PHYSICAL REVIEW B VOLUME 14, NUMBER 12 15 DECEMBER 1976

Pair spectra, edge emission, and the shallow acceptors in melt-grown ZnSe

V. Swaminathan* and L. C. Greene

Air Force Materials Laboratory, Electromagnetic Materials Division, Wright-Patterson Air Force Base, Ohio 45433

(Received 25 June 1976)

The nature of edge emission bands in the photoluminescence spectra of as-grown, annealed, and electron-irradiated melt-grown ZnSe crystals at 4.2°K has been investigated. Five different edge emission bands associated with donor-acceptor pair recombination are identified. These bands have their zero-phonon peaks at 4566, 4587, 4595, 4606, and 4625 Å. A high-energy series, free-to-bound recombination band, is observed at 77°K in association with the band at 4625 Å. The bands at 4566, 4587, and 4595 Å are seen only in annealed crystals; the band at 4625 Å is seen only in as-grown crystals; whereas the band at 4606 Å is observed in annealed and as-grown crystals. Discrete pair lines have been resolved only for the bands at 4566 and 4587 Å. It is recognized that the band at 4606 Å is the previously studied group-III-donor–$\mathrm{Li_{Zn}}$ recombination band and that the band at 4587 Å is the as yet unidentified complex pair band reported by Dean and Merz. A study of the bound exciton lines occurring with the edge emission indicates that the band at 4625 Å arises from group-III-donor–$\mathrm{Na_{Zn}}$ recombination. The acceptor ionization energy, E_A, of $\mathrm{Na_{Zn}}$ is deduced to be 122 meV. From the analysis of the discrete pair lines associated with the bands at 4566 and 4587 Å and from the results of electron irradiation and annealing experiments it is suggested that these two bands involve the same donor and acceptor and that the shorter-wavelength band arises from preferential pairing and the longer-wavelength band from random pairing of the donor and acceptor centers. The donor and the acceptor are tentatively assigned to be the doubly ionized zinc interstitial, Zn_i, and the singly ionized complex $(\mathrm{Na_{Zn}}\,V_{\mathrm{Se}})$, respectively. The ionization energy of the complex center, $(\mathrm{Na_{Zn}}\,V_{\mathrm{Se}})$, is estimated from the corresponding bound exciton line to be 80–100 meV. The pair band at 4595 Å is tentatively assigned to a group-III-donor–$(\mathrm{Li_{Zn}}\,V_{\mathrm{Se}})$ transition, and this acceptor has $E_A = 110$–130 meV, estimated from the corresponding bound exciton line.

I. INTRODUCTION

The low-temperature photoluminescence spectra of II-VI compounds near the band edge exhibit well-developed structure consisting of many sharp lines and broad bands. Based on the most extensive studies of these spectra in CdS, which normally crystallizes in the hexagonal (wurtzite) structure, the sharp lines have been attributed to the radiative decay of free excitons and excitons bound to localized donor or acceptor impurities.[1] The origin of the so-called broad "edge emission" bands has been the subject of investigation for many years.[2] Often two series of LO-phonon assisted bands are observed separated by a few hundredths of an eV. The high-energy series (HES) is generally seen at high temperatures (typically liquid-nitrogen temperature) and high excitation intensities, while the low-energy series (LES) is prominent at very low temperatures (typically liquid-helium temperature) and at low excitation intensities. It is now generally accepted that the HES arises from the recombination of free electrons with holes bound to acceptors ("free-to-bound" recombination), and that the LES involves recombination of distant donor-acceptor (*D-A*) pairs.[3,4] A unique characteristic of the LES bands is that they exhibit sharp line structure due to transitions at pairs with different discrete values for the separation between the donor and the acceptor. Such structured *D-A* pair spectra have been identified in several II-VI compounds.[2] It is the chemical identification of the donors and the acceptors involved in the LES bands in cubic ZnSe that is the subject of the present investigation.

In this paper we report the results of low-temperature photoluminescence measurements of undoped ZnSe and ZnSe doped with Li, Na, K, Ag, Al, Ga, In, In and Na, LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, or KI. The chemical doping experiments are supplemented by parallel studies of the effects of postgrowth annealing treatments and electron irradiation on the photoemission. The information thus obtained along with the results of the optical measurements of previous investigators enable us to propose models for the chemical identity of the defect centers in the *D-A* pair recombination in ZnSe.

II. BACKGROUND

A. Bound excitons

Merz *et al.*[5] examined in detail the optical properties of substitutional donors in ZnSe. They identified for Al, Ga, In, Cl, and F, the I_2 lines resulting from the radiative recombination of excitons bound to neutral donors and the corresponding I_3 lines (excitons bound to the ionized donors). Three I_1 lines (excitons bound to neutral acceptors), I_1^x, I_1^y, and I_1^{DEEP} have also been identified.[6,7]

The I_1^x line has been associated with a substitutional lithium acceptor $\mathrm{Li_{Zn}}$.[7] The origin of the other two lines is less certain, though it has been suggested that I_1^y and I_1^{DEEP} may be associated with sodium and a native defect, respectively.[5,7] (See also Ref. 10.)

