

- ⁶J. S. Berkes, S. W. Ing, Jr., and W. J. Hillegas, *J. Appl. Phys.* **42**, 4908 (1971).
⁷J. Dresner and G. B. Stringfellow, *J. Phys. Chem. Solids* **29**, 303 (1968).
⁸J. Feinleib, J. deNeufville, S. C. Moss, and S. R. Ovshinsky, *Appl. Phys. Lett.* **18**, 254 (1971).
⁹N. Morimoto, *Mineral. J. (Sapporo)* **1**, 160 (1954).
¹⁰A. A. Vaipolin, *Kristallografiya* **10**, 596 (1965) [*Sov. Phys.-Crystallogr.* **10**, 509 (1966)].

- ¹¹C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory* (Benjamin, New York, 1964), p. 120.
¹²M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952).
¹³L. C. Cusachs, *J. Chem. Phys. Suppl.* **43**, S157 (1965).
¹⁴This degeneracy is based on the layer symmetry, and not the crystal symmetry. The former is discussed by R. Zallen, M. L. Slade, and A. T. Ward, *Phys. Rev. B* **3**, 4257 (1971).
¹⁵M. E. Sharfe, *Phys. Rev. B* **2**, 5025 (1970); M. D. Tabak and P. J. Warter, Jr., *Phys. Rev.* **173**, 899 (1968).

PHYSICAL REVIEW B

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Pair Spectra and the Shallow Acceptors in ZnSe

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Donor-acceptor pairs associated with the three effective-mass-like donors Al, Ga, and In have been observed in the photoluminescence spectra of ZnSe. The previously determined binding energies of these donors are ~ 28 meV. Under conditions of weak excitation, the distant pair band peaks at an energy of ~ 2.69 eV. The identification of discrete pair lines indicates that both the donor and acceptor are on the same sublattice. The shift of all pair lines by 0.05–0.1 meV to lower energy when crystals are doped with the Li^6 isotope proves that the acceptor is substitutional Li, with a binding energy $E_A = 114 \pm 2$ meV. A second shallow acceptor, tentatively assigned to Na, has $E_A \sim 90$ –100 meV, estimated from the corresponding bound-exciton line. Another more complex pair spectrum is reexamined. The discrete pair lines for this system exhibit a doubling of all lines, but the chemical identity of the donor and acceptor producing this spectrum remains undetermined.

I. INTRODUCTION

The observation and analysis of the many sharp lines appearing in donor-acceptor pair spectra is a powerful tool for understanding the nature of the common donors and acceptors in a compound semiconductor. This recombination process, where an electron on a donor recombines with a hole on an acceptor, was first suggested by Prener and Williams¹ to interpret broad green and red luminescence bands in ZnS. However, detailed evidence for this process was not obtained until the characteristic sharp-line structure resulting from many different discrete pairs was observed and analyzed in GaP.^{2,3} The kinetics of pair recombination is now well understood,⁴ and a large amount of detailed information about impurities in GaP has resulted from studies of pair spectra.⁵⁻⁷ Discrete pair lines have also been observed in BP,⁸ AlSb,⁹ and SiC.^{10,11} More recently, pair spectra have also been observed in several II-VI compounds.¹²⁻¹⁶

This paper is the third of a series on the optical properties of ZnSe. In the first¹² (hereafter referred to as DM), analysis of a discrete-line pair spectrum indicated that the donor and acceptor were on the same sublattice, but it could not be determined whether the Zn or Se site was involved, and the impurities responsible were not chemically identified. The second paper¹⁷ (re-

ferred to as MKNS) presented a detailed study of the optical properties of excitons bound to the common simple donors in ZnSe, and the binding energy was determined for five shallow donors: Al, Ga, In, Cl, and F. The present paper is a continuation of the work reported by MKNS. For the three metal-ion donors Al, Ga, and In, pair spectra have been observed with discrete lines. Analysis of these pair lines proves that for each pair both the donor and the acceptor belong to the same sublattice; the acceptor must therefore also be on the Zn site. When crystals are grown in the presence of the Li^6 isotope, the resulting energy shift of the pair lines proves that the acceptor is substitutional Li. Finally, the pair spectrum reported by DM is reexamined in light of the above results, and the differences between this pair system and those involving the three metal ions are discussed.

II. EXPERIMENTAL

Most of the experimental techniques used in this work have already been described by MKNS. The crystals were grown from the vapor phase using a technique which has previously been described.¹⁸ Crystals were doped with Li and Na by adding the carbonates of these alkali metals to the ZnSe charge, along with excess Zn. Successive growth runs without additional doping are an essential feature of this technique. A few attempts were also

made to diffuse Li and Na into the crystals after growth by sealing them in quartz ampoules with the alkali metal.

Photoluminescence was excited with an argon-ion laser operating in the uv. The crystals were immersed in liquid helium which could be pumped below the λ point. The laser radiation was usually focused on the surface of the sample to excite the discrete pair lines, which require intense excitation for their observation. To study the pair bands themselves weak excitation (i. e., unfocused laser light) was used.

