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Calculations of $2p$ -Exciton States in Semiconductors with Degenerate Bands*

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Using a method previously introduced to treat s states, we analyze the $2p$ -excited states of direct excitons in semiconductors. The splitting of the four $2p$ levels, due to the degeneracy of the valence bands, are given by simple analytical expressions. The symmetry of these levels are discussed for the zinc-blende, diamond, and NaCl structures. Results are given for all semiconductors for which the valence-band parameters are known. Since the actual experimental situation is poor, suggestions are made as to which substances should be investigated in order to appreciate these splittings.

I. INTRODUCTION

Very recently, two-photon spectroscopy has gained increasing importance as a powerful method of studying electronic properties of solids.^{1,2} Two-quantum absorption is a nonlinear optical phenomenon in which two quanta are simultaneously absorbed in an electronic or excitonic transition. Since the selection rules for two-photon transitions^{3,4} are very different from those appropriate to one-photon transition,⁵ the two methods are complementary. Moreover, since more state symmetries are observable in two-quantum absorption, one expects that more information concerning energy levels in solids can be obtained from two-quantum absorption than from single-quantum absorption. For excitons, the different selection rules involved in the two-quantum experiments^{3,4} allow the observation of p states forbidden in the one-photon case. It is therefore evident that an accurate knowledge of these states is necessary to correctly interpret the results of the experimental analysis. Because of the anisotropy and the degeneracy of the valence bands⁶ in all cubic semiconductors one cannot apply the simple hydrogenic model for the determination of these states; further, such degeneracy produces a splitting of the p states¹ which is clearly neglected if one uses the simple model.

In a previous set of papers,⁷⁻⁹ we have set forth a method which solves the exciton problem in the case of degenerate bands, and we have applied it to treat the exciton ground state and the excited

s -like states. In this paper we extend the method to treat the p -like excited states. We obtain very simple analytical expressions for the splitting of the various $2p$ states. Section II is a short analysis of the symmetry of the various states. In Sec. III we review briefly the general formulation of the problem and the method of solution, and in Sec. IV we apply the method to treat the $2p$ states. In Sec. V we discuss and summarize the results of the present investigation.

II. GROUP-THEORETICAL ANALYSIS

We now briefly describe the symmetry¹⁰ of the p states in the diamond, zinc-blende, and NaCl structures. The exciton wave function can be written¹¹

$$\psi(\vec{r}_e, \vec{r}_h) = \sum_i \chi^{(i)}(\vec{r}_e - \vec{r}_h) \phi_h^{(i)}(\vec{r}_h) \phi_e(\vec{r}_e), \quad (1)$$

where ϕ_e and $\phi_h^{(i)}$ are the Bloch functions for the electron and the hole, respectively, χ is the envelope function which describes the relative electron-hole motion, and i runs over the degenerate valence-band states. The symmetry of the exciton wave function is determined by the direct product of the irreducible representations for the envelope, hole, and electron wave functions.

For diamond crystals, the point group is O_h . The symmetry of the degenerate valence band at $\vec{k} = 0$ is Γ_8^+ and the conduction-band minimum is Γ_2^- (Γ_8^- double-group notation). For the p states, in which we are interested, the envelope function has Γ_{15} symmetry and therefore we have

$$\Gamma_8^+ \otimes \Gamma_{15} \otimes \Gamma_6^- = E_1 \oplus E_2 \oplus E_3 \oplus E_4, \quad (2)$$

where

$$E_1 = \Gamma_1 + \Gamma_{25} \quad (\text{twofold degenerate without electron spin}), \quad (3a)$$

$$E_2 = \Gamma_2 + \Gamma_{15} \quad (\text{twofold degenerate without electron spin}), \quad (3b)$$

$$E_3 = \Gamma_{12} + \Gamma_{15} + \Gamma_{25} \quad (\text{fourfold degenerate without electron spin}), \quad (3c)$$

$$E_4 = \Gamma_{12} + \Gamma_{15} + \Gamma_{25} \quad (\text{fourfold degenerate without electron spin}). \quad (3d)$$

For the zinc-blende case, the point group is Γ_d , the symmetry of the degenerate valence-band maximum is Γ_8 , and the conduction-band minimum is Γ_1 (Γ_6 double group). The exciton p -like level symmetries are exactly the same as in the diamond case.