B. Edge emission

The first detailed report of edge emission bands in zinc selenide was made by Reynolds *et al.*[8] In their type-II zinc selenide crystals a series of broad bands with a leading peak at 4598 Å observed at 4.2°K was attributed to donor-acceptor (D-A) pair recombination.[9] They designated this peak as $L10$. This may have been the same band that Dean and Merz[6] reported at a somewhat longer wavelength, which they called Q. They also reported another band near 4587 which they called R. Liang and Yoffe[10] observed in Mn-ion bombarded hexagonal ZnSe a band at 4608 Å. Iida[11] reported a band at 4588 Å and calculated the acceptor ionization energy $E_A = 100$ meV and the donor ionization energy $E_D = 26$ meV.

The first observation of structured D-A pair spectra in ZnSe was made by Dean and Merz[6] (DM). They reported two bands, X0-4587 (R) and X0-4606 (Q), in undoped crystals annealed at 600–700°C in zinc atmospheres. [The notation used in this paper immediately identifies the peak in question. X means LES (Y for HES), the zero indicates the zero-phonon peak, and the number gives the approximate wavelength. A letter in parentheses indicates the notation used in the reference under discussion.] The observed fine structure was associated with X0-4587 and $E_A + E_D \simeq 140$ meV was estimated. (This band is referred to as DM spectrum in the literature.[2,7]) From the thermal quenching behavior of the bands Dean and Merz[6] proposed that the donor and acceptor involved in X0-4587 have comparable ionization energies, i.e., $E_A \simeq E_D \simeq 70$ meV. They also noted that the individual pair lines were split into two lines with a splitting of 0.3 meV.

Merz *et al.*[7] studied in detail the pair spectra in ZnSe doped with Li and Al, Ga, or In. They identified three pair spectra all with $E_A + E_D$ close to 140 meV and all involving $\mathrm{Li_{Zn}}$—proved by the observation of an isotope shift of the pair lines when crystals were doped with the ^{6}Li isotope—and the shallow donors $\mathrm{Al_{Zn}}$, $\mathrm{Ga_{Zn}}$, or $\mathrm{In_{Zn}}$. The I_1^x(Li) bound-exciton line which occurred with these bands was thus associated with $\mathrm{Li_{Zn}}$. Based on the close similarity of the DM spectrum (neglecting the doubling of lines in the DM pairs) and the three group-III-donor–$\mathrm{Li_{Zn}}$ bands, Merz *et al.*[7] suggested that the original hypothesis that the DM spectrum might arise from a deep donor ($E_D \simeq 70$ meV) was probably erroneous and that the DM pair lines really merged into[6,7] X0-4606 (Q), the $\mathrm{Al_{Zn}}$-$\mathrm{Li_{Zn}}$ pairs. Dean,[2] however, argued against this explanation and contended that the donor involved in the DM spectrum is a deeper donor than the shallow group-III donors, and that the acceptor involved is not $\mathrm{Li_{Zn}}$, but might be an axial defect.

Chatterjee *et al.*[12] and Rosa and Streetman[13] in their photoemission studies observed that X0-4587 (R) responded to Na doping. Therefore, they suggested that this band is due to $\mathrm{Al_{Zn}}$-$\mathrm{Na_{Zn}}$ pair recombination and estimated from the peak position of the HES band associated with X0-4587 an acceptor ionization energy of 100 meV for $\mathrm{Na_{Zn}}$. Bouley *et al.*[14] also obtained a similar value for $E_A(\mathrm{Na_{Zn}})$ from their photoemission studies on ZnSe : Ga + Na. These authors, however, did not observe the discrete pair lines associated with X0-4587. The above mentioned hypothesis, that the donor and acceptor involved in X0-4587 are a group-III donor and $\mathrm{Na_{Zn}}$, respectively, fails to explain the characteristics of the DM spectrum. First, E_D of a group-III donor is only $\simeq 30$ meV,[5] as compared to $E_D \simeq 70$ meV estimated for the donor in DM spectrum.[6] Second, a simple substitutional acceptor such as $\mathrm{Na_{Zn}}$ could not account for the doubling of the pair lines in DM spectrum.[2,6]

Gezci and Woods[15] recently reported in undoped ZnSe three different series of pair bands at 10°K with their zero-phonon wavelengths at 4630 (S), 4615 (S') and 4590 (S'') Å. Pair lines associated with any of these bands were not detected. The bands at 4630 and 4615 Å were seen in crystals grown in zinc atmosphere, and the bands at 4630 4590 Å were seen in crystals grown in excess selenium. By comparison with the studies in CdS by Bryant *et al.*,[16] Gezci and Woods[15] tentatively suggested that the bands at 4615 and 4590 Å were associated, respectively, with random and preferential pairing of the same donor and acceptor centers. They also noted that the band at 4630 Å disappeared after the as-grown samples were heated in molten zinc at 850°C. Table I summarizes the edge emission bands in ZnSe reported in literature.