III. PAIR SPECTRA

A typical donor-acceptor pair spectrum is shown in low resolution in Fig. 1(a). The I_1^{DEEP} , I_1^{X} , and I_2 lines arise from the recombination of excitons bound to neutral acceptors and donors.¹⁷ At lower energies, strong phonon replicas of the two I_1 lines occur, separated by the energy of the LO phonons, 31.9 ± 0.1 meV. In addition to these strong bound-exciton lines and their phonon replicas, there are a large number of sharp closely spaced pair lines which merge into a broad band, Q_0 . Two LO-phonon replicas of this band are also seen, denoted by Q_1 and Q_2 . To a first approximation, the energy of an individual pair line is given by

$$h\nu = E_g - (E_A + E_D) + e^2/\epsilon r, \quad (1)$$

where E_g is the band gap, E_A and E_D are the acceptor and donor binding energies, ϵ is the dielectric constant, and r is the donor-acceptor (or "shell") separation. For close pairs, a polarization interaction must also be considered. Dis-

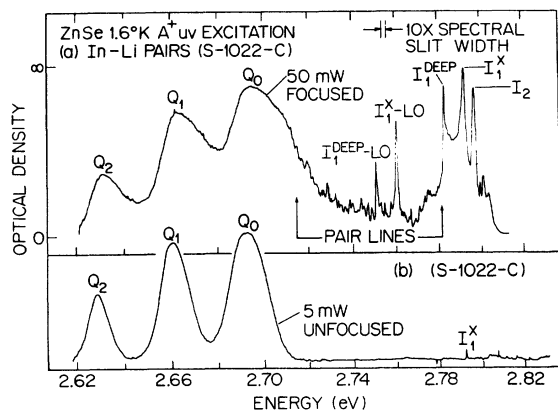


FIG. 1. Photoluminescence intensity vs photon energy of a crystal showing discrete pair lines in the region indicated, and the associated pair band (Q_0) and its LO-phonon replicas (Q_1 and Q_2). The sharp lines above 2.78 eV are bound-exciton lines. (a) and (b) show the same crystal under conditions of strong and weak excitation, respectively.

TABLE I. Inequivalent sites and their degeneracies for type-I pair spectrum. The shell number is defined in Ref. 3. The number of inequivalent sites and their degeneracies have been calculated for shells 1-500 by R. A. Faulkner (unpublished) for both type-I and type-II pairs. These results, which have been used in the present work for identification of observed lines, correct several errors which appeared in earlier papers (e. g., Refs. 3 and 5) caused by ignoring the lack of inversion symmetry in the zinc-blende lattice (T_d symmetry).

Shell number	Number of inequivalent sites	Degeneracies	Number of lines observed (Fig. 2)
10	1	24	1 ^a
11	2	12, 12	2
12	2	12, 12	2
13	3	24, 24, 24	3
14	0	...	0
15	2	24, 24	2
16	1	12	1
17	3	12, 12, 24	2
18	3	12, 12, 6	3 ^a
19	4	24, 24, 12, 12	4
20	1	24	1
21	2	24, 24	1 ^{a,b}
22	2	12, 12	2
23	2	24, 24	2
24	2	4, 4	1
25	4	24, 24, 12, 24	3
26	1	24	1
27	6	12, 12, 12, 12, 24, 24	3
28	2	24, 24	2
29	1	24	1
30	0	...	0

^aObserved in the Ga-Li pair system.

^bThese lines are obscured by I_1^{X} -LO.

crete pair lines result because r can take on only discrete values, determined by the lattice constants and structure of the material. Fine structure can arise for each pair line if there are inequivalent sites in a given shell. If the intensity of the exciting light is low, distant pair recombination dominates, and only the broad "distant pair band" Q_0 is observed, as seen in Fig. 1(b).

The pair lines shown in Fig. 1(a) can be clearly resolved, as shown in Fig. 2. The identification of individual lines in this spectrum is made on the basis of type-I pairs, for which both the donor and acceptor are on the same sublattice. Significantly poorer results are obtained when one tries to fit the data to a type-II assignment (pairs on different sublattices). The shell numbers of pair lines are given in parentheses. Fine structure splittings for close pairs are indicated. The numbers not in parentheses indicate the total number of pairs with a given separation; i. e., within a given shell. Gaps in this spectrum expected to occur for "shells" having no lattice sites³ are denoted by G. Table I lists the degeneracies of inequivalent sites predicted on the basis of a type-I spectrum for shells numbered 10 through 30, and the corresponding number of lines actually observed. Closer pairs are not observed because

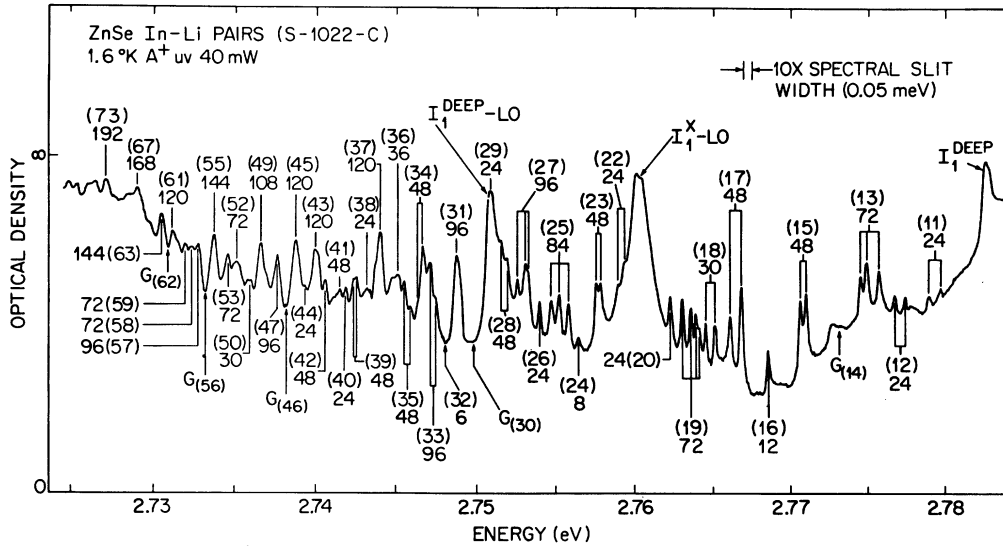


FIG. 2. High-resolution luminescence spectrum of the pair lines shown in Fig. 1(a). The lines are identified according to a type-I pair spectrum, for which both the donor and acceptor are on the same lattice site. The brackets indicate inequivalent sites with the same separation (same shell); the shell number for each separation is given in parentheses. The numbers not in parentheses give the total number of pairs in each shell. Empty shells, for which gaps in the spectrum are anticipated, are denoted by G. The gap at (32) is not a true gap, but this shell has only six equivalent sites and should therefore be very weak. The fine structure degeneracies for each shell are given in Table I.