For the NaCl structure, the point group is O , the symmetry of the degenerate valence-band maximum is Γ_8^- and the conduction-band minimum is Γ_1 (Γ_6^+ double group). One therefore gets

$$\Gamma_8^- \otimes \Gamma_{15} \otimes \Gamma_6^+ = E_1 \oplus E_2 \oplus E_3 \oplus E_4, \quad (4)$$

where

$$E_1 = \Gamma_1 + \Gamma_{15}, \quad (\text{twofold degenerate without electron spin}), \quad (5a)$$

$$E_2 = \Gamma_2 + \Gamma_{25}, \quad (\text{twofold degenerate without electron spin}), \quad (5b)$$

$$E_3 = \Gamma_{12} + \Gamma_{15} + \Gamma_{25}, \quad (\text{fourfold degenerate without electron spin}), \quad (5c)$$

$$E_4 = \Gamma_{12} + \Gamma_{15} + \Gamma_{25}, \quad (\text{fourfold degenerate without electron spin}). \quad (5d)$$

Not all the above levels are observable in general in a two-quantum absorption experiment, since they obey selection rules. A single photon represents, in the long-wavelength limit, a perturbation of symmetry Γ_{15} and therefore only excitons of Γ_{15} symmetry are observed in one-photon experiments. In two-photon absorption the perturbation can have many complications which depend on the polarization of the two quanta. For example, in the NaCl structure Γ_{15} exciton states are observed only when the two quanta are not polarized parallel to each other. We will not discuss the selection rules here because it would be quite lengthy, but we refer to the excellent works of Inoue and Toyozawa³ and Bader and Gold.⁴

III. FORMULATION OF THE PROBLEM

Crystals with diamond and zinc-blende structure have very similar band structures.⁶ Most of them, and these are the ones for which the present investigation applies, have a direct gap at $\vec{k} = 0$, where the conduction band has a nondegenerate minimum and the valence band has a threefold degenerate maximum, neglecting the spin. The inclusion of spin and spin-orbit interaction alters the bands by splitting the sixfold degenerate valence-band states into an upper fourfold ($J = \frac{3}{2}$) and a lower twofold ($J = \frac{1}{2}$) state represented by the spin-orbit splitting Δ . Since the spin-orbit splitting Δ is almost always large, compared with the exciton binding energy,¹² its contribution to the main (upper fourfold band) excitons is very small, as seen in our previous work.⁸ Therefore, in order to simplify the analysis, we will neglect such terms. The exciton Hamiltonian, in the relative electron-hole system, is therefore (neglecting the electron spin)

$$H_{\text{ex}}(\vec{p}) = \left(\frac{p^2}{2m_e^*} - \frac{e^2}{\epsilon r} \right) I - H_v(p), \quad (6)$$

where \vec{p} is the relative electron-hole momentum, m_e^* is the electron effective mass, ϵ is the static dielectric constant, r is the electron-hole distance, I is the 4×4 unit matrix, and H_v is the well-known 4×4 matrix¹³ which describes the hole kinetic energy near $\vec{k} = 0$.

Equation (6) differs for the diamond and zinc-blende structure because of linear terms in \vec{p} which appear in H_v in the latter case.¹⁴ We have previously⁸ seen that such terms are negligible and therefore we will neglect them in our present treatment.