III. EXPERIMENTAL PROCEDURE

A. Sample preparation

The majority of the ZnSe crystals used in this investigation were grown from the melt and were obtained from Eagle-Picher Industries, Inc. In a few cases thin prismatic plates grown by the vapor-transport method of Greene and Geesner[17] were also used. Both undoped zinc selenide and zinc selenide doped with Li, Na, K, Ag, Al, Ga, In, In and Na, LiCl, LiBr, LiI, NaCl, NaBr, NaI,

TABLE I. Summary of edge emission bands in ZnSe.

Zero-phonon peak wavelength in Å	Remarks	Reference
4598	At 4.2 °K, no pair lines, unknown impurities	8
4608 (hexagonal)	At 4.2 °K, no pair lines, Mn-ion bombarded, unknown impurities	10
4588	At 4.2 °K, no pair lines, $E_A+E_D \simeq 126$ meV, $E_A \simeq 100$ meV, unknown impurities	11
~4587	At 4.2 °K, pair lines doubling of the individual pair lines, $E_A+E_D \simeq 140$ meV, $E_A \simeq E_D \simeq 70$ meV, unknown impurities	6 (DM spectrum)
~4606	At 4.2 °K, no pair lines, $E_A+E_D \simeq 150$ meV	6
~4606	At 4.2 °K, pair lines $E_A+E_D \simeq 140$ meV, Al_{Zn}-Li_{Zn}, Ga_{Zn}-Li_{Zn}, In_{Zn}-Li_{Zn} pairs	7
~4587	At 4.2 °K, no pair lines, $E_A+E_D \simeq 137$ meV $E_A \simeq 100$ meV, Na-doped ZnSe	12,13
4630, 4615, 4590	At 10 °K, no pair lines, unknown impurities, $E_A \simeq 122$ meV for 4630	15

KCl, KBr, or KI were studied. Samples along with zinc or selenium pellets were annealed in evacuated and sealed quartz ampoules in the temperature range 300–930 °C. The excess zinc or selenium was kept at a lower temperature than the sample to establish the required vapor pressures of these elements. After they had been annealed, the samples were either quenched in water or furnace cooled. No change in the results was observed for the two cooling methods.

B. Electron irradiation

Some annealed crystals were also electron irradiated to study the effects of irradiation on the pair bands. The irradiation was done at liquid-nitrogen temperature in a Van de Graaff accelerator at an energy of 1 MeV to an electron fluence of 10^{16} e/cm^2.

C. Spectroscopy

Optical measurements were made on cleaved surfaces. The crystals were immersed in liquid helium or liquid nitrogen in a glass Dewar. The spectra were analyzed with a Bausch and Lomb 2-m grating spectrograph. The highest linear reciprocal dispersion was 0.7 Å/mm under the most favorable experimental conditions, though the majority of the experiments were carried out at a reciprocal dispersion of 4 Å/mm. The fluorescence was excited with a 500-W Osram high-pressure mercury lamp equipped with a filter designed to pass the ultraviolet light. If the excitation intensity was to be varied, Special Optics calibrated quartz neutral density filters were used. All data were taken photographically on Kodak type 103 a-F films.

IV. RESULTS

The chemical analysis of the samples used in this investigation is given in Table II. The optical results are presented as densitometer traces of the photographic films, and where appropriate the exposure times are indicated. All optical transitions are given in wavelengths. (The photon energies are obtained using the relation $h\nu = 12\,395.926/\lambda$, where $h\nu$ is in eV and λ is in Å.)

A. Undoped ZnSe

A typical spectrum from an undoped ZnSe crystal is shown in Fig. 1. The prominent bound exciton lines are I_2, $I_1^x(\mathrm{Li})$, $I_1^y(\mathrm{Na})$, and I_1^{DEEP}. The I_2 (4430.63 Å) line is associated with an alkali metal interstitial donor and the exciton binding energy E_{Bx} for this line is 4.5 meV.[18] (E_{Bx} is the energy separation of the line from the free exciton line taken to be 2.8023 eV in our work.) The $I_1^x(\mathrm{Li})$ line is believed to arise from the decay of an exciton bound to a substitutional lithium acceptor $\mathrm{Li}_{\mathrm{Zn}}$.[7] The $I_1^y(\mathrm{Na})$ has been tentatively associated with $\mathrm{Na}_{\mathrm{Zn}}$.[12,13] The E_{Bx} for the two lines are, $E_{Bx}(\mathrm{Li}) = 9.8$ meV and $E_{Bx}(\mathrm{Na}) = 9.2$ meV. These two I_1 lines appear as triplets in high resolution.[7] The I_1^{DEEP} line ($E_{Bx} = 19.2$ meV) is believed to be associated with a native acceptor, for example, a zinc vacancy or a complex involving a native defect.[6,7] These I_1 lines in ZnSe exhibit the strong series of LO-phonon replicas, which is characteristic of the I_1 lines in CdS and CdSe.[19]