they overlap with the strong bound-exciton spectrum.

The spectrum shown in Fig. 2 was observed in a crystal which was doped with In during growth; the correlation with donor doping will be discussed further in Sec. IV. Similar spectra have been obtained from crystals doped with Al or Ga. The energies of the pair lines are plotted as a function of lattice separation in Fig. 3 for these three pair spectra. The values of $E_A + E_D$ for each pair system, obtained by extrapolating the Coulomb term (solid curve) to $r \rightarrow \infty$, are indicated on the figure.

IV. DONORS ASSOCIATED WITH THE PAIRS

During the course of these experiments, indistinct pair spectra were occasionally seen in nominally undoped samples. However, the three pair systems plotted in Fig. 3 were obtained when the crystals were purposely doped with Al, Ga, or In. The procedure used for doping was described in detail by MKNS. Briefly, a doping run was generally made by adding a small amount of the impurity of interest to the furnace tube; the resulting crystals were usually heavily overdoped, showing only strong unresolved lines in the luminescence spectrum. Subsequent runs were then made without adding more of the impurity, relying on the contamination of the furnace tube. Usually the pair lines were discernible best in the more heavily doped of these runs, whereas the bound-exciton lines were still broad from overdoping. As the doping level decreased in further furnace

runs, the pair lines became weak, and the bound-exciton lines and two-electron transitions grew sharp and dominant. In a few cases of undoped or low-doped crystals, two interleaved pair spectra could be discerned. The presence of the donors Ga and In in nominally undoped samples, and the erratic appearance of the Al donor under various growth conditions, have already been discussed by MKNS. It is not surprising that pair spectra are also occasionally seen in these undoped crystals. However, the best pair spectra (denoted in Fig. 3 as Al-Li, Ga-Li, and In-Li pairs) were obtained when the crystals were purposely doped with Al, Ga, or In, respectively.

If it is assumed that the same acceptor is involved in each of these three pair spectra, then the difference in the values of $E_A + E_D$ listed in Fig. 3 gives the difference in the donor binding energies. Agreement with the results of MKNS for the donor energies falls within the experimental error (± 1 meV) of extrapolating the Coulomb curve. In fact, it is possible to measure these energy differences more accurately by measuring the energy differences of actual pair lines ($\Delta h\nu_r$) at several lattice separations, using the more distant pair lines. Then, for a given lattice separation r , we have

$$\begin{aligned} \Delta h\nu_r &= [E_g - (E_A + E_D^{(2)}) + e^2/\epsilon r] \\ &\quad - [E_g - (E_A + E_D^{(1)}) + e^2/\epsilon r] \\ &= E_D^{(1)} - E_D^{(2)} \equiv \Delta E_D \end{aligned} \quad (2)$$