Equation (6) can be written explicitly as follows⁸:

$$H_{\text{ex}}(\vec{p}) = \begin{vmatrix} P+Q & L & M & 0 \\ L^\dagger & P-Q & 0 & M \\ M^\dagger & 0 & P-Q & -L \\ 0 & M^\dagger & -L^\dagger & P+Q \end{vmatrix}, \quad (7)$$

where

$$P = \frac{p^2}{2\mu_0} - \frac{e^2}{\epsilon r} \quad (\text{s-like}), \quad (8a)$$

$$Q = \frac{p_x^2 + p_y^2 - 2p_z^2}{2\mu_1} \quad (\text{d-like}), \quad (8b)$$

$$L = -i \frac{(p_x - ip_y)p_z}{2\mu_2} \quad (\text{d-like}), \quad (8c)$$

$$M = \sqrt{3} \frac{p_x^2 - p_y^2}{2\mu_1} - i \frac{p_x p_y}{2\mu_2} \quad (\text{d-like}), \quad (8d)$$

where the masses μ_0 , μ_1 , and μ_2 are simply related to the Luttinger¹⁵ parameters γ_1 , γ_2 , and γ_3 and to the Dresselhaus-Kip-Kittel¹⁶ parameters

A, B, and C by the simple relationships

$$\frac{1}{\mu_0} = \frac{1}{m_e^*} + \frac{\gamma_1}{m_0} = \frac{1}{m_e^*} - \frac{2}{\hbar^2} A, \quad (9a)$$

$$\frac{1}{\mu_1} = \frac{\gamma_2}{m_0} = -\frac{1}{\hbar^2} B, \quad (9b)$$

$$\frac{1}{\mu_2} = 2\sqrt{3} \frac{\gamma_3}{m_0} = \frac{2}{\hbar^2} (C^2 + 3B^2)^{1/2}, \quad (9c)$$

m_0 being the free-electron mass.

In accord with the fact that the operators (8a)–(8d) have different symmetry properties, we write Eq. (7) as

$$H_{\text{ex}} = H_s + H_d, \quad (10)$$

where H_s and H_d are 4×4 matrices which contain only s - and d -like operators, respectively, i. e.,

$$H_s = \begin{vmatrix} p & 0 & 0 & 0 \\ 0 & P & 0 & 0 \\ 0 & 0 & P & 0 \\ 0 & 0 & 0 & P \end{vmatrix} \quad (11a)$$

and

$$H_d = \begin{vmatrix} Q & L & M & 0 \\ L^\dagger & -Q & 0 & M \\ M^\dagger & 0 & -Q & -L \\ 0 & M^\dagger & -L^\dagger & Q \end{vmatrix}. \quad (11b)$$

In accord with our previous work⁷⁻⁹ we treat H_s as the unperturbed Hamiltonian and consider H_d as a perturbation.

IV. CALCULATION FOR THE $2p$ STATES

Exact solutions of the unperturbed Hamiltonian H_s are easily found because the operator P represents the Hamiltonian of a hydrogen atom with reduced mass μ_0 and the dielectric constant ϵ . The eigenfunctions are

$$|n, l, m, i\rangle = |n, l, m\rangle |i\rangle, \quad (12)$$

where $|n, l, m\rangle$ is the usual hydrogen-atom wave function¹⁷ and $|i\rangle$ is a four-component spinor as defined in Ref. 8. The corresponding eigenvalues are

$$E_{n,i} = 1/n^2, \quad i = 1, 2, 3, 4$$

where we have used effective units; i. e., for the energies

$$R_0 = \mu_0 e^4 / 2\hbar^2 \epsilon^2 \quad (13)$$

and for the length

$$a_0 = \epsilon \hbar^2 / \mu_0 e. \quad (14)$$

We now consider H_d as a perturbation. Consistent with our previous work⁷⁻⁹ we will consider only

the first nonvanishing contribution; in this case the first order. Here, as in the case of s states, since one has four series of p states with the same energy, we use degenerate first-order perturbation theory. The resulting secular determinant is diagonal, however, and nondegenerate perturbation theory can be used. The analysis becomes more elegant if the perturbation Hamiltonian H_d is expressed in terms of irreducible tensor operators.¹⁸