Figure 1(a) shows also the edge emission bands. In the undoped crystals two different D-A pair bands, $X0$-4606 and $X0$-4625, were seen. At liquid-helium temperature the high-energy series (HES), free to bound transitions, associated with these pair bands was not observed. At liquid-nitrogen temperature an HES associated with $X0$-4625 was identified; however, no HES associated with $X0$-4606 was detected. No discrete pair lines associated with either of these bands were observed.

The effects of the annealing experiments on the emission spectra are shown in Figs. 1(b) and 1(c). For the undoped crystals annealing in zinc or selenium atmospheres did not produce any difference in the pair bands, and so only the results of the annealing treatments in selenium are given. As the annealing temperature increases from 730 to 930 °C the $X0$-4625 band disappears completely, and the $X0$-4606 remains as the strong transition. This high-temperature annealing treatment also destroys the $I_1^y(\mathrm{Na})$ line. Once again no structure on the pair band was observed for the annealed samples.

B. ZnSe: Doped with lithium

Figure 2 shows the pair spectra observed in as grown and annealed ZnSe : Li samples. As is evident in the figure only one pair band, $X0$-4606, was seen for samples annealed in the temperature range 300–500 °C. The dominant acceptor line associated with $X0$-4606 in these samples is the $I_1^x(\mathrm{Li})$. However, some samples annealed at 900 °C in zinc showed a significant change in the emission spectra as shown in Fig. 2(d). A new $I_1(\mathrm{Li})$ line

TABLE II. Impurity concentrations in melt-grown ZnSe crystals (ppm).[a]

No.	Li	Na	K	Ag	Al	Ga	In	Dopant(s)
1	< 0.1	0.5	< 0.1	< 0.1	2.0	< 1.0	< 1.0	Undoped
2	6.0	< 0.1	< 0.1	< 0.1	< 1.0	< 1.0	< 1.0	Li
3	< 0.1	5.0	< 0.1	< 0.1	< 1.0	< 1.0	< 1.0	Na
4	< 0.1	< 0.1	< 0.1	80.0	1.0	< 1.0	< 1.0	Ag
5	< 0.1	< 0.1	2.0	< 0.1	1.0	< 1.0	< 1.0	K
6	< 0.1	< 0.1	< 0.1	< 0.1	50.0	< 1.0	< 1.0	Al
7	< 0.1	< 0.1	< 0.1	< 0.1	< 1.0	30.0	< 1.0	Ga
8	< 0.1	< 0.1	< 0.1	< 0.1	< 1.0	< 1.0	50.0	In
9	< 0.1	6.0	< 0.1	< 0.1	< 1.0	< 1.0	50.0	In + Na
10	8.0	0.5	0.1	0.1	3.0	< 1.0	< 1.0	LiCl
11	4.0	0.1	< 0.1	0.1	1.0	< 1.0	< 1.0	LiBr
12	4.0	0.3	< 0.1	0.2	2.0	< 1.0	< 1.0	LiI
13	< 0.1	3.0	< 0.1	0.1	1.0	< 1.0	< 1.0	NaCl
14	< 0.1	2.0	< 0.1	0.1	5.0	< 1.0	< 1.0	NaBr
15	< 0.1	1.0	< 0.1	0.1	10.0	< 1.0	< 1.0	NaI
16	< 0.1	1.0	0.1	< 0.1	5.0	< 1.0	< 1.0	KCl
17	< 0.1	0.5	0.1	0.1	5.0	< 1.0	< 1.0	KBr
18	< 0.1	0.1	< 0.1	0.1	2.0	< 1.0	< 1.0	KI

[a] Analyses by emission spectroscopy.

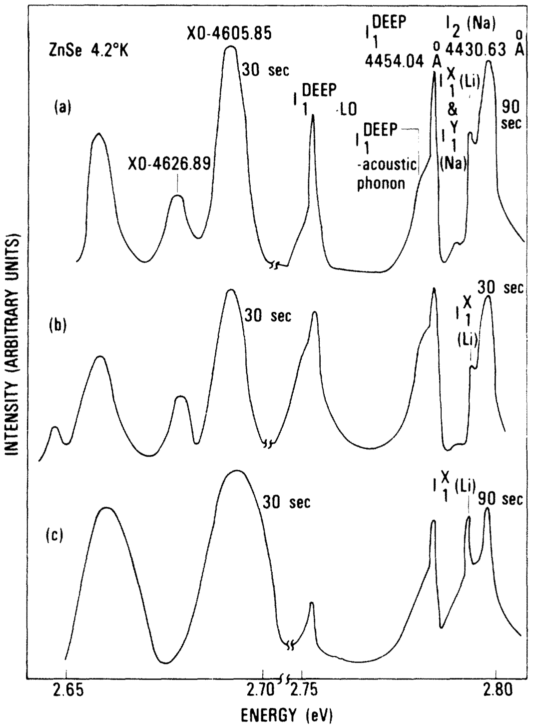

FIG. 1. Bound excitons and pair bands in undoped cubic ZnSe single crystal. (a) Untreated; (b) annealed at 730 °C and $P_{Se_2} = 0.28$ atm; (c) annealed at 930 °C and $P_{Se_2} = 1.10$ atm.