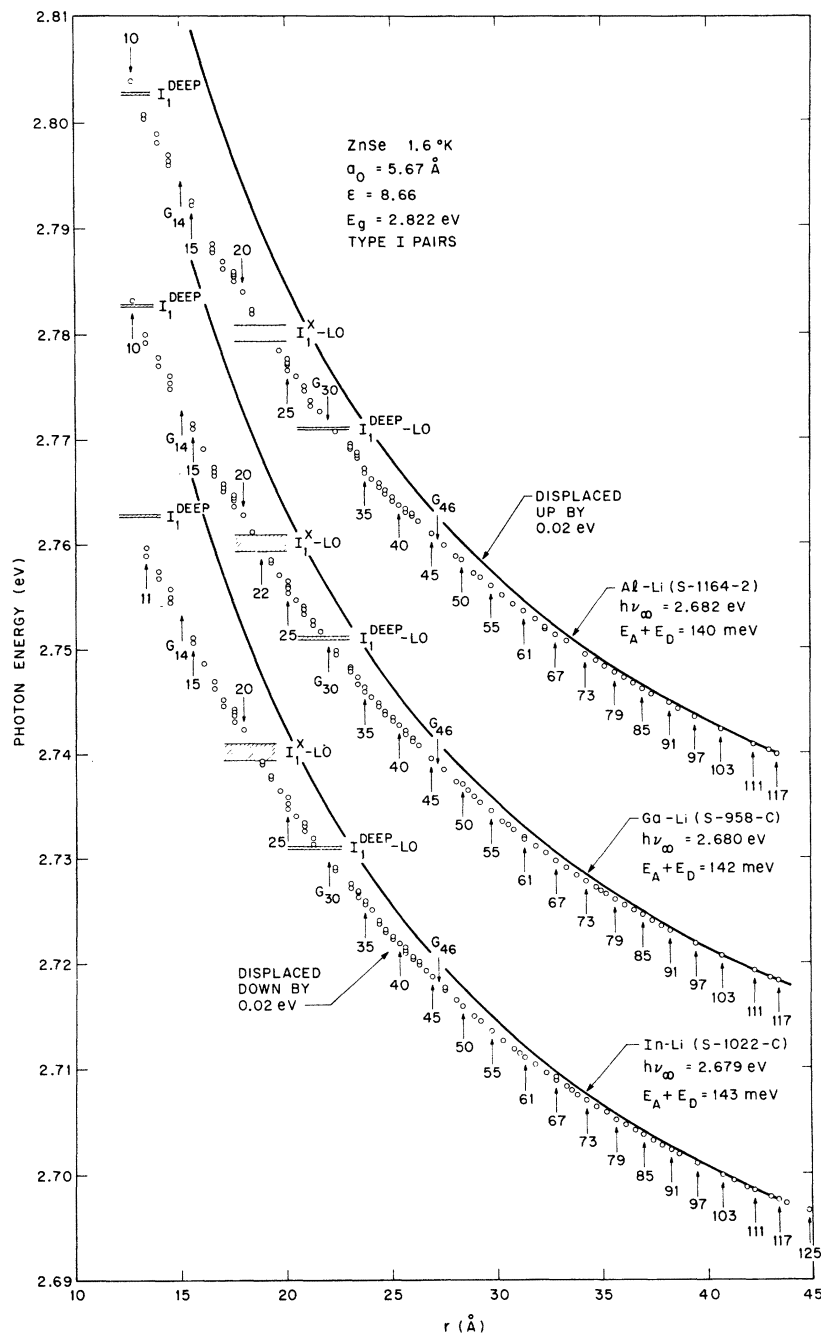


FIG. 3. Photon energy of the discrete pair lines vs lattice separation for the three pair spectra observed when crystals are doped with Al, Ga, and In. The shell numbers for many of the lattice spacings are indicated by arrows, as are the gaps in the spectra (denoted by G) predicted on the assumption of type-I pairs. The positions and widths of the bound-exciton lines I_1^{DEEP} , $I_1^{\text{X-LO}}$, and $I_1^{\text{DEEP-LO}}$ are indicated by shaded bands because they overlap with the pair lines. The solid curves are a plot of the Coulomb term $e^2/\epsilon r$, fit to the data points at large separations. By extrapolating the Coulomb curve the value of $h\nu_\infty$ and hence $E_A + E_D$ can be determined for each pair system. The data points and solid curves have been displaced for the Al-Li and In-Li systems for clarity. Systematic deviations from Eq. (1) occur for pair separations less than $\sim 30 \text{ \AA}$ (\sim shell 55) because of polarization interactions.

for two donors of binding energy $E_D^{(1)}$ and $E_D^{(2)}$. The differences in donor binding energy between the Al and Ga donors ($\Delta E_D^{\text{Al-Ga}}$) and between the Ga

and In donors ($\Delta E_D^{\text{Ga-In}}$) obtained in this way for five shells in the pair spectra are tabulated in Table II. Comparison is also made with the same energy

TABLE II. Differences in donor binding energies (all energies in meV).

(a) Determined from the pair spectra		
Shell number	ΔE_D^{Al-Ga}	ΔE_D^{Ga-In}
97	1.6 ± 0.1	0.9 ± 0.1
103	1.6 ± 0.1	0.9 ± 0.1
111	1.6 ± 0.1	0.9 ± 0.1
115	1.7 ± 0.1	0.8 ± 0.1
117	1.6 ± 0.1	0.9 ± 0.1
Avg.	1.6 ± 0.1	0.9 ± 0.1
(b) Determined from the two-electron transitions (Ref. 17)		
Donor	$E_{2p}-E_{1s}$	ΔE_D
Al	19.14 ± 0.04	} $\Delta E_D^{Al-Ga} = 1.6 \pm 0.1$
Ga	20.72 ± 0.04	
In	21.69 ± 0.04	

differences obtained by MKNS to ± 0.1 meV from the two-electron transitions. The excellent agreement of these results combined with the doping experiments proves that (i) the donors involved in the three pair spectra are the three simple substitutional group-III donors Al, Ga, and In, and (ii) the same acceptor is present as a common contaminant in each of these pair spectra. More than one acceptor could be involved only if the difference of their hole binding energies is ≤ 0.1 meV. The acceptor must also be on a Zn site, since the pair spectra are all type I.

V. ACCEPTORS

A. Li Acceptor Associated with the Pairs

The binding energy for the acceptor participating in the pair spectra can be determined by subtracting the values of E_D measured by MKNS from

TABLE III. Li-acceptor binding energy.

Donor	$E_A + E_D$ (meV) (Fig. 3)	E_D (meV) (Ref. 17)	Li acceptor E_A (meV)
Al	140 ± 1	26.3 ± 0.6	114 ± 2
Ga	142 ± 1	27.9 ± 0.6	114 ± 2
In	143 ± 1	28.9 ± 0.6	114 ± 2

the sums $E_A + E_D$ given in Fig. 3. This is done in Table III, yielding $E_A = 114 \pm 2$ meV. The most obvious candidate for a simple shallow acceptor at a Zn site in ZnSe is substitutional Li, which has a covalent radius very close to that of Zn,¹⁹ and should therefore fit easily into the ZnSe lattice. Li and Na have been found to be the only soluble shallow acceptors in CdS and CdSe,²⁰ and the covalent radius of Li is much closer to that of Zn than Cd. Attempts to dope ZnSe with Li, as discussed below, tend to confirm this identification.