Using the standard definitions¹⁸ we get

$$Q = -\frac{1}{\sqrt{6}} \frac{1}{\mu_1} T_0^2, \quad (15a)$$

$$L = -\frac{i}{6\mu_2} T_{-1}^2, \quad (15b)$$

$$M = \left(\frac{1}{2\sqrt{3}} \frac{1}{\mu_1} - \frac{1}{12\mu_2} \right) T_2^2 + \left(\frac{1}{2\sqrt{3}} \frac{1}{\mu_1} + \frac{1}{12\mu_2} \right) T_{-2}^2, \quad (15c)$$

and therefore

$$L^\dagger = -\frac{i}{6\mu_2} T_1^2 \quad (15d)$$

and

$$M^\dagger = \left(\frac{1}{2\sqrt{3}} \frac{1}{\mu_1} + \frac{1}{12\mu_2} \right) T_2^2 + \left(\frac{1}{2\sqrt{3}} \frac{1}{\mu_1} - \frac{1}{12\mu_2} \right) T_{-2}^2, \quad (15e)$$

where T_q^l is the q component of the irreducible tensor T^l of rank l formed from the symmetric reducible second-rank tensor with vanishing trace

$$T_{ij} = 3p_i p_j - \delta_{ij} p^2. \quad (16)$$

Since, for simplicity, we work in effective units (i. e., $E_{2p} = \frac{1}{4}$), we rewrite Eqs. (15a)–(15e) as

$$Q = \left(\frac{2}{3} \right)^{1/2} \frac{\mu_0}{\mu_1} T_0^2, \quad (17a)$$

$$L = \frac{i}{3} \frac{\mu_0}{\mu_2} T_{-1}^2, \quad (17b)$$

$$M = \left(\frac{1}{6} \frac{\mu_0}{\mu_2} - \frac{1}{\sqrt{3}} \frac{\mu_0}{\mu_1} \right) T_2^2 - \left(\frac{1}{\sqrt{3}} \frac{\mu_0}{\mu_1} + \frac{1}{6} \frac{\mu_0}{\mu_2} \right) T_{-2}^2, \quad (17c)$$

and similarly for L^\dagger and M^\dagger . In order to determine the perturbation corrections to the unperturbed $2p$ level, we must diagonalize the determinant

$$A = \begin{vmatrix} \langle P_1 | H_d | P_1 \rangle & \langle P_1 | H_d | P_0 \rangle & \langle P_1 | H_d | P_{-1} \rangle \\ \langle P_0 | H_d | P_1 \rangle & \langle P_0 | H_d | P_0 \rangle & \langle P_0 | H_d | P_{-1} \rangle \\ \langle P_{-1} | H_d | P_1 \rangle & \langle P_{-1} | H_d | P_0 \rangle & \langle P_{-1} | H_d | P_{-1} \rangle \end{vmatrix}, \quad (18)$$

where $|P_m\rangle = |2, 1, m\rangle$ using the notation (12). All the matrix elements involved in Eq. (18) are of the

type

$$\langle LM' | T_q^2 | LM \rangle. \quad (19)$$

Such matrix elements are easily evaluated using the Wigner-Eckart theorem¹⁸:

$$\langle LM' | T_\mu^2 | LM \rangle = (-1)^{L-M'} \begin{pmatrix} L & 2 & L \\ -M & q & M \end{pmatrix} (L \| T^2 \| L). \quad (20)$$

By doing this, we have separated the matrix element [Eq. (19)] into two parts: one part (||) which is independent of M , M' , and q is called the reduced matrix element of the tensor T^2 and which therefore has to be evaluated only once; another part, the 3- j symbol which depends on M , M' , and q in a very simple known way.

The reduced matrix element (||) is easily evaluated:

$$(L \| T^2 \| L) = \sqrt{3} \frac{[L(2L+1)(2L+2)]^{1/2}}{[(2L-1)(2L+3)]^{1/2}} \times \int_0^\infty R_{2L}(r) \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2} \right) R_{2L}(r) r^2 dr. \quad (21)$$

In our case, $L=1$ and therefore

$$(L \| T^2 \| L) = -3/2\sqrt{5}. \quad (22)$$

In order to diagonalize the matrix (18) we have to solve the system of equations

$$(A) \cdot \begin{bmatrix} f_1 \\ f_2 \\ \vdots \\ \vdots \\ f_{12} \end{bmatrix} = \begin{bmatrix} f_1 \\ f_2 \\ \vdots \\ \vdots \\ f_{12} \end{bmatrix}. \quad (23)$$

