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Capture Modes Revealed by the Study of Line Intensities in GaP Pair Spectra

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The capture mechanisms preceding photon emission by donor-acceptor pairs were clarified by the study of spectral-line intensities. Strong violations of the rule "equal intensities per donor-acceptor pair" were found in GaP under conditions of low excitation. Abrupt changes of intensity with changing separation of the donor-acceptor pair were attributed to changes in capture mode, and were related to critical dissipation energies in the capture process. The closing of capture channels and phonon resonance capture adequately explained the two kinds of observed intensity anomalies. An accurate calculation of the critical energies required the evaluation of multipole, van der Waals, and polarization energies. This led to a unique method of determining the polarizability of impurity atoms in solids. The measured polarizabilities of donors and acceptors in GaP are smaller than predicted by the model of a hydrogenic atom in a dielectric continuum.

I. INTRODUCTION

The many sharp lines of donor-acceptor (DA) pair spectra have been studied extensively in GaP [1-7] and in other semiconductors.[8] The photon energy depends on the DA separation primarily because of the monopole Coulomb interaction[9] of the DA ions after electron-hole recombination. The multiline nature of the spectrum is then explained by the fact that only discrete values of DA separations are permitted by the lattice structure. The possible positions of donors about a given acceptor (or of acceptors about a donor) can be grouped into equidistant shells.[10] The shell number m can be identified for each line by fitting the spectrum, and it is then convenient to use the number m to tag the spectral line.[1,2]

Analysis of the spectral-line *energies* gives information on a variety of semiconductor properties, such as donor and acceptor ionization energies,[6] van der Waals interactions,[3] the dielectric constant,[11] and multipole moments of the substituted atoms.[12]

Spectral-line *intensities* have not received as much attention.[13] In this paper we show that analysis of line intensities yields considerable information on capture processes. We exhibit several examples of abrupt changes in intensity with changing m in GaP pair spectra, and we interpret the data in terms of changes in capture mode. The analysis also provides a unique way of measuring the polarizability of impurity atoms in solids.

Lax[14,15] discussed the capture of electrons and holes by independent donors and acceptors, and summarized the experimental information available in 1960. In pair spectra, however, photon emission is preceded by the two-step capture of an electron and a hole by an *interacting* donor and acceptor. This double capture is like the capture by independent ions only in the limit of distant pairs (very large m). For most values of m, the DA interaction has a strong influence on capture that is most easily discussed by considering the two units of energy given to the lattice in the two capture steps. These are not the donor and acceptor ionization energies E_D and E_A, but are quantities E_{L1} and E_{L2}, defined below (see Fig. 1), that depend on the order of capture (electron first or hole first) and on the DA separation.

The DA interaction energies must be considered in the various stages of the capture process. Depending on the charge states of the donor and acceptor these are the monopole Coulomb, polarization, and van der Waals energies defined in Fig. 1. They are all functions of the distance between donor and acceptor, hence functions of m. The Coulomb and van der Waals energies can be obtained by analysis of the spectral-line energies, but the polarization energy can only be obtained from an interpretation of line intensities.

The line intensities in DA spectra have previously been studied as a function of excitation intensity.[4] At high excitation, many DA pairs are saturated, i.e., the rate-limiting step in light production is the radiative recombination. Line intensities can then be explained in terms of the number of contributing sites and the overlap of electron and hole wave functions.[4] There is no dependence on capture rates for saturated pairs. However, the close pairs we shall consider are

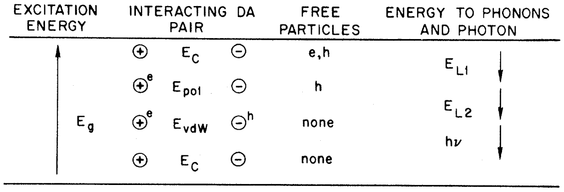

FIG. 1. Schematic of excitation-recombination cycle using the e-h capture branch. Circled charges are the DA ions, and the arrows indicate successive steps in the cycle, excitation being one step and recombination three. The DA interaction energy is shown for each stage of the cycle.

seldom saturated. In order to make certain of this, we used low excitation rates in the range where the relative intensities of the close-pair lines are not a function of the excitation intensity, i.e., the transitions are unsaturated. Differences in capture rates for different m then show up as intensity differences.

We look especially for the sudden changes in intensity with changing m that indicate a change in capture mode. We interpret such changes in terms of certain critical values of the energy units E_{L1} or E_{L2}. For example, one critical value of E_{L1} is the value zero for hole-first capture, which occurs at a particular m. At smaller m, the necessity of electron-first capture reduces the capture rate by an order of magnitude in two spectra shown here. Another critical condition occurs when E_{L2} becomes equal to the energy of a TO or LO phonon. Three examples are given in which this phonon resonance enhances the capture rate.

The complete excitation-emission cycle is examined in Sec. II to see how the DA interactions and the energy balance determine the dependence of the capture mode on the shell number m. Examples from GaP spectra are presented in Sec. III, and some of the results are compared with theory in Sec. IV. In the Appendix a multipole analysis of DA pair interactions[16] is used to improve the earlier assignment[5] of the Cd-O pair lines.

II. DEPENDENCE OF CAPTURE CROSS SECTIONS ON DA SEPARATION

Before a DA pair can emit a photon through electron-hole recombination, the donor must capture an electron and the acceptor a hole, a double capture that may occur in either order. We will call the electron-first process "e-h capture" and the hole-first process "h-e capture." Cross sections are written σ_1 for first capture and σ_2 for second. Thus, the total capture probability is determined by the four cross sections σ_1(e-h), σ_1(h-e), σ_2(e-h), and σ_2(h-e). In the limit of large DA separations, σ_1(e-h) and σ_2(h-e) are equal, as are the other pair, but when DA interaction is significant these cross sections are usually quite different, and they vary with shell number m. Both σ_1(e-h) and σ_1(h-e) tend to decrease with decreasing m, but not necessarily monotonically. For shallow donors and acceptors, both eventually go to zero for small m, but usually at different values of m. The two second-capture cross sections have a considerably weaker dependence on m.

In Sec. II A we consider the energy balance in DA luminescence, and we define the energies E_{L1} and E_{L2} that are important in determining cross sections. The change of E_{L1} and E_{L2} with changing m is discussed in Sec. II B, and in Sec. II C the observed dependence of the capture rate on the square of the DA separation is made plausible for the region dominated by the Lax capture mechanism.