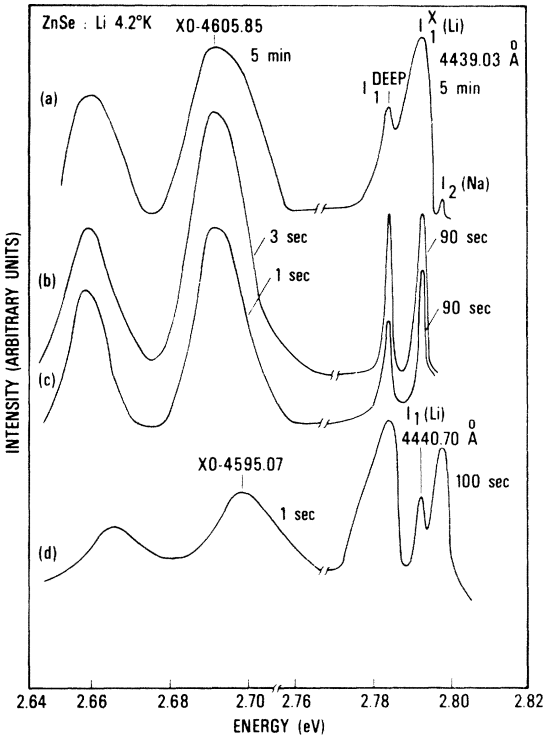

FIG. 2. Bound excitons and pair bands in Li-doped cubic ZnSe single crystal. (a) Untreated; (b) annealed at 500 °C and $P_{Zn} = 3.90 \times 10^{-4}$ atm; (c) annealed at 300 °C and $P_{Se_2} = 1.90 \times 10^{-5}$ atm; (d) annealed at 900 °C and $P_{Zn} = 0.90$ atm.

(4440.7 Å) and a new pair band X0-4595 appeared in these crystals. The exciton binding energy for I_1(Li) is 10.9 meV. Discrete pair lines were not seen with these bands.

C. ZnSe doped with Al, Ga, or In

The as-grown ZnSe containing Al, Ga, or In showed pair bands X0-4625, X0-4621, or X0-4631, respectively, as shown in Figs. 3(a)–3(c). On annealing these crystals at 830 °C in zinc, all these three bands are replaced by a new set of bands, X0-4606(Al), X0-4613(Ga), and X0-4615(In). [Figures 3(d)–3(f).] The I_1^x(Li) is seen to be associated with these bands. In order to ascertain the possibility of the pair bands in the as-grown samples being associated with sodium, the pair spectra were studied in samples containing group-III donors and Na. An example is shown in Fig. 3(c). The peak position of the band in ZnSe : In + Na is the same as of the band in as-grown ZnSe : In. This suggests that the as-grown ZnSe : Al, Ga, or In contains more Na than Li. Once again discrete pair lines were not observed for these bands.

D. ZnSe doped with sodium

A typical spectrum observed in the as-grown ZnSe : Na is presented in Fig. 4(a). Apart from the strong I_1^y(Na) line, another I_1 line denoted as I_1(Na) appeared at an energy of 1.0 meV higher than the I_1^y(Na) line. In high resolution the I_1(Na) line, like I_1^x(Li) and I_1^y(Na), appeared as a triplet in vapor-grown crystals. This new line is always seen in samples doped with sodium, and the E_{Bx} for this line is 8.3 meV. The pair band observed in the as-grown samples is X0-4625. The band X0-4606 is seen as a shoulder to X0-4625, but the phonon bands of X0-4606 are not seen. At liquid-nitrogen temperature an HES, Y0-4619, associated with X0-4625 is observed [Fig. 4(b)].