The above 12×12 system factorizes into four 3×3 subsystems. After straightforward calculations one gets

$$\begin{cases} -af_1 & +cf_{11} & = \lambda f_1 \\ & +2af_8 & +bf_{11} & = \lambda f_8 \\ cf_1 & +b^*f_8 & +af_{11} & = \lambda f_{11} \end{cases}, \quad (24a)$$

$$\begin{cases} af_2 & +bf_5 & +cf_2 & = \lambda f_2 \\ b^*f_2 & +2af_5 & & = \lambda f_5 \\ cf_2 & & -f_{12} & = \lambda f_{12} \end{cases}, \quad (24b)$$

$$\begin{cases} af_3 & & +af_9 & = \lambda f_3 \\ & -2af_6 & -bf_9 & = \lambda f_6 \\ df_3 & -b^*f_6 & -af_9 & = \lambda f_9 \end{cases}, \quad (24c)$$

$$\begin{cases} -af_4 & -bf_7 & +df_{10} & = \lambda f_4 \\ -b^*f_4 & -2af_7 & & = \lambda f_7 \\ df_4 & & +af_{10} & = \lambda f_{10} \end{cases}, \quad (24d)$$

where

$$a = \frac{1}{10} \frac{\mu_0}{\mu_1}, \quad (25a)$$

$$b = \frac{i}{10\sqrt{2}} \frac{\mu_0}{\mu_2}, \quad (25b)$$

$$c = \frac{1}{10} \left(\sqrt{3} \frac{\mu_0}{\mu_1} - \frac{1}{2} \frac{\mu_0}{\mu_1} \right), \quad (25c)$$

$$d = \frac{1}{10} \left(\sqrt{3} \frac{\mu_0}{\mu_1} + \frac{1}{2} \frac{\mu_0}{\mu_2} \right). \quad (25d)$$

It is easy to see that (24a) and (24b) have the same eigenvalues given by

$$\lambda^3 - 2a\lambda^2 - (a^2 + |b|^2 + c^2)\lambda + a(2a^2 - |b|^2 + 2c^2) = 0, \quad (26)$$

and that (24c) and (24d) also give the same solutions given by

$$\lambda^3 + 2a\lambda^2 - (a^2 + |b|^2 + d^2)\lambda - a(2a^2 - |b|^2 + 2d^2) = 0. \quad (27)$$

By solving Eq. (26) we get

$$\lambda_1 = \frac{1}{20} \left(4 \frac{\mu_0}{\mu_1} - \sqrt{3} \frac{\mu_0}{\mu_2} \right), \quad (28a)$$

$$\lambda_2 = \frac{1}{40} \left\{ \sqrt{3} \frac{\mu_0}{\mu_2} + \left[3 \left(\frac{\mu_0}{\mu_2} \right)^2 + 64 \left(\frac{\mu_0}{\mu_1} \right)^2 \right]^{1/2} \right\}, \quad (28b)$$

$$\lambda_3 = \frac{1}{40} \left\{ \sqrt{3} \frac{\mu_0}{\mu_2} - \left[3 \left(\frac{\mu_0}{\mu_2} \right)^2 + 64 \left(\frac{\mu_0}{\mu_1} \right)^2 \right]^{1/2} \right\}. \quad (28c)$$

By solving Eq. (27) we have

$$\lambda_4 = -\frac{1}{20} \left(4 \frac{\mu_0}{\mu_1} + \sqrt{3} \frac{\mu_0}{\mu_2} \right), \quad \lambda_5 = \lambda_2, \quad \lambda_6 = \lambda_3. \quad (28d)$$