A. Energy Balance Equations

An excitation energy $\gtrsim E_g$ is required to produce an electron-hole pair, and in DA luminescence this energy is returned in three steps. The energy E_{L1} is given to the lattice[17] in the first capture process, E_{L2} in the second, and, finally, a photon of energy $h\nu$ is emitted. These three energies are all functions of m because of DA interactions. As the number of ions change from two to one to zero, the interaction changes from Coulomb to polarization to van der Waals. For a DA pair, these interactions are all attractive; hence the Coulomb, polarization, and van der Waals energy E_C, E_{pol}, and E_{vdW} are all negative quantities. The other energies are positive by definition. The complete excitation recombination cycle is shown in Fig. 1, from which the following relationships are obtained. They are written for an e-h capture. If the capture is h-e, the ionization energies E_D and E_A should be interchanged.

$$E_{L1} = E_D + E_C - E_{\text{pol}} , \tag{1}$$

$$E_{L2} = E_A + E_{\text{pol}} - E_{\text{vdW}} , \tag{2}$$

$$h\nu = E_g - (E_D + E_A) + E_{\text{vdW}} - E_C . \tag{3}$$

Unless otherwise stated we take $E_C = -e^2/\epsilon r$ to be the dominant monopole term in the Coulomb interaction between the ionized DA pair.[18]

B. Dependence of Capture Cross Section on E_{L1} and E_{L2}

Of the three interaction energies, E_{pol} and E_{vdW} are small except for close pairs (small m). However, $-E_C$ is about 50 meV at $m = 50$ and is more than 100 meV at $m = 10$. In the region of well-resolved spectral lines, $-E_C$ is therefore comparable with E_D or E_A and gives E_{L1} a strong dependence on m. The size of E_{L1}, in turn, determines the possible mechanisms of first capture, hence the magnitude of the cross section σ_1.

The way in which the capture mode may change with changing *m* is illustrated in Fig. 2. At large *m*, E_{L1} is positive even when the binding energy of a shallow excited state is used in place of E_D. Therefore, the Lax cascade capture mechanism is permitted, and a large σ_1 is expected at low temperatures. An estimate of the dependence of σ_1 on DA separation for large *m* is given below.

At medium *m*, Fig. 2(b) indicates that the excited states may no longer be able to bind an electron, i.e., the ground-state binding energy E_D is required in Eq. (1) to keep E_{L1} positive. When *m* falls in this range, σ_1 is reduced.

For a particular *m*, the situation illustrated in Fig. 2(c) may obtain, in which E_{L1} is equal to the energy of an optical phonon ($\hbar\omega$). We then expect a large σ_1, for what we call resonance capture, because the emission of only one phonon is required.

Finally, Fig. 2(d) shows that E_{L1} may vanish for small *m*, making capture impossible. Here the $E_{\rm pol}$ term may also be important. With unequal E_D and E_A, σ_1 vanishes first for the impurity with the smaller ionization energy, shutting off one of the two recombination channels. At still smaller *m*, σ_1 may vanish also for the other impurity, with the result that the DA pair can no longer function as a luminescence center except as a result of exciton capture.[19]

Figure 2 may also be used to illustrate second-capture processes, but E_{L2} has no dependence on E_C, and therefore varies with *m* much less rapidly than E_{L1} does. Even for small *m*, E_{L2} is not reduced enough to bring about the situation of Fig. 2(d), i.e., second capture is never impossible.

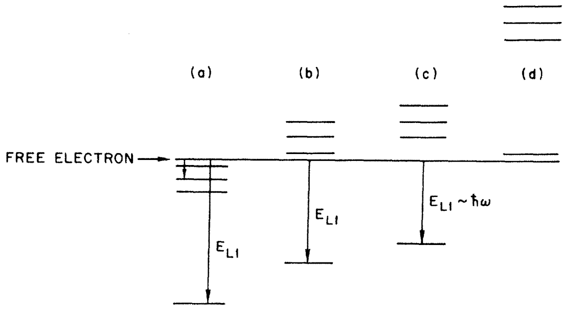

FIG. 2. Schematic of first capture (in e-h branch) as a function of DA separation. The relative energies of free and bound electrons depend on the shell number *m*. (a) Capture into ground *or* excited states (large *m*); $E_{L1} \approx E_D$; (b) capture into ground state only (medium *m*); $E_{L1} < [E_D(n=1) - E_D(n=2)]$; (c) phonon resonance capture (at *m* for which $E_{L1} = \hbar\omega_{\rm TO}$ or $\hbar\omega_{\rm LO}$); (d) capture not possible (small *m*), E_{L1} is negative. Similar considerations apply also to second capture, but E_{L2} varies much less than E_{L1} and the situation shown in (d) does not occur.

C. Capture into Excited States (Lax Mechanism)

We can now use Eq. (1) to account for the dependence of capture probability on DA separation for large *m*. Lax[14] showed that the large observed capture cross sections of donors or acceptors at low temperatures can be explained by capture into the large orbits of the shallow excited states. A limitation to finite-sized orbits is imposed by the condition $E_{in} \geqslant kT$, where E_{in} is the binding energy of the isolated impurity state with principal quantum number *n*, and kT is the thermal energy. For the low-temperature capture by a donor in the presence of an ionized acceptor, $-E_c > kT$ except for the most distant pairs; so instead of $E_{in} \geqslant kT$ we take $E_{in} \geqslant -E_c + E_{\rm pol}$, where $E_{\rm pol}$ refers to the *n*th excited state of the impurity. This is the requirement for positve $E_{L1}(n)$, i.e., we require energy to be *given* to the lattice on capture of an electron into the *n*th state.[20] For large DA separations $E_{\rm pol}$ is negligible, and we note that $-E_{in}$ is half the Coulomb interaction energy of the donor with its orbital electron. Therefore, the limiting impact parameter for capture is $\sim \frac{1}{2} r$, half the DA separation.

This simple estimate[21] yields a σ_1 proportional to r^2. If first capture is the rate-limiting step, the double-capture process will also be proportional to r^2. Such a dependence on DA separation was previously suggested by Thomas *et al.*[4] "on intuitive grounds," and was suported by experimental evidence.

The above estimate was obtained by considering *n* as a continuous quantum number, but as *r* decreases the discrete nature of the quantum states becomes more significant. For sufficiently small *m*,

$$E_{i2} < -E_C + E_{\rm pol}\,,$$

and only capture into the ground state is possible. Since $E_{in} \propto n^{-2}$, one would expect a sudden drop in cross section by a factor 16 when E_{L1} is reduced to the point that only ground-state capture is possible. This reduction factor may be considerably larger for those donors or acceptors where the central cell interaction produces a large increase in binding energy only for the ground state E_{i1} (E_i).

For most impurities E_{i2} is $\approx$ 10 to 20 meV,[22] and hence the reduced capture cross sections would be found at very large *m*, where the spectral lines are not resolved.