However, the definitive proof that Li is the acceptor associated with the Al, Ga, and In pairs is the observation of the isotope shifts of the pair lines when crystals are doped with the Li^6 isotope. Such shifts have clearly established the identity of the Li acceptor in CdS, and their origin is at least qualitatively understood.²⁰ Figure 4 compares pair spectra obtained from ZnSe crystals lightly doped with In and either the Li^6 isotope or naturally abundant Li (mostly Li^7). For the crystal doped with Li^6 , all the pair lines are shifted ≤ 0.1 meV to lower energy, as can be seen by comparison with the calibration line and the In two-electron transitions also shown in the figure. The decrease in the isotope shift from 0.09 meV (shell

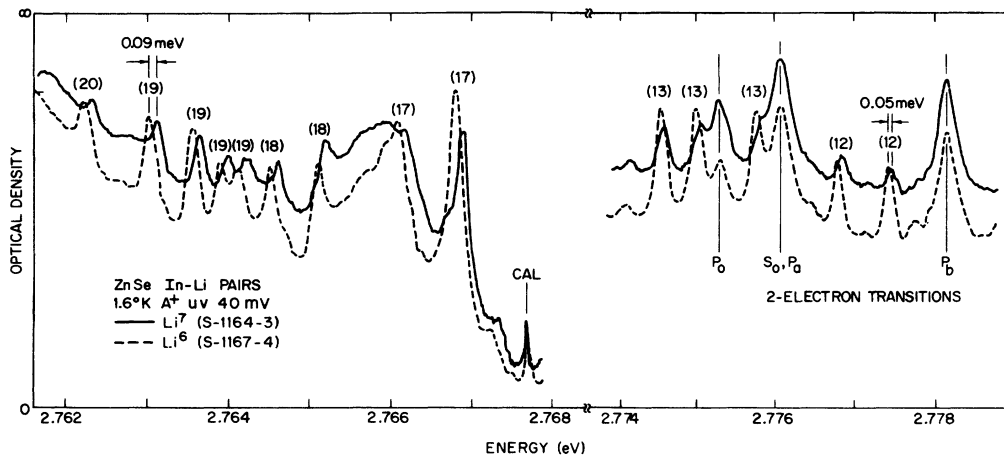


FIG. 4. Portions of the donor-acceptor pair line spectra for crystals lightly doped with In and either the naturally abundant Li (mostly Li^7) (solid line) or Li^6 isotope (broken line). The In two-electron transitions p_0 , s_0 and p_a , and p_b (which have been identified in Ref. 17) and the calibration line occur at the same energy in both spectra, as expected. The isotope shift of the pair lines, which varies from 0.09 (shell 19) to 0.05 meV (shell 12), proves unambiguously that substitutional Li at a Zn site is the acceptor participating in the three pair spectra shown in Figs. 2 and 3. The resolution used for these spectra is given by the half-width of the calibration line.

19) to 0.05 meV (shell 12) is expected, because for close pairs the hole becomes delocalized from the Li acceptor due to repulsion from the donor. This isotope shift proves unambiguously the participation of Li in this pair spectrum, and since the same simple acceptor at a Zn site is involved in all three pair systems, it must be substitutional Li.

B. Excitons Bound to Neutral Acceptors (I_1 Lines)

1. Lithium

Halsted and Aven²¹ have found that the binding energy for an exciton bound to a neutral donor (E_{BX}) in many of the II-VI compounds is related to the acceptor binding energy E_A by $E_{\text{BX}}/E_A \approx 0.1$. This relationship was verified by Henry *et al.*²⁰ for the shallow Li and Na acceptors in CdS and CdSe (cf. Table IV). Using this rule, one would expect to find an I_1 line associated with the ZnSe donor-Li pair spectra at an energy of ~ 10 or 11 meV below the energy of the free exciton. In fact, the binding energies E_{BX} for the two dominant I_1 lines in ZnSe, I_1^{X} and I_1^{DEEP} , are 9.5 and 18.8 meV, respectively. (These are the separations of the lowest-energy components of the lines from the free-exciton energy taken to be 2.8015 eV; cf. MKNS.)

Very little can be said about the I_1^{DEEP} line on the basis of the experiments reported in this paper. Both the I_1^{DEEP} and I_1^{X} lines exhibit the strong series of LO-phonon replicas which is characteristic of the I_1 lines in CdS and CdSe,²⁰ and it was pointed out by DM that the I_1^{DEEP} line (referred to as the I_1 line in that work) showed typical I_1 behavior for various heat treatments. In contrast to this behavior, the I_1^{X} line (called I_X by DM) increases when the samples are heated in Zn vapor, at least for the Wright-Patterson (WP) crystals studied by DM. It was reported by DM that there appeared to be a correlation between the I_1^{X} line and the pair spectrum reported in that work (which will henceforth be referred to as the DM pair system). However, in the crystals grown at Bell Laboratories for the present paper (grown by vapor transport in the presence of excess Zn), the I_1^{X} line is always present, and is intense when the Al-Li, Ga-Li, or In-Li pair systems are observed. Because of this correlation, the expected exciton binding energy for this line, and the structure of the I_1^{X} line discussed below, we now believe that the I_1^{X} line results from the recombination of an exciton bound to the neutral Li acceptor; whether or not it is also associated with the more complicated DM pairs is presently uncertain.

Under conditions of high resolution, the I_1^{X} line is found to be a triplet. (This can be seen in Fig. 1 of MKNS.) As the temperature is increased from

1.6 to 4.2 °K, the relative intensities of the higher-energy components increase. This thermalization indicates that the splitting is in the excited state of the bound-exciton complex. The triplet structure could arise from transitions from the $J = \frac{5}{2}$, $\frac{3}{2}$, and $\frac{1}{2}$ excited states of the bound-exciton complex (two holes and one electron) to the $J = \frac{3}{2}$ ground state (a single hole). However, it must be emphasized that this model can be corroborated only by studying its piezo- or magneto-optical behavior.