In conclusion we therefore have the following solution:

$$E_1^d = -\frac{1}{20} \left(4 \frac{\mu_0}{\mu_1} + \sqrt{3} \frac{\mu_0}{\mu_2} \right) \text{ (twofold)}, \quad (29a)$$

$$E_2^d = \frac{1}{20} \left(4 \frac{\mu_0}{\mu_1} - \sqrt{3} \frac{\mu_0}{\mu_2} \right) \text{ (twofold)}, \quad (29b)$$

$$E_3^d = \frac{1}{40} \left\{ \sqrt{3} \frac{\mu_0}{\mu_2} + \left[3 \left(\frac{\mu_0}{\mu_2} \right)^2 + 64 \left(\frac{\mu_0}{\mu_1} \right)^2 \right]^{1/2} \right\} \text{ (fourfold)}, \quad (29c)$$

$$E_4^d = \frac{1}{40} \left\{ \sqrt{3} \frac{\mu_0}{\mu_2} - \left[3 \left(\frac{\mu_0}{\mu_2} \right)^2 + 64 \left(\frac{\mu_0}{\mu_1} \right)^2 \right]^{1/2} \right\} \text{ (fourfold)}. \quad (29d)$$

It is useful to express the above results in terms of the same parameters, μ and δ , used in describing the acceptor impurity problem.¹⁹ By doing so,

moreover, we can determine very easily the symmetry of the above states. Since

$$\mu = \frac{\sqrt{3}}{5} \frac{\mu_0}{\mu_2} + \frac{4}{5} \frac{\mu_0}{\mu_1}, \quad (30a)$$

$$\delta = \frac{1}{2\sqrt{3}} \frac{\mu_0}{\mu_2} - \frac{\mu_0}{\mu_1}, \quad (30b)$$

we can rewrite expressions (29a)–(29d) as

$$E_1^d = -\frac{1}{4}\mu \quad (\text{twofold}), \quad (31a)$$

$$E_2^d = -\frac{1}{20}(\mu + \frac{24}{5}\delta) \quad (\text{twofold}), \quad (31b)$$

$$E_3^d = \frac{1}{40}[3\mu + \frac{12}{5}\delta + \frac{1}{5}(625\mu^2 + 720\mu\delta - 600\delta^2)^{1/2}] \quad (\text{fourfold}), \quad (31c)$$

$$E_4^d = \frac{1}{40}[3\mu + \frac{12}{5}\delta - \frac{1}{5}(625\mu^2 + 720\mu\delta - 600\delta^2)^{1/2}] \quad (\text{fourfold}). \quad (31d)$$

As $\delta \rightarrow 0$, i. e., neglecting the cubic term in the exciton Hamiltonian,¹⁹ we get

$$E_2^d = E_4^d \quad (32)$$

and therefore we see that

$$E_1^d \rightarrow P_{1/2}, \quad (33a)$$

$$E_2^d \rightarrow P_{3/2}, \quad (33b)$$

$$E_2^d + E_4^d \rightarrow P_{5/2}, \quad (33c)$$

using the notation of Ref. 19.

Therefore, the symmetries of the four $2p$ states (29a)–(29d) are, say, for the diamond structure (including the electron spin),

$$E_1 \rightarrow \Gamma_1 + \Gamma_{25}, \quad (34a)$$

$$E_2 \rightarrow \Gamma_2 + \Gamma_{15}, \quad (34b)$$

$$E_3 \rightarrow \Gamma_{12} + \Gamma_{15} + \Gamma_{25}, \quad (34c)$$

$$E_4 \rightarrow \Gamma_{12} + \Gamma_{15} + \Gamma_{25}, \quad (34d)$$

and similarly for the zinc-blende and NaCl structures. In conclusion, the energy expression for the four $2p$ states is given by

$$E_i = R_0 (\frac{1}{4} + E_i^d), \quad i = 1, 2, 3, 4 \quad (35)$$

where E_i^d are given by expressions (29a)–(29d).

TABLE I. Results for Ge and III-V compounds. All the quantities are defined in the text. The energy unit is meV.