The effects of annealing on the edge emission from these crystals are presented in Fig. 5. For the annealing treatments in the temperature range 700–930 °C the edge emission spectra are similar for the crystals treated in zinc or selenium atmospheres. Figure 5(a) shows the spectrum from a crystal annealed at 930 °C in zinc vapor. This high-temperature heat treatment destroys com-

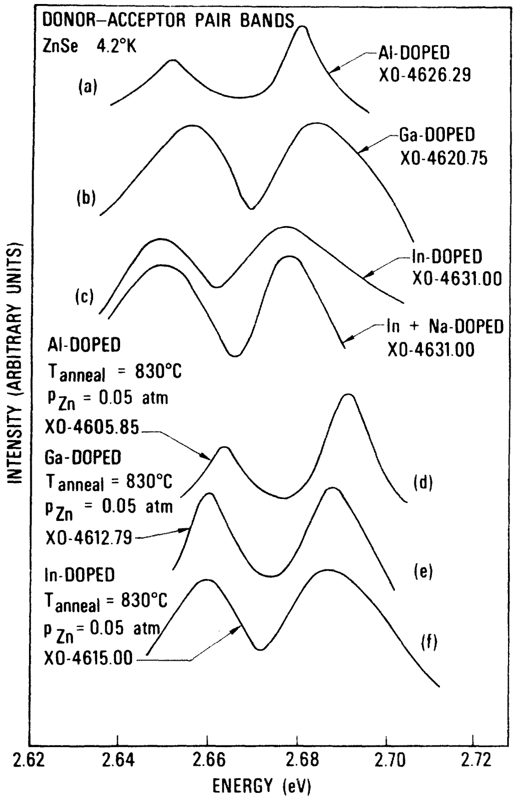

FIG. 3. Pair bands in cubic ZnSe single crystals doped with Al, Ga, In, or In and Na. (a) untreated ZnSe:Al (b) untreated ZnSe:Ga; (c) untreated ZnSe:In and untreated ZnSe:In + Na; (d) Al-doped ZnSe annealed at 830 °C and $P_{Zn} = 0.05$ atm; (e) Ga-doped ZnSe annealed at 830 °C and $P_{Zn} = 0.05$ atm; (f) In-doped ZnSe annealed at 830 °C and $P_{Zn} = 0.05$ atm.

pletely the I_1^y(Na) and I_1(Na) lines and the pair band *X*0-4625, while the I_1^x(Li) line along with the pair band *X*0-4606 are brought out as the dominant transitions. This annealing condition, however, did not produce the discrete pair lines.

Annealing the sodium-doped crystal in the temperature range 300–500 °C produced significant and interesting results. The exciton lines I_1^y(Na) and I_1(Na) and the band *X*0-4625 are destroyed in samples annealed at 300 °C [Fig. 5(b)], while samples annealed at 500 °C [Fig. 5(c)] exhibit the exciton lines I_1^y(Na) and I_1(Na). Apart from the I_1^x(Li) line and *X*0-4606, which are introduced by the low-temperature anneal, two new pair bands *X*0-4566 and *X*0-4587 are observed. The band *X*0-4566 is detected in samples annealed at 300 °C in selenium, while *X*0-4587 is seen in samples annealed at 500 °C in zinc. All the three pair bands showed a displacement of 2–3 Å to longer wavelengths when the excitation intensity was reduced to one-tenth of the maximum.

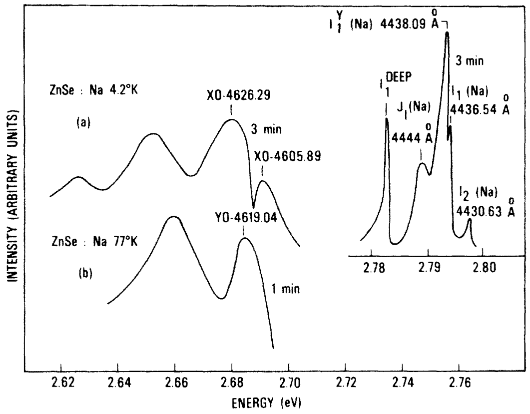

FIG. 4. Low-temperature "edge" photoluminescence spectra of untreated Na-doped cubic ZnSe single crystal. (a) Bound excitons and pair bands at 4.2 °K; (b) free-to-bound recombination band at 77 °K.