III. EXPERIMENTAL RESULTS

Our experimental work on pair spectra consists of a study of selected spectral regions that show a strong dependence of line intensity on DA separation. The greatest intensity changes are observed when the exciting light is relatively weak; hence the *m* dependence of line intensity is attributed to the *m* dependence of the double-capture rate. The strong *m* dependence we examine here is seen only infrequently. For the most part, pair spectra have been successfully analyzed on the assumption of weak *m* dependence.[2,5] The intensity ratio of two nearby lines is then given approximately by the ratio of the numbers of equivalent pairs contributing to the two lines, as determined by the lattice geometry. In other words, the usual rule[7] is "equal intensities per donor-acceptor pair." Our interest is limited to portions of spectra in which a strong violation of this rule is observed. Each of these portions is considered to be evidence of a change in capture mode.

To identify the reason for the change in capture mode we evaluate E_{L1} and E_{L2}, using Eqs. (1) and (2). For the spectra shown here we know E_A, E_D, and E_C. As for the small quantities E_{po1} and E_{vdW}, we can make an estimate of the former and an approximate measurement of the latter. A consideration of these energies enables us to identify the critical change in E_{L1} or E_{L2} that forces a change in capture mode, hence in the double-capture rate. We thus obtain a measure of the relative effectiveness of certain capture mechanisms.

The sudden intensity changes reported here fall into two categories. In the first, called a "cutoff," there is an abrupt decrease of line intensity with decreasing *m*, and we can show that the cutoff is due to the closing of a capture channel. In the second, called a "resonance," the line intensity is enhanced for one or two values of *m*. The spectra showing a cutoff in one capture channel are described in Sec. III A, those showing a cutoff in both capture channels in Sec. III B, and those showing a phonon resonance in Sec. III C.

A. Intensity Cutoff in Infrared Pair Spectra

For examples of intensity cutoff, the three spectra of Ref. 5 were reexamined under low excitation. In each spectrum one impurity is the very deep donor O, with E_D = 895.5 meV,[23] a value large enough to ensure $E_{L1} > 0$ for the e-h capture channel for all spectral lines. On the other hand, E_{L1} should go to zero for the h-e capture channel at different values of *m* in the three spectra, for E_A is, respectively, 48, 64, and 96.5 meV for C, Zn, and Cd.[24]

The pair spectra[25] of Fig. 3 were recorded photographically, using excitation intensities as low as possible, consistent with adequate resolution of the weak lines.[26] In the Cd-O pair spectrum [Fig. 3(a)], the rule of equal intensities per donor-acceptor pair would predict $I_a/I_b = 2$ for the two components of shell $m = 11$, but we measure $I_a/I_b \cong 0.25$. Lines with $m < 11$ are too weak to appear in this spectrum,[27] so there is an intensity cutoff between lines 11b and 11a, as indicated by the letter C in Fig. 3(a). The corresponding lines in the Zn-O spectrum are shown in Fig. 3(c), with $I_a/I_b \cong 1.5$, close to the expected ratio for constant-capture cross section.

The lines 11a and 11b are shell *substructure* components that must be identified by a multipole field analysis, given earlier for the Zn-O spectrum,[16] and given in the Appendix for Cd-O. Both substructure components have $m = 11$; hence they have the same value of the monopole Coulomb energy, but when the multipole terms are added they differ in total Coulomb energy by 6.1 meV for Cd-O, as shown in Table I.

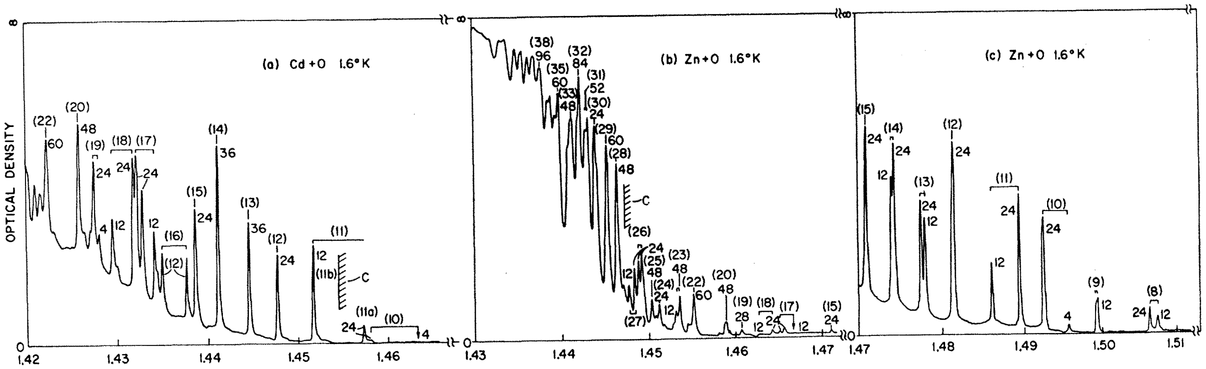

FIG. 3. Densitometer recordings from photographic plates of portions of (a) the Cd-O; (b) and (c) the Zn-O type-II infrared DA pair spectra in GaP. The bracketed integers denote the shell numbers *m*. The unbracketed integers denote the numbers of pairs within a given shell or, for close pairs, within a given shell subcomponent. The bars C mark positions at which the pair line intensities show abrupt decreases with increase in transition energy. The linewidth is limited by the instrumental resolution employed, as is true also in Figs. 4–6.

TABLE I. Data used in Eq. (4) to place limits on E_{pol}. E_{L1}, E_i, and E_{pol} all refer to the bracketed atom in each line. E_C includes multipole terms for Cd-O. All energies are in meV.

Spectrum	Line	$E_{L1}(\ )$	$E_i(\ )$	$-E_C$	$-E_{\mathrm{pol}}(\ )$
(Cd)-O	11b	>0	96.5	104.6	>8.2
(Cd)-O	11a	<0	96.5	110.7	<14.0
(Zn)-O	28	>0	64	66.4	>2.4
(Zn)-O	27	<0	64	67.7	<3.7
Zn-(S) or Cd-(S)	10	>0	104	113.5	>9.5
Zn-(S) or Cd-(S)	9	<0	104	120	<16

The tentative assumption that E_{L1} is positive for 11b and negative for 11a permits us to use Eq. (1) to calculate limits for the only unkown E_{pol}. Hence, for the h-e channel

$$-E_{\mathrm{pol}}=E_{L1}-E_A-E_C\,. \tag{4}$$

For the h-e channel the capture order of Fig. 1 is reversed, and the polarizable atom is the acceptor. If we find a reasonable value for E_{pol}, we may conclude that the likely reason for the intensity cutoff is that $\sigma_1(\text{h-e})\gg\sigma_1(\text{e-h})$; in other words the closing of the h-e capture channel for $h\nu>1.455$ eV forces the donor-acceptor pair to operate in the relatively slow electron-first capture mode.