	ϵ	μ_0	μ	δ	R_0	E_1	E_2	E_3	E_4	E_{2s}
AlSb	9.9 ^a	0.010 ^b	0.022 ^b	0.009 ^b	1.44	0.35	0.36	0.37	0.36	0.36 ^c
		0.010 ^d	0.039 ^d	-0.001 ^d	1.45	0.35	0.36	0.37	0.36	0.36 ^c
GaP	11.1 ^e	0.075 ^b	0.093 ^b	0.084 ^b	8.30	1.88	1.87	2.27	2.07	2.13 ^c
		0.081 ^d	0.236 ^d	0.021 ^d	8.91	1.70	2.08	2.65	2.14	2.43 ^c
GaAs	12.5 ^f	0.048 ^b	0.159 ^b	0.035 ^b	4.16	0.87	0.97	1.17	1.02	1.08 ^c
		0.048 ^d	0.215 ^d	0.001 ^d	4.22	0.83	1.01	1.24	1.01	1.13 ^c
		0.045 ^g	0.226 ^g	0.001 ^g	3.90	0.76	0.93	1.15	0.93	1.04 ^c
GaSb	15.2 ^h	0.035 ^b	0.184 ^b	0.033 ^b	2.05	0.42	0.48	0.59	0.50	0.54 ^c
		0.032 ^d	0.280 ^d	0.005 ^d	1.87	0.34	0.44	0.57	0.44	0.52 ^c
		0.031 ⁱ	0.237 ⁱ	0.042 ⁱ	1.82	0.35	0.41	0.54	0.44	0.49 ^c
InP	12.1 ^j	0.053 ^b	0.189 ^b	0.035 ^b	4.96	1.01	1.15	1.43	1.21	1.31 ^c
		0.052 ^d	0.276 ^d	-0.001 ^d	4.82	0.87	1.14	1.47	1.14	1.34 ^c
InAs	11.8 ^k	0.018 ^b	0.240 ^b	0.009 ^b	1.74	0.33	0.41	0.52	0.42	0.47 ^c
		0.017 ^d	0.259 ^d	-0.001 ^d	1.68	0.31	0.40	0.51	0.40	0.46 ^c
		0.016 ^l	0.288 ^l	0.000 ^l	1.57	0.28	0.37	0.48	0.37	0.44 ^c
InSb	16.8 ^h	0.012 ^b	0.212 ^b	0.006 ^b	0.56	0.11	0.13	0.16	0.13	0.15 ^c
		0.010 ^d	0.300 ^d	0.004 ^d	0.49	0.09	0.11	0.15	0.12	0.14 ^c
		0.010 ^m	0.308 ^m	0.019 ^m	0.48	0.08	0.11	0.15	0.11	0.14 ^c
Ge	15.4 ⁿ	0.026 ^d	0.236 ^d	0.023 ^d	1.49	0.28	0.35	0.44	0.36	0.40 ^c
		0.025 ^o	0.256 ^o	0.034 ^o	1.44	0.27	0.33	0.43	0.35	0.40 ^c

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TABLE II. Results for cubic II-VI compounds. All the quantities are defined in the text. The energy unit is meV.

	ϵ	μ_0	μ	δ	R_0	E_1	E_2	E_3	E_4	E_{2s}
ZnS	8.1 ^a	0.178 ^b 0.228 ^d	0.089 ^b 0.385 ^d	0.137 ^b -0.047 ^d	36.87 47.41	8.58 7.29	7.88 11.48	10.32 15.52	9.11 10.65	9.61 ^c 15.29 ^c
ZnSe	8.7 ^e	0.125 ^b 0.132 ^d	0.126 ^b 0.339 ^d	0.055 ^b 0.019 ^d	22.43 23.67	4.90 3.91	5.17 5.41	6.21 7.52	5.58 5.57	5.77 ^c 6.95 ^c
ZnTe	10.1 ^a	0.079 ^b 0.081 ^d	0.116 ^b 0.192 ^d	0.029 ^b 0.000 ^d	11.43 10.83	2.53 2.19	2.71 2.60	3.13 3.12	2.83 2.60	2.92 ^c 2.85 ^c
CdTe	9.7 ^a	0.079 ^b 0.070 ^d	0.0116 ^b 0.253 ^d	0.029 ^b -0.023 ^d	11.43 10.10	2.53 1.89	2.71 2.45	3.13 3.04	2.83 2.37	2.92 ^c 2.76 ^c

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V. RESULTS AND DISCUSSION

We now apply the results of Sec. IV to investigate the direct $2p$ -exciton levels in diamond and zinc-blende crystals for which band parameters are available. In Tables I and II we give the results of an investigation for the III-V and II-VI compounds, respectively. In these tables we give the binding energies E_1 , E_2 , E_3 , and E_4 of four $2p$ states obtained using Eq. (35). Also given are the parameters used for the calculations; i. e., the dielectric constant ϵ , the band parameters μ_0 , μ , and δ , together with the effective rydberg R_0 . We have also included the energy of the $2s$ -exciton level in order to compare it with the energy of the $2p$ states.