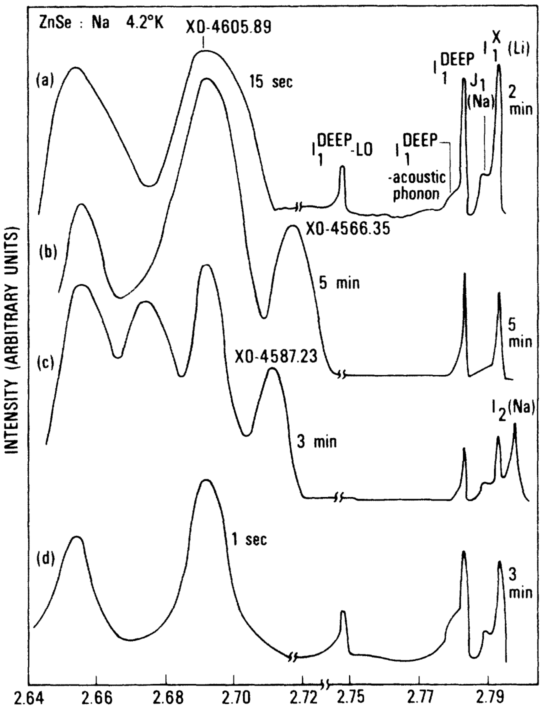

FIG. 5. Bound excitons and pair bands in Na-doped cubic ZnSe single crystal. (a) Annealed at 930 °C and $P_{Zn} = 0.76$ atm; (b) annealed at 300 °C and $P_{Se_2} = 1.88 \times 10^{-5}$ atm; (c) annealed at 500 °C and $P_{Zn} = 3.9 \times 10^{-4}$ atm; (d) annealed at 500 (300 °C) and $P_{Zn} = 3.9 \times 10^{-4}$ atm ($P_{Se_2} = 1.88 \times 10^{-5}$ atm) and electron irradiated at 77 °K with 1.0-MeV electrons to a fluence of 10^{16} e/cm^2

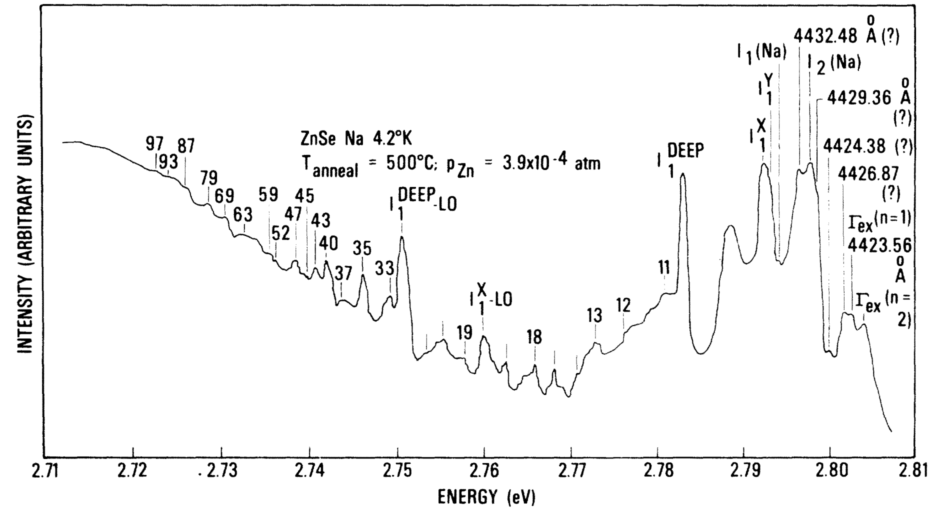

FIG. 6. Donor-acceptor pair lines in Na-doped cubic ZnSe single crystal which has been annealed at 500 °C and $P_{Zn} = 3.9 \times 10^{-4}$ atm. The luminescence was excited with 500-W high-pressure mercury lamp. The new I_2 lines introduced by the annealing treatment are not identified. At least one of them might be associated with native donors.

In addition to introducing two new bands the low-temperature annealing treatments induced also drastic changes in the pair bands. For the first time in our experiments and for the first time in Na-doped ZnSe the discrete pair lines associated with at least one of the pair bands were observed. Though the structured pair spectra were observed for samples annealed either at 300 °C or at 500 °C for excess zinc or excess selenium conditions, the best spectra were observed for samples annealed at 500 °C in zinc. Figure 6 shows the fine structure on the high-energy tail of the pair band *X*0-4587. The individual lines in this spectrum are easily identified on the basis of type-I pairs, for which both the donor and acceptor are on the same sublattice. The peak energies of these lines are analyzed according to usual procedures.[20] The transition energy of an individual pair line is given by

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

where E_g is the band gap, E_A and E_D are the acceptor and donor binding energies, ϵ is the low-frequency dielectric constant, e is the electronic charge, and r is the donor-acceptor separation (or "shell" radius). Figure 7 is a plot of the energies of the pair lines, calculated according to Eq. (1), as a function of r. The shell radius, r, was calculated with the lattice constant $a = 5.67$ Å.[21] In Eq. (1) the band-gap energy at liquid-helium temperature was taken to be 2.819 eV,[22] and the Coulomb interaction energies $e^2/\epsilon r$ were calculated assuming $\epsilon = 8.66$.[23] Systematic deviations from Eq. (1) occur for pair separations less than ~30 Å. This deviation from the Coulomb curve has been observed in the type-I, group-III-impurity–Li, *D*-*A* pair spectra in ZnSe[6,7] and the deviations have been attributed to polarization interactions.[24] By