The Zn-O spectrum in Fig. 3(b) has a similar intensity cutoff between the lines $m=28$ and 27. Multipole terms are negligibly small for this larger DA separation (19.8 Å for $m=27$ instead of 12.4 Å for $m=11$). The Coulomb energy is shown in Table I, and we again use Eq. (4) to place limits on E_{pol}. The polarization energy is expected to vary as r^{-4}, and $(19.8/12.4)^{-4}=0.15$, so the polarizabilities found for the Zn and Cd atoms are not very different.[28] The magnitudes of these and other polarizabilities will be compared with those given by Lax's formula[14] in Sec. IV.

For $m\leq 27$, the Zn-O intensities are greatly reduced, but are again roughly m independent down to $m=10$ [Fig. 3(c)]. For close DA pairs our capture model is not very useful because we do not have simple analytic expressions for the various interaction energies defined in Fig. 1. An alternative model of electron or hole capture by a dipole[29] may then be more appropriate but the dipole model does not appear to be very useful in predicting capture rates.

No intensity cutoff was observed in the C-O pair spectrum. With $E_A=48$ meV, the cutoff would be expected near $m=50$, where the lines of the spectrum are not well resolved.

We have attributed the large intensity change in the Cd-O and Zn-O spectra to the fact that $\sigma_1(\text{e-h})\gg\sigma_1(\text{h-e})$. A large first-capture inequality is not expected in general, but is thought to be due to the small capture cross section of the very deep donor O. Capture of an electron into an excited state of O is not possible for the pertinent values of m, and capture into the ground state requires the dissipation of a very large energy in multiphonon or photon emission.[17] On the other hand, $\sigma_2(\text{h-e})$ need not be small because second capture into excited states *is* possible. This explains why electron capture by O may be fast in the h-e channel but slow in the e-h channel.

A comparable intensity cutoff has not been observed in the green pair spectra that are produced when both donor and acceptor are shallow. An example is given in Sec. III B.

B. Double Cutoff in Green Pair Spectra

With the donor O replaced by S ($E_D=104$ meV),[30] the spectra of Fig. 4 were obtained[31] for comparison with Fig. 3. The cross section $\sigma_1(\text{h-e})$ does not depend significantly on the change in donor, so h-e capture must again become impossible for $m\leq 27$ in the Zn-S spectrum. No intensity cutoff is observed, however, because the replacement of O by S increases $\sigma_1(\text{e-h})$.

The comparison of Cd-S with Cd-O is somewhat different because the multipole splitting of $m=11$ is very small in Cd-S. The closing of the h-e capture channel therefore occurs between $m=11$ and 10 and apparently reduces the intensity by a factor of 2, a small reduction compared with that observed for Cd-O. The further cutoff between $m=10$ and 9 is discussed below. In view of the arguments presented in Sec. III A, we would expect $\sigma_1(\text{h-e})$ to be comparable with $\sigma_1(\text{h-e})$ for Cd-S pairs, in contrast to Cd-O pairs.

A new intensity cutoff, due to the closing of the second-capture channel, is now observed in both Zn-S and Cd-S between $m=10$ and 9. This is not unexpected, for $E_D(\text{S})$ is only 7.5 meV greater than $E_A(\text{Cd})$. It is vital to our interpretation that the cutoff occur at the same m value in both spectra of Fig. 4, for $\sigma_1(\text{e-h})$ depends only on the common donor S. With both capture channels closed for $m\leq 9$, the possibility of exciton capture[7] explains the appearance of the remaining weak lines.

The cutoff in the Zn-S spectrum was used by Hopfield to estimate $E_D(\text{S})$, neglecting $E_{\mathrm{pol}}(\text{S})$.[7] We now have better data, and a separate determination of $E_D(\text{S})$; we therefore use the cutoff and Eq. (1) to place limits on $E_{\mathrm{pol}}(\text{S})$, as shown in Table I.[32]

C. Enhanced Capture Due to Phonon Resonance

Figure 5 shows a different kind of intensity anomaly. In the unsaturated C-S and Mg-S spectra most lines obey the approximate rule of equal intensities

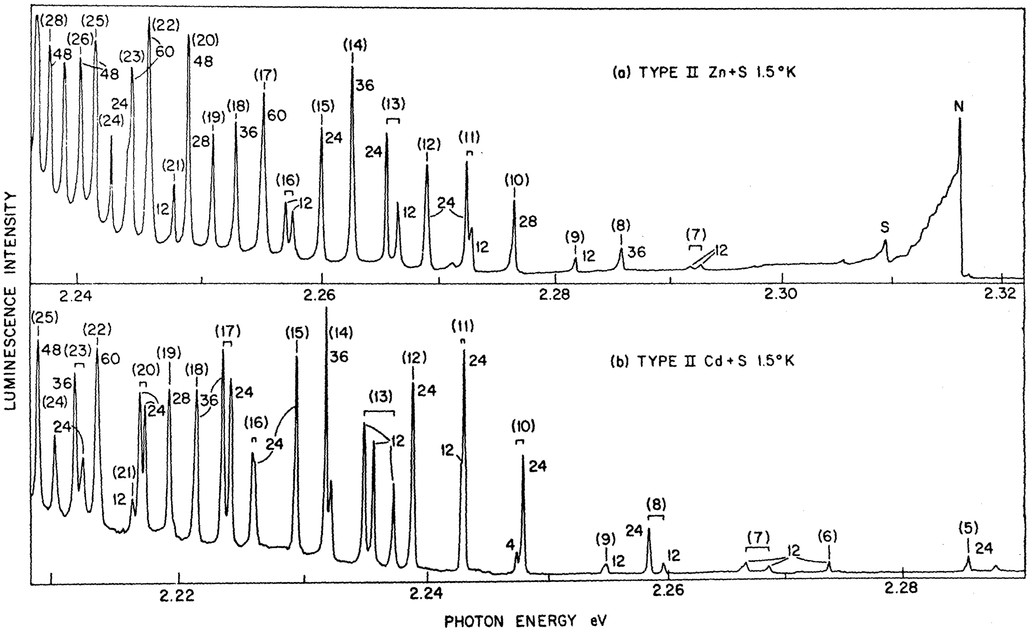

FIG. 4. Photoelectric recordings of portions of (a) the Zn-S and (b) the Cd-S unsaturated green DA pair spectra in GaP. The nomenclature is like that of Fig. 3, except that there are additional lines due to the radiative decay of excitons at neutral S donors and at N isoelectronic traps. Note that the energy scale for spectrum (b) has been shifted to the right by 0.03 eV to allow for the effect of the larger ionization energy of the Cd acceptor.