Chemical doping experiments were attempted to confirm this identification of the I_1^{X} line with the Li acceptor. When a small amount of Li_2CO_3 was added to the furnace tube, the crystals were found to be heavily overdoped; broad luminescence bands were observed near the band edge and intense pair bands were seen. Analysis of these crystals by emission spectroscopy showed that they contained ~ 50 -ppm Li, compared with < 1 -ppm Li for undoped material. In crystals grown during subsequent runs, relying on Li contamination, the I_1^{X} line was usually found to dominate the spectrum; the concentration of Li in these crystals varied between 1 and 5 ppm. The Al-Li or Ga-Li pair spectra were also usually observed in these crystals lightly doped with Li.

Similar results were obtained when Li was diffused into undoped samples. For diffusion temperatures of 600 or 450 °C, only strong, broad-band luminescence was observed. When Li was diffused at 300 °C, discrete lines could be seen. The I_1^{X} line dominated the bound-exciton spectrum, and Ga-Li pair lines could be distinguished.

2. Sodium

Another weak triplet occasionally appears in the luminescence spectra of ZnSe at an energy of 1 meV higher than the I_1^{X} triplet. The three components of this line have approximately the same intensity distribution as the components of I_1^{X} , and

TABLE IV. Shallow acceptor and exciton binding energies.

	Acceptor	E_{BX} (meV)	E_A (meV)	E_{BX}/E_A
ZnSe	Li	9.5	114 ± 2	0.083
	(Na) ^a	8.5	$(90-100)^b$	$(0.1)^b$
	I_1^{DEEP}	18.8	$(\sim 200)^b$	$(0.1)^b$
CdS	Li ^c	17.67	165 ± 6	0.107
	Na ^c	17.50	169 ± 6	0.103
CdSe	Li or Na ^c	9.15	109 ± 6	0.084

^aThe chemical identification of Na is inconclusive, as discussed in the text.

^bFor these cases, E_A was estimated assuming $E_{\text{BX}}/E_A \sim 0.1$.

^cDetermined by Henry *et al.*, Ref. 20.

also thermalize as a function of temperature. It is tempting to associate this triplet with the Na substitutional acceptor, the other soluble shallow acceptor in CdS. The exciton binding energy for this line is $E_{BX} = 8.5$ meV, leading to an anticipated acceptor binding energy for Na of $E_A \sim 90$ – 100 meV, i. e., less binding than for the Li acceptor. In CdS the Na acceptor is deeper than Li, whereas the two appear to be indistinguishable in CdSe (cf. Table IV). Attempts to confirm this chemical identification of the I_1^X line by doping with Na were inconclusive, however, which may result from the poor fit of the Na atom into the ZnSe lattice.

VI. DM PAIR SPECTRUM

During the course of this work, the pair spectrum reported by DM has been observed indistinctly in a few Bell Laboratories crystals, but usually interleaved with one of the simple pair spectra discussed above. The I_1^X bound-exciton line, attributed to Li, is thought to be associated with the simple pair spectra. Whether or not Li also participates in the DM pairs is presently unknown. In the WP crystals, individual DM pair lines have been resolved better than in the original work, probably because the less penetrating uv-focused-laser excitation samples a smaller region of the crystal. The energies of the discrete DM pair lines have therefore been measured more ac-

curately. It was found that this spectrum closely resembles the three simple pair spectra plotted in Fig. 3, but that each line in the simple spectra is split into two lines in the DM spectrum. This is illustrated in Fig. 5, where portions of the In-Li pair spectrum which have clearly resolved pair lines are plotted below the corresponding portions of the DM pair spectrum. The doubling of the DM pair lines is evident from the figure. The splitting of each pair of lines is approximately 0.3 meV, although the splitting appears to be slightly smaller for the higher-energy lines. In most cases the lower-energy line of each pair appears to be stronger, and the lines do not appear to thermalize between 4.2 and 1.6 °K.

The energies of the individual DM pair lines have been plotted as a function of lattice separation in Fig. 6 of the original paper (DM). The spectrum is also type I. A value of $E_A + E_D = 141$ meV was obtained from that plot, which agrees to within experimental error with the more accurate value obtained in the present work: $E_A + E_D = 140 \pm 1$ meV. The DM pair lines are very close in energy to the Al-Li pairs.

In addition to the doubling of the DM pair lines, there appears to be another important difference between the DM pairs and the other three simple spectra: the large energy difference between the positions of the peaks of the distant pair bands, R_0 for the simple pairs, and the band denoted R_0 in