We can see that the perturbation in the case of p states is even more important than the case of s states. In fact, such a perturbation as H_4 not only shifts the energy of the states considered here, but also introduces a splitting.

Unfortunately, the experimental situation is poor at present, and it is not possible to compare our results with the experimental data. $2p$ states have been observed by Frohlich *et al.*² in some alkali halides and in ZnO.²⁰ In this case only one of the four $2p$ states has been observed. Furthermore, the band parameters necessary for the calculation are not available and for that reason we cannot compute the $2p$ levels for such substances. Stafford and Park²² have very recently investigated the two-photon spectrum in KI and have observed two separate $2p$ levels: One of them is interpreted as being due to a phonon-assisted process. Our method can be applied to alkali-halide crystals because the

effective-mass approximation, which we use, is supposed to work fairly well for the excited $2p$ states. However, also for KI, the band parameters μ_0 , μ_1 , and μ_2 needed for the calculation are not known, and therefore we cannot compute such levels. We think, however, that it is possible that the two levels observed by Stafford and Park²² are simply two of the four $2p$ states. The argument is the following: In semiconductors, i. e., II-VI compounds, where the exciton binding energy is of the order of 30 meV, the splitting among the various $2p$ states is of the order of 2 meV. Everything else being equal, the splitting among the $2p$ states scales linearly with exciton binding energy, thus in KI, where the binding energy is of the order of 300 meV, the splitting could be about 20 meV, which is in qualitative agreement with the splitting observed by Stafford and Park²² (22 meV). It is clear, however, that only when the valence-band parameters μ_0 , μ_1 , and μ_2 are known can one have quantitative conclusions.

For the semiconductors for which the valence-band parameters are known, no experimental data are available. We think that the split $2p$ states can hardly be observed in the III-V compounds, both because of the very small gap of the material and because of the small splitting among these states. However, II-VI compounds look much more promising, especially ZnS and ZnSe.

It is clear that there is much room for both theoretical and experimental efforts in the future, which could prove to be very useful in better understanding the nature of these solids, since two-quantum experiments give much information which is not obtainable with the one-quantum experiments.

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X-Ray Photoemission Measurements of GaP, GaAs, InAs, and InSb

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X-ray-induced electron-emission measurements were used to determine the energy levels of core electrons in GaP, GaAs, InAs, and InSb. The investigated energy range extends from the bottom of the valence band to about 1400 eV below the Fermi level. Samples were cleaned by using argon-ion bombardment, and the gold $4f_{7/2}$ electron level was used to provide an energy reference level. Chemical shifts were determined by comparing the results with previously published experimental values for the pure elements. Several spin-orbit-splitting values were experimentally determined. Two maxima in the conduction-band density of states were located with respect to the bottom of the conduction band by comparing the photoemission data for the outermost core d and p electrons with transition energies measured by uv absorption, uv reflectivity, and electron-energy-loss experiments. One maximum is located between 0, 8 and 1.4 eV above the bottom of the conduction band depending on the compound and the other is located between 3 and 4 eV.

I. INTRODUCTION

We present the results of our x-ray-induced electron-emission studies of the electron-core levels of GaP, GaAs, InAs, and InSb. Similar measurements on several of the II-VI compounds have previously been reported.¹

Section II includes a brief description of the apparatus and principles of operation along with a

more detailed description of sample preparation and energy calibration. Sample preparation included cleaning by ion bombardment and energy calibration was based on the $4f_{7/2}$ energy level of gold.

The results of our measurements are listed in Sec. III which is divided into three sections. Section III A is concerned with the actual location of the measured energy levels. We list our results