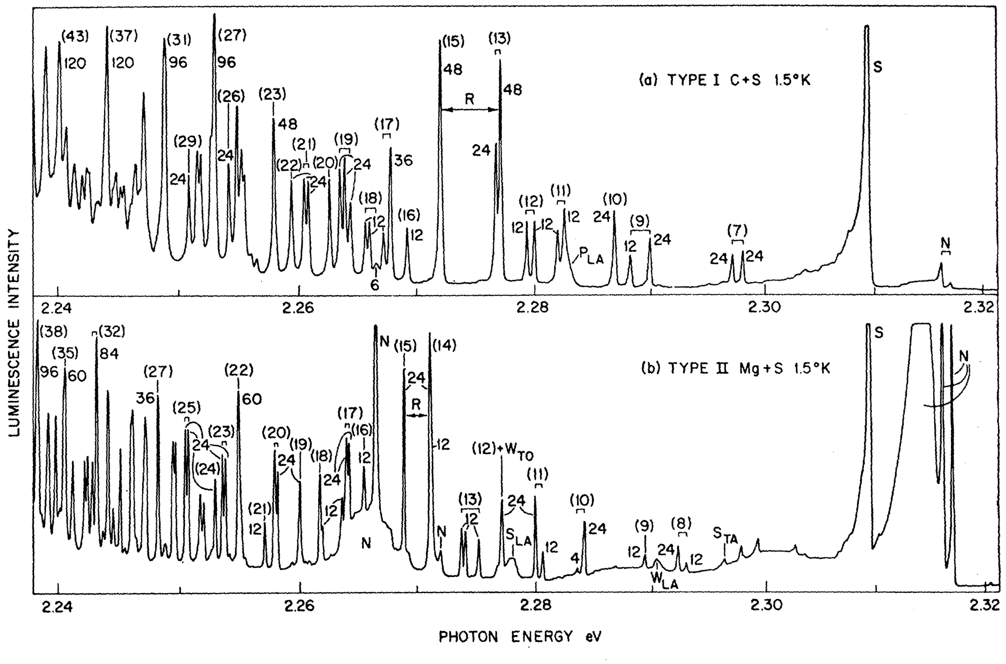

FIG. 5. Photoelectric recordings of portions of (a) the C-S and (b) the Mg-S unsaturated green DA pair spectra in GaP. The nomenclature is like that of Fig. 4, except that there are additional lines due to unknown centers (P and W). Regions in which the DA pair lines are stronger than anticipated from the indicated number of pair sites are denoted by R.

TABLE II. Data used in Eq. (2) for E_{L2}. The unknown $E_{\rm pol}$ refers to the bracketed donor atom, which captures first, and it is adjusted to make E_{L2} equal to a TO or LO phonon energy. The DA separation at resonance is taken as the average separation of pairs with enhanced capture rates. All energies are in meV.

Spectrum	Lines	av r (Å)	E_{L2}	E_A	$-E_{\rm vdW}$	$-E_{\rm pol}(\ )$
C-(S)	13-15	14.41	45.5	48	5	7.5
Mg-(S)	14-15	14.35	50.2	53.5	5	8.3
C-(Se)	15	14.92	45.5	48	5	7.5

per donor-acceptor pair, but m = 15 and 13 in C-S[33] and m = 15 and 14 in Mg-S (marked R in Fig. 5) are distinctly stronger than expected.[34] The fact that no such enhanced intensity was observed in Zn-S and Cd-S (Fig. 4) suggests that the effect is related to hole capture. C and Mg are shallow acceptors with E_A = 48 and 53.5 meV, respectively,[35] and the h-e capture channel is closed (E_{L1} negative) in the region of enhanced intensity. The cross section of interest is therefore σ_2(e-h).

We calculate E_{L2}(e-h), using Eq. (2), and find the values shown in Table II. The $E_{\rm vdW}$ was measured by fitting the spectra using Eq. (3) and $E_{\rm pol}$-(S) was first estimated by using the limits on $E_{\rm pol}$-(S) in Table I. Finally, the suggestion of resonance with a TO or LO phonon[36] was used to adjust $E_{\rm pol}$ to the value shown. Confidence in our interpretation of the enhanced intensity therefore requires the final value of $E_{\rm pol}$ (S) to be a reasonable one. A discussion of $E_{\rm pol}$ and a comparison with theory are given in Sec. IV.

Figure 6 shows C-Se and Zn-Se pair spectra for comparison with C-S and Zn-S. Replacement of S by Se should make little difference in capture processes, for E_D(Se) is only ≈ 2 meV less than E_D(S). A phonon resonance is observed for m = 15 in C-Se as in C-S, but m = 13 is now off resonance.[37] Zn-Se is consistent with Zn-S in that no resonance is seen.

The absence of resonance for the deeper acceptors is easily explained. Equation (2) shows that E_{L2} differs from E_A only by the *difference* between the two small quantities $E_{\rm pol}$ and $E_{\rm vdW}$. Hence, the requirement for resonance is that E_A be only *slightly* larger than $\hbar\omega_{\rm TO}$ or $\hbar\omega_{\rm LO}$. For C, with E_A = 48 meV, E_{L2} can be reduced to $\hbar\omega_{\rm TO}$ = 45.5 meV, but there cannot be a resonance with LO, for which $\hbar\omega$ = 50.2 meV. For Mg, with E_A = 53.5 meV, E_{L2} is reduced to 50.2 meV at m = 15 and 14, but never reaches 45.5 meV for resonance with TO.

We have not observed capture enhancement by phonon resonance when $E_{L1} = \hbar\omega_{\rm TO}$ or $\hbar\omega_{\rm LO}$. For the impurities used (except O), E_{L1} is always less than these phonon energies except at large m where the spectral lines are unresolved.

The second-capture channel is closed for $m \leq 9$ in all our S or Se spectra, but there is not always