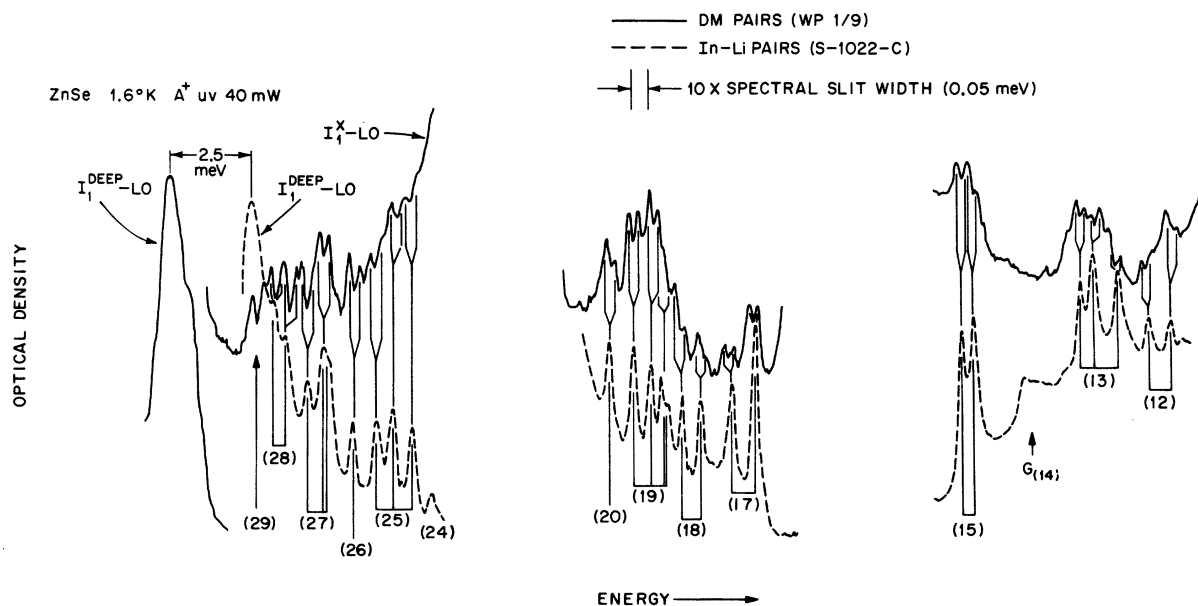


FIG. 5. Comparison of portions of the DM pair spectrum (solid line) with the corresponding In-Li pair lines (broken line). The portions of the In-Li spectrum shown here are taken from Fig. 2. The shell numbers are indicated in parentheses. For each line in the In-Li pair spectrum, two lines are seen in the DM system, with a splitting of ~ 0.3 meV. To make this comparison, the two spectra have been shifted by 2.5 meV, as indicated by the apparent separation of the $I_1^{\text{DEEP-LO}}$ lines, which should appear at the same energy.

Ref. 12 for the DM pairs, which peaks ~ 17 meV above Q_0 . On the basis of the thermal quenching behavior of Q_0 and R_0 , the following suggestion was advanced by DM: The Q_0 band involves impurities with a large difference in binding energies (this has been confirmed by MKNS and this paper: $E_D \approx 28$ meV and $E_A = 114$ meV), but the donor and acceptor responsible for R_0 are probably more comparable in energy. Thus, the donor participating in the DM pairs was expected to be considerably deeper than the effective-mass-like donors identified thus far. However, the discrete pair lines associated with Q_0 , reported in Sec. IV above, were not observed by DM.

This model of a deep donor participating in the DM pairs is inconsistent with the close similarity of the line spacing and fine structure of the discrete DM pair lines and the other pair systems (neglecting the unexplainable doubling of lines in the DM pairs). If the donor on the DM pairs were considerably deeper than the shallow donors Al, Ga, and In, the pattern of individual lines and their deviation from the Coulomb curve should be significantly altered, which is not the case.

It now seems likely that this apparent contradiction results from an erroneous identification of R_0 as the distant pair band for the DM pair lines. Well-resolved DM pair lines have been seen in only a few WP crystals, in which both the Q_0 and R_0 bands are present. It is quite difficult in such cases to determine unambiguously which of the two bands is the distant pair peak. Crystals containing the DM and Al-Li pair lines have been studied under a variety of excitation intensities; the results for intermediate excitation (weak but resolvable pair lines, fairly strong pair bands) are shown in Fig. 6. The Al-Li pairs behave as expected; discrete lines merge into a very broad continuous band peaking just below 2.70 eV. The appearance of the DM pairs is quite different; the band R_0 rises rather abruptly, with discrete pair lines observable quite close to its peak. It is possible that R_0 is another unrelated band (with the thermal and excitation behavior reported by DM) and that the DM pair lines actually merge into Q_0 . From these results the authors can draw no definite conclusions regarding the distant pair peak for the DM pairs, nor have the chemical identities of the donor and acceptor been determined for this system. However, we have established that the second pair spectrum shifted 2.0 ± 0.2 meV to lower energy, reported by DM, is the Ga-Li system, with Q_0 as its distant pair peak. If Q_0 is also the distant pair peak for the DM pairs, then this system may also involve the Li acceptor and a Zn-site donor, which must however give rise to a doubling of all pair lines.

VII. SUMMARY AND CONCLUSIONS

Three separate donor-acceptor pair systems have been studied in this paper. The well-resolved fine structure of individual pair lines in each spectrum closely agrees with a type-I assignment, indicating that both the donor and acceptor are on the same sublattice. Doping experiments show that the three donors involved are Al, Ga, and In, whose binding energies have been determined by MKNS. From this it can be concluded that the acceptor must be the same in all three cases, must be located at a Zn site, and has a binding energy $E_A = 114 \pm 2$ meV. The acceptor has been positively identified as substitutional Li by the observation of isotope-shifted pair lines when crystals are doped with Li⁶.

