefore even carbon has a considerable central-cell correction. This conclusion is supported by previous observation of an acceptor $X$ with binding energy 2 meV lower[8] than carbon. Thus even this shallowest acceptor due to an axial center of yet uncertain origin has an appreciable central-cell correction. By combining recent data[9] of the sulfur donor $E_D(\text{S}) = 107$ meV, the ionization energy of infinitely distant pairs[7] $h\nu(\infty) = 2.1884$ eV, and our result for the carbon acceptor, we obtain the energy gap $E_g = h\nu(\infty) + E_D(\text{S}) + E_A(\text{C}) = 2.3423$ eV with an estimated error of $< 1.5$ meV. This value, together with the free exciton energy[10] $E_{gx} = 2.3285$ eV, leads to the free exciton binding energy $E_x = E_g - E_{gx} = 13.8$ meV. This is larger than previous estimates[10] but smaller than theoretical prediction[11] probably because of omission of the "camel's back."[12]

We find $J^* - J$ directly from the deviation of the acceptor energies from their value at large $R$. $J$ can be obtained from D-A luminescence spectra,[7] but rather inaccurately because the large Coulomb term must first be subtracted. The interaction is analogous to the binding of a molecule (apart from the absence of exchange terms), and the present experiment provides a unique method of investigating the bond strength as a function of pair separation. Alternative descriptions of $J$ and $J^*$ are the attractive Van der Waals interac-

tion, or the effect of D-A overlap which is repulsive at large $R$ and attractive at small $R$.[4,7] $J$ is negative at all $R$ for C-S pairs,[7] and therefore the Van der Waals term dominates the ground-state transition. The $2P$ levels generally show a larger interaction which may be partially due to an increased polarizability of the acceptor. However, the small positive shift of two of the carbon $2P$ levels (Fig. 2) cannot be explained in this way but is predicted from the model of D-A overlap. The reason for the dominance of overlap is the larger Bohr radius compared to the ground state. The value of $R$ when $J^* - J$ changes sign suggests an effective Bohr radius of 15–20 Å. In the Mg-Te spectra, no change of sign is observed (Fig. 3). $J^* - J$ decreases substantially faster than in the C-S spectra, presumably because the Van der Waals interaction is larger when Te is substituted for S[13] and dominates even the $2P$ levels.

Excited states of the deeper acceptors Be, Mg, Zn, and Cd in GaP have recently been measured in absorption,[14] suggesting increased acceptor binding energies. Our own preliminary absorption data on GaP:C, however, agree with our excitation data.

Finally, we return to the carbon level at 36.6 meV and the magnesium level at 35.0 meV, both of which are very weakly $R$ dependent. This behavior is in complete contrast to the $2P$ levels and implies a state with a much smaller Bohr radius causing a weaker interaction with the donor. This observation confirms that they are $1S_{1/2}$ levels as has already been suggested from electronic Raman scattering.[3]

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