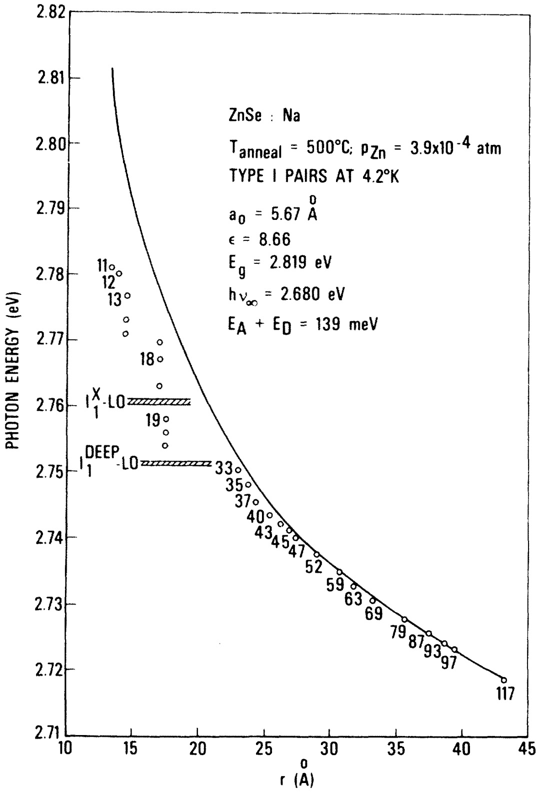

FIG. 7. Photon energy of the discrete pair lines vs the donor-acceptor (or "shell") radius for the pair spectrum in Fig. 6. The shell numbers as predicted on the assumption of type-I pairs are indicated by arrows. The positions and width of the bound exciton lines I_1^X – LO and I_1^{DEEP} – LO are indicated. The solid curve is a plot of the Coulomb term $e^2/\epsilon r$. Systematic deviations from Eq. (1) occur for pair separations less than ~30 Å (~ shell 50) because of polarization interactions.

extrapolating the Coulomb curve to $r \rightarrow \infty$ in Fig. 7 we obtain $E_A + E_D \simeq 139$ meV. It should be mentioned that the analysis of the discrete pair lines seen in samples annealed at 300 °C in selenium vapor also yielded the same value for $E_A + E_D$.

E. Electron irradiation of annealed ZnSe:Na

In order to determine whether any of the two new bands *X*0-4566 and *X*0-4587 or the band *X*0-4606 involves a native defect, the Na-doped crystals annealed at 300 or 500 °C were electron irradiated at liquid-nitrogen temperature. Immediately following the irradiation the photoemission spectra were obtained from the crystals at liquid-helium temperature. Electron irradiation introduced dramatic changes in the pair spectra as shown in Fig. 5(d). The two annealing induced pair bands *X*0-4566 and *X*0-4587 and the discrete pair lines are completely destroyed by irradiation.

F. Other dopants

The pair spectra from zinc-selenide crystals doped with silver did not show any new band that could be associated with Ag, even though the Ag acceptor bound exciton lines have been identified.[25] Potassium showed limited solubility in ZnSe; only a free-to-bound transition that may be attributed to recombination of an electron bound to an interstitial K donor with a hole in the valence band was observed. Doping with the alkali halides also did not give rise to any new pair band. For all these dopants the pair bands observed were either *X*0-4625 or *X*0-4606 or both and the dominant acceptor lines were I_1^x(Li) and/or I_1^y(Na).

V. DISCUSSION

It is evident from the results of our investigation that there are at least five clearly defined series of LO-phonon-assisted edge emission bands in the low-temperature photoluminescence spectra of melt-grown cubic ZnSe. The wavelengths of the five bands are *X*0-4566, *X*0-4587, *X*0-4595, *X*0-4606, and *X*0-4625. Of these five bands only one or, at the most, two are detected in any one crystal depending upon the dopant and the state of the crystal. The bands are prominent only at 4.2 °K and they shift to longer wavelengths as the excitation intensity is reduced. These two features together with the observation of previous investigators that in [6,12,13]ZnSe the HES bands associated with the LES bands are not observed at 4.2 °K, in contrast to the usual behavior of II-VI compounds,[26,27] indicate that all the five bands are *D*-*A* pair recombination bands. Even at 77 °K the HES bands are not observed except for *X*0-4625 for which a free-to-bound transition at 4619 Å was detected. In this section we discuss the origin of these different edge emission bands. By comparing the bound-exciton transitions that occur with the edge emission, we attempt to identify the centers that are involved in both processes and to suggest models for the chemical nature of these centers.

A. Discrete pair lines in Fig. 6

A characteristic feature of a pair recombination band is the presence of discrete lines. An analysis of this fine structure according to Eq. (1) will yield a value for $E_A + E_D$. This together with some knowledge of the bound exciton lines and of the ionization energies of either the donor or the acceptor will help to identify the chemical species involved. In previous investigations[6,7] on ZnSe where structured pair spectra were observed the luminescence was always excited by focused Ar$^+$ laser radiation, and the crystals used where strain-free vapor-grown crystals, which are essential for high-resolution optical studies. When unfocused laser light or a Hg-arc excitation was used, and when the measurements were made on