Two bound-exciton lines in the luminescence spectrum have been tentatively identified as the recombination of excitons bound to the neutral Li and Na acceptors, although the evidence for the latter assignment is far from conclusive. The acceptor binding energies for these two impurities, $E_A = 114 \pm 2$ meV (Li) and $E_A \sim 90$ –100 meV (Na?), are in reasonable agreement with the estimated effective-mass binding energy for acceptors in ZnSe, $E_0 \approx 107 \pm 15$ meV.²² The soluble alkali atoms therefore appear to be shallow acceptors in ZnSe, as is the case in CdS and CdSe. A third deep bound exciton usually seen in ZnSe is believed to correspond to a deep acceptor ($E_A \sim 200$ meV) because of its exciton binding energy, strong

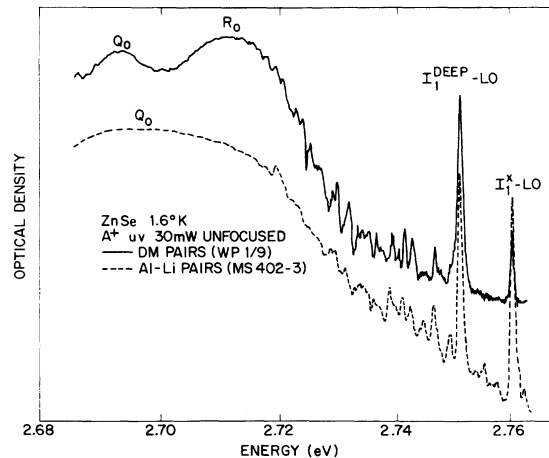


FIG. 6. Low-resolution spectra of the DM pair system (solid line) and the Al-Li pair system (broken line) using an excitation intensity which is intermediate between the strong excitation of Fig. 1(a) and the weak excitation of Fig. 1(b). Under these conditions the discrete pair lines and bands are observable. From comparisons of this sort it is difficult to determine which of the bands Q_0 or R_0 is the distant pair peak associated with the DM pair lines.

phonon replicas, and behavior with annealing. This acceptor may arise from native defects.

Another pair spectrum, the first for which individual pair lines have been identified in any II-VI compound, has been reexamined under conditions of better resolution. It was found that each pair line in any of the three simpler pair spectra is doubled in the DM pairs. The original suggestion that this spectrum might arise from a deep donor seems to be inconsistent with the similarity of line spacing and fine structure with the other pair systems. The chemical identities of the donor and acceptor responsible for this spectrum have not been determined.

On the basis of the evidence presented here, the hopes for converting ZnSe to low-resistivity *p*-type material do not look promising. Li, and possibly Na, are the only soluble shallow acceptors that have been observed. In CdS it was found

that Li and Na compensate themselves, and it was suggested that they may do so by forming shallow interstitial donors.²⁰ The same mechanism is possible in ZnSe. The other alkali acceptors are believed to be insoluble in ZnSe, and the group-V acceptors are known to be deep.²³⁻²⁵

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¹J. S. Prener and F. E. Williams, *J. Electrochem. Soc.* **103**, 342 (1956).

²J. J. Hopfield, D. G. Thomas, and M. Gershenson, *Phys. Rev. Lett.* **10**, 162 (1963).

³D. G. Thomas, M. Gershenson, and F. A. Trumbore, *Phys. Rev.* **133**, A269 (1964).

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

⁵F. A. Trumbore and D. G. Thomas, *Phys. Rev.* **137**, A1030 (1965).

⁶P. J. Dean, C. H. Henry, and C. J. Frosch, *Phys. Rev.* **168**, 812 (1968).

⁷P. J. Dean, C. J. Frosch, and C. H. Henry, *J. Appl. Phys.* **39**, 5631 (1968).

⁸F. M. Ryan and R. C. Miller, *Phys. Rev.* **148**, 858 (1966).

⁹M. R. Lorenz, T. N. Morgan, G. D. Pettit, and W. J. Turner, *Phys. Rev.* **168**, 902 (1968).

¹⁰W. J. Choyke, D. R. Hamilton, and L. Patrick, *Phys. Rev.* **133**, A1163 (1964).

¹¹W. J. Choyke and L. Patrick, *Phys. Rev. B* **2**, 4959 (1970).

¹²P. J. Dean and J. L. Merz, *Phys. Rev.* **178**, 1310 (1969).

¹³C. H. Henry, R. A. Faulkner, and K. Nassau, *Phys. Rev.* **183**, 798 (1969).

¹⁴C. H. Henry, K. Nassau, and J. W. Shiever, *Phys. Rev. Lett.* **24**, 820 (1970).

¹⁵D. C. Reynolds and T. C. Collins, *Phys. Rev.* **188**, 1267 (1969).

¹⁶Unpublished work of P. J. Dean (CdTe), C. H. Henry (CdSe), and J. L. Merz (ZnTe).

¹⁷J. L. Merz, H. Kukimoto, K. Nassau, and J. W. Shiever, *Phys. Rev. B* **6**, 545 (1972).

¹⁸K. Nassau and J. W. Shiever, *J. Cryst. Growth* **13/14**, 375 (1972).

¹⁹R. T. Anderson, *Chemical Periodicity* (Reinhold, New York, 1960).

²⁰C. H. Henry, K. Nassau, and J. W. Shiever, *Phys. Rev. B* **4**, 2453 (1971).

²¹R. E. Halstead and M. Aven, *Phys. Rev. Lett.* **14**, 64 (1965).

²²This was calculated using the static dielectric constant $\epsilon = 8.66$ and the hole effective mass $m_h = 0.6m_e$ (where m_e is the mass of an electron); cf. Ref. 17.

²³B. Tell, *J. Appl. Phys.* **41**, 3789 (1970).

²⁴R. K. Watts, W. C. Holton, and M. de Wit, *Phys. Rev. B* **3**, 404 (1971).

²⁵A. R. Reinberg, W. C. Holton, M. de Wit, and R. K. Watts, *Phys. Rev. B* **3**, 410 (1971).