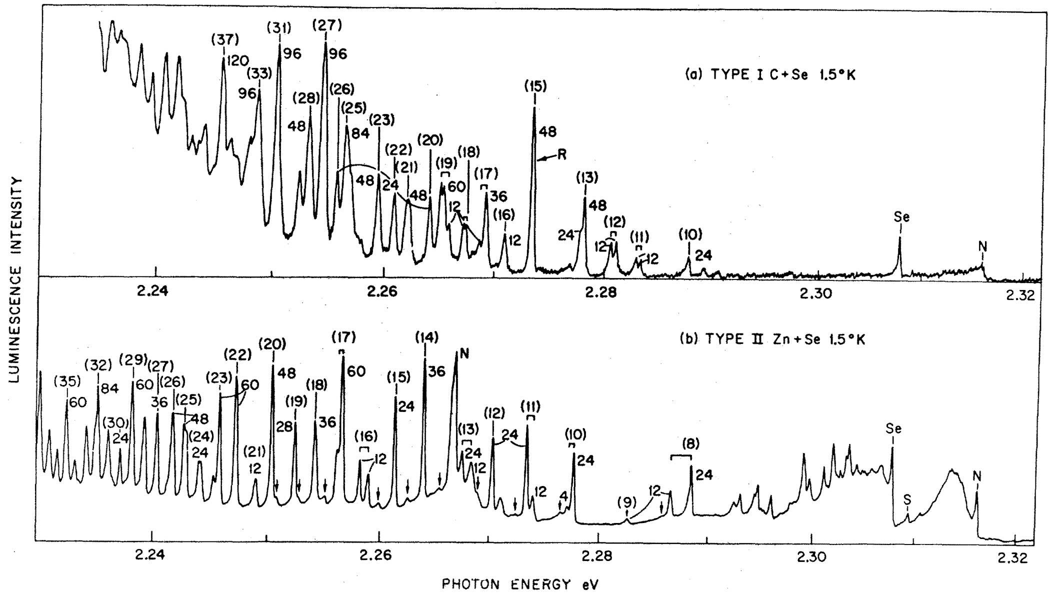

FIG. 6. Photoelectric recordings of portions of (a) the C-Se and (b) the Zn-Se unsaturated green DA pair spectra in GaP. The nomenclature is like that of Fig. 5. Line 15 in the C-Se pair spectrum, marked R, is unexpectedly strong according to the indicated numbers of pair sites. No such effect is found in the Zn-Se pair spectrum. The weak lines, indicated by vertical arrows in the Zn-Se pair spectrum, are due to Zn-S pair transitions.

an intensity cutoff in the exciton-capture region. The rate of exciton capture depends not only on capture cross sections but also on the exciton density. Thus, the relative intensity of lines with $m \leq 9$ depends on additional factors not considered here, such as sample purity and particle lifetimes.

IV. DISCUSSION

In this section it is shown that the deduced values of E_{pol} in Tables I and II are reasonable in magnitude and consistent with each other, supporting our interpretation of the intensity anomalies. However, the deduced E_{pol} is smaller than predicted by Lax's formula, which is based on the model of a hydrogenlike atom in a dielectric continuum.[14] It is possible that the calculated E_{pol} is too large for close pairs, for the calculated E_{vdW} is known to be much too large under these circumstances.

A. Comparison of Experimental and Calculated E_{pol}

An approximate value of E_{pol} for a hydrogenlike atom in GaP is obtained by assuming unity effective mass $(m^* = m_0)^{38}$ and the corresponding ionization energy $E_0 = 118$ meV. Using the known value of E_{pol} of the hydrogen atom (monopole-dipole approximation) and considering only the effect of the dielectric[14] with $\epsilon = 10.75$,[11] we find a factor ϵ^{-2} from Lax's Eq. (6.2) and a factor ϵ^4 from Lax's Eq. (6.5), giving

$$-E_{\text{pol}}(m_0,\, E_0) = -\epsilon^2 E_{\text{pol}}(\text{H}) = (5.53\times 10^5/r^4)\,\text{meV Å}^{-4}\,. \tag{5}$$

This value of $-E_{\text{pol}}$ is shown as the straight line in Fig. 7 for comparison with the plotted experimental values from Tables I and II. It should be remembered that the r^{-4} dependence of E_{pol} given in Eq. (5) is rigorous only for large r compared with the orbital diameter of the neutral center.

A correction to Eq. (5) for effective mass m^* and true ionization energy E_1 is made by using Lax's Eq. (6.5).

$$E_{\text{pol}}(m^*, E_i)/E_{\text{pol}}(m_0, E_0) = (m_0/m^*)\;(E_0/E_i)^2\;. \tag{6}$$

Values of E_i for the polarizable atoms Zn, Cd, Se, and S are, respectively, 64, 96.5, 102, and 104 meV. The large correction for the E_i of Zn (>3) spoils the apparent agreement of Fig. 7. The smaller corrections for the other atoms increase the discrepancy between calculated and experimental values. Use of an effective mass $m^* < m_0$ would further increase the disagreement.

There is some doubt[14] about what value of effective mass to use in Eq. (6), so no further adjustments are made in the theoretical E_{pol}. Recent values proposed for the effective masses are $m^* = 0.33m_0$ for the electron,[30] and $m^* = 0.3m_0$ for the hole.[39] These values would yield ionization energies of 39 meV for donors and 35 meV for acceptors. The actual E_i are, in most cases, closer to 118 meV, the magnitude for $m^* = m_0$.

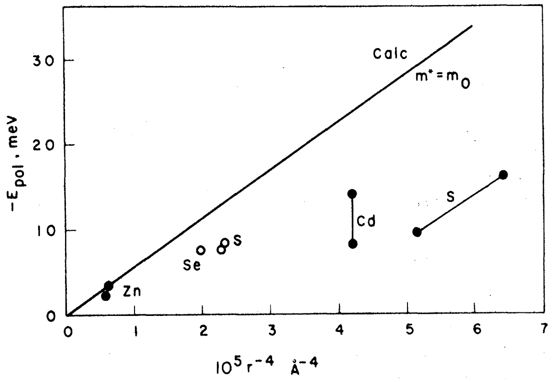

FIG. 7. Comparison of calculated and experimental values of E_{pol}. The calculated value, linear in r^{-4}, is drawn for effective mass $m^* = m_0$, with $E_i = E_0 = 118$ meV, the ionization energy for unity effective mass. The experimental values are for four different atoms, as indicated. The E_{pol} limits in Table I are plotted and joined. The single values of E_{pol} from Table II are shown as open circles.

We conclude that the experimental values of E_{pol} are smaller than calculated values by factors of order 3 or more. However, there is fairly good consistency among the E_{pol} values, and this gives support to our interpretation of the data.

The validity of the calculated E_{pol} is in doubt when the DA separation is not much larger than the size of the polarizable atom. The calculated Bohr radii are ≈ 6 Å for $m^* = m_0$. S is the only atom for which we have obtained limits on E_{pol} at two different DA separations, and it appears from Fig. 7 that the polarizability is less for the closer pairs (larger r^{-4}). The failure of the calculated E_{vdW} for close pairs is quite obvious in the experimental data and is discussed in Sec. IV B.

B. Evaluation of E_{vdW}

Equation (3) is used in the initial fitting of a DA pair spectrum. Inclusion of the term $E_{\text{vdW}} \propto r^{-6}$ improves the fit, but only for rather large r (often for $r > 20$ Å).[1-3] The large and increasing disagreement shown in Refs. 1–3 for $r < 15$ Å indicates that the usual (dipole-dipole) formula for E_{vdW} is invalid for close pairs. In this region the observed E_{vdW} is very much *less* than the value predicted for dipole-dipole interaction. A similar failure of the formula for E_{pol} is plausible, but the experimental data for E_{pol}, unlike those for E_{vdW}, are too few to fix the interval in which failure occurs. We cannot tell, at present, whether or not this accounts for some or all of the disagreement shown in Fig. 7.

The evaluation of the dipole-dipole component of E_{vdW} by fitting pair spectra is difficult. At small m the calculated values are invalid, and at large m the van der Waals interaction is negligible. The E_{vdW} term is therefore used only in a limited portion of the spectrum, where it appears as a correction to the much larger Coulomb energy term. Thus, a small error in E_C can lead to a large percentage error in E_{vdW}. The uncertainty in E_C is almost entirely due to the uncertainty in the dielectric constant. In previous work, values of $\epsilon = 10.18$[1-3] and $\epsilon = 11.1$[6] have been used. We now use the recent low-temperature value of $\epsilon = 10.75$,[11] and we note that this leads to considerably smaller E_{vdW} than reported in Ref. 3.

V. SUMMARY

Eight examples of abrupt intensity changes with changing shell number m have been given. These have been explained in terms of critical values of the energies E_{L1} and E_{L2} and the resulting changes of capture mode. Many critical values of E_{L1} and E_{L2} are reached *without* an observed intensity change, for one of the following reasons. (i) The intensity of saturated pairs does not depend on capture rates. (ii) Many of the capture-mode changes are predicted to occur at large m, where the spectral lines are unresolved. (iii) The closing of one capture channel has no great effect on the intensity unless capture is slow in the second channel. (iv) The closing of both capture channels has no great effect unless exciton capture is slow.

E_{L1} is a function of the relatively large Coulomb energy E_C, and therefore has a strong dependence on m. E_{L2} is not a function of E_C and has a weak dependence on m, hence does not reach as many critical values as E_{L1} does. In the examples given, E_{L2} reaches the critical phonon resonance only for impurities with relatively small ionization energies.

Identification of an intensity change with a certain critical value of E_{L1} or E_{L2} puts limits on E_{pol}, the only unknown in Eqs. (1) and (2). Values of E_{pol} obtained in this way are plotted and found to be smaller than the calculated values. The reason for this disagreement is not clear. There is a strong dependence of the measured E_{vdW} on the value used for the dielectric constant.

APPENDIX

After the infrared spectra of Ref. 5 were published it was shown that shell *substucture* components could be identified by means of a multipole analysis of the final-state interaction, i.e., the interaction between donor and acceptor ions.[16] For the Zn-O spectrum this analysis led to a reassignment of some shell numbers, the new assignments being used in Figs. 3(b) and 3(c). We now present a similar analysis of the Cd-O spectrum in order to identify the substructure components in Fig. 3(a).

The leading multipole terms permitted by the symmetry of the zinc-blende lattice have the directional properties of third- and fourth-order lattice harmonics.

$$V_3 + V_4 = k_3\, xyz / r^7 + k_4 (x^4 + y^4 + z^4 - 0.6 r^4) / r^9 \,. \quad \text{(A1)}$$

If V_3 and V_4 are positive, they increase the final-state energy and should therefore be subtracted from the right-hand side of Eq. (3) if E_C refers to the monopole term only. The coefficients k_3 and k_4 are determined by fitting the spectrum. We take $k_3 = -2.4 \times 10^5$ Å^4 meV, the same as that used for the Zn-O spectrum, consistent with the belief that it should be attributed to the O donor. The value $k_4 = 2.8 \times 10^6$ Å^5 meV is 50% larger than for Zn-O, and is thought to be due to the Cd ion, since the term V_4 is negligible in the C-O spectrum.[12]

Table III shows the calculated values of V_3 and V_4 for $8 < m < 18$. The substructure is not well resolved for larger m, and the calculated V_3 and V_4 fail to fit the data for smaller m. (The fit for $m = 10$ is also poor.)

The failure of the calculated V_3 and V_4 for close pairs probably arises from our omission of multipole terms for the initial state (before electron-hole recombination). The initial-state interaction for distant pairs is E_{vdW}, calculated for spherical atoms. For close pairs, however, overlapping of the wave functions leads to distortions that induce multipole components. Thus, fitting the data for close pairs would require extra multipole terms with complex dependence on m. Other evidence of overlapping wave functions is the additional splitting of some lines, e.g., $m = 9$. Such splittings are probably due to *j-j* interaction between the bound electron and hole.[40] For $m = 9$, $r \approx 11$ Å, which is less than twice the approximate Bohr radius of ≈ 6 Å.

Figure 8 shows that a fairly good fit to the data in Table III is possible with the inclusion of V_3 and V_4. The apparent paucity of spectral lines is partly explained by our failure to resolve the predicted close doublets for $m = 14$ and $m = 13$(a and c). In addition, reexamination of the data disclosed that 10b had been incorrectly identified in Ref. 5 as an excited-state line (ES). The only missing line now is 13b, a line that may also be missing in the Zn-O spectrum.[16]

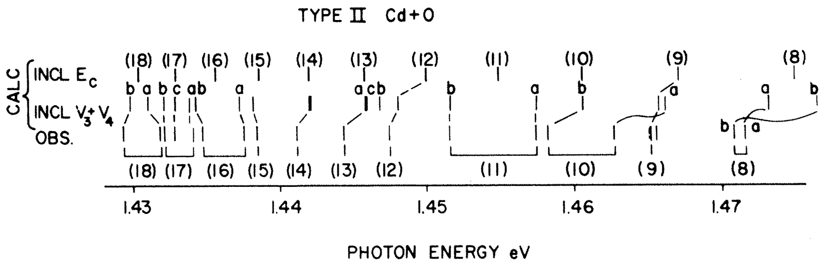

FIG. 8. Comparison of observed and calculated energies of some spectral lines in the Cd-O pair spectrum in GaP, with two degrees of refinement in the calculated values. In the top line, only the Coulomb interaction energy is considered with $\epsilon = 10.75$ and $(E_A + E_D) = 992$ meV. The middle line also includes the effect of the multipole terms V_3 and V_4 defined in the text.

TABLE III. Calculated monopole term $-E_c$ and multipole terms V_3 and V_4, and comparison of the calculated and observed photon energies in the Cd-O infrared pair spectrum in GaP. The reassigned shell numbers and the corresponding set $\langle uvw \rangle$ are given in columns 1 and 2, the old shell numbers (Ref. 5) are in column 9. The theoretical intensities (numbers of sites) are given in column 8.

New shell m	Set $\langle uvw \rangle$	$-E_c$ (meV)	V_3 (meV)	V_4 (meV)	Calc. (eV)	Obs. (eV)	Calc. intensity	Old shell m
8a	731	127.9	−0.9	+2.6	1.4732	1.4714	24	8
8b	$5\bar{5}3$		+3.3	−4.9	1.4765	1.4708	12	8
9	$7\bar{3}3$	120.1	+1.8	−0.5	1.4658	1.4654	12	9
10a	555	113.5	−2.4	−3.3	1.4662	1.4626	4	?
10b	$7\bar{5}1$		+0.7	−0.8	1.4606	1.4583	24	ES
11a	753	107.9	−1.4	−1.4	1.4577	1.4575	24	10
11b	911		−0.1	+3.4	1.4516	1.4517	12	11
12	$9\bar{3}1$	103	+0.3	+1.6	1.4481	1.4476	24	12
13a	933	98.8	−0.6	+0.5	1.4459	1.4444	12	13
13b	771		−0.3	−0.7	1.4468	...	12	Not seen
13c	$7\bar{5}5$		+1.2	−1.4	1.4460	1.4444	12	13
14a	951	95.0	−0.3	+0.1	1.4422	1.4411	24	•••
14b	$7\bar{7}3$		+0.8	−0.9	1.4421	1.4411	12	14
15	$9\bar{5}3$	91.6	+0.6	−0.2	1.4382	1.4385	24	14
16a	775	88.6	−0.8	−0.9	1.4373	1.4376	12	15
16b	$11,\bar{1},1$		0	+1.3	1.4343	1.4349	12	16
17a	955	85.9	−0.6	−0.4	1.4339	1.4342	12	16
17b	11,3,1		−0.1	+0.8	1.4322	1.4323	24	17
17c	$9\bar{7}1$		+0.2	−0.2	1.4329	1.4329	24	17
18a	973	83.4	−0.4	−0.3	1.4311	1.4319	24	17
18b	$11,\bar{3},3$		+0.2	+0.4	1.4298	1.4296	12	18

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[1] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters 10, 162 (1963).

[2] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. 133, A269 (1964).

[3] F. A. Trumbore and D. G. Thomas, Phys. Rev. 137, A1030 (1965).

[4] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. 140, A202 (1965).

[5] P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. 168, 812 (1968).

[6] P. J. Dean, C. J. Frosch, and C. H. Henry, J. Appl. Phys. 39, 5631 (1968).

[7] J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

[8] F. M. Ryan and R. C. Miller, Phys. Rev. 148, 858 (1966), in BP; M. R. Lorenz, T. N. Morgan, G. D. Pettit, and W. J. Turner, *ibid.* 168, 902 (1968), in AlSb.

[9] Other smaller multipole interactions will be considered later.

[10] The grouping into shells and the type of spectrum depend on whether donor and acceptor substitute on the same sublattice (type I), or on different sublattices (type II). Shell $m=1$ comprises the closest pairs permitted by the lattice structure. For the relation between DA separation and shell number m see Ref. 1 or 2.

[11] L. Patrick and P. J. Dean, Phys. Rev. 188, 1254 (1969).

[12] L. Patrick, Phys. Rev. Letters 21, 1685 (1968).

[13] There are some exceptions. Intensities in the broadband part of the spectrum were thoroughly investigated in a study of recombination kinetics by Thomas *et al.* (Ref. 4). Hopfield proposed to use the intensity cutoff

at small m to evaluate the ionization energy of the deeper member of the DA pair (Ref. 7).

[14] M. Lax, Phys. Rev. 119, 1502 (1960).

[15] M. Lax, J. Phys. Chem. Solids 8, 66 (1959).

[16] L. Patrick, Phys. Rev. 180, 794 (1969).

[17] The entire energies E_{L1} and E_{L2} are not necessarily given to the lattice. For example, most of the energy E_{L1} may appear as electromagnetic radiation for deep donors or acceptors. Efficient electron-capture luminescence has been observed for the abnormally deep donor O in GaP [P. J. Dean and C. H. Henry, Phys. Rev. 176, 928 (1968)].

[18] $E_C = -e^2/\epsilon r$, where r is the DA separation, and $\epsilon = 10.75$ is the low-temperature dielectric constant of Ref. 11.

[19] Hopfield shows (Ref. 7) that a close DA pair may capture an exciton even though it cannot capture the electron and hole separately.

[20] The full energy E_{L1} is eventually given to the lattice or dissipated in other ways as the electron drops into the ground state.

[21] The Thomson theory discussed by Lax (Ref. 14) would give σ_1 proportional to r^3.

[22] Deduced from effective-mass values considered later. The deep donor O is an exception.

[23] Revised value of E_D from Ref. 11.

[24] Revised values of E_A obtained with the use of new data discussed in Ref. 11.

[25] We have maintained the customary order in naming impurities. The donors O, S, and Se are usually named second. Some authors prefer to invert this order for reasons of consistency with the "donor-acceptor" class name.

[26] Most of the oscillator strength of these deep DA pair transitions is contained in phonon replicas (Ref. 5), unlike the shallow DA pair spectra in GaP (Ref. 2).

[27] Stronger excitation and longer photographic exposure times brought out lines down to $m = 6$ in Ref. 5.

[28] There is considerable uncertainty in E_{pol} (Cd) because the position of the cutoff is not sharply defined, and in E_{pol} (Zn) because the small value depends strongly on the accuracy of E_A.

[29] R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spectr. 4, 51 (1960).

[30] A. Onton, Phys. Rev. 186, 786 (1969).

[31] The greater intensity of these line spectra and the more favorable spectral region permitted the use of photomultipliers as detectors.

[32] These limits would be altered slightly if the multipole terms were added to E_C.

[33] The C-S spectrum is type I and therefore has no line for $m = 14$ (see Ref. 1).

[34] It is necessary to measure line *areas* in making these comparisons. Note that the stronger component of line 11 in Fig. 5(a) and lines 12 and 15–18 in Fig. 5(b) are distorted by the presence of overlapping extraneous luminescence.

[35] An analysis of the Mg-S pair spectrum shows that $E_A(\text{Mg}) - E_A(\text{C}) = 5.5$ meV. This analysis will be reported elsewhere.

[36] The phonon energies were measured by A. S. Barker, Jr., Phys. Rev. 165, 917 (1968).

[37] In the absence of a careful fitting of the C-Se spectrum it was assumed that $-E_{\text{vdW}} = 5$ meV (Table II) because of the similarity to C-S.

[38] To minimize a notational difficulty, carrier masses appear only as m^* or m_0, never as m, the shell number symbol.

[39] This value is an average between the light and heavy hole masses calculated by R. A. Faulkner (private communication) from the valence-band parameters of M. L. Cohen and T. K. Bergstresser [Phys. Rev. 141, 789 (1966)], assuming infinite spin-orbit splitting.

[40] Splittings of this type are most significant in the Cd-O pair spectrum, and were not seen in the C-O spectrum, where both impurities have small spin-orbit splittings. A large j-j splitting has been observed for the $m = 1$ line in the Cd-O spectrum by C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. 166, 754 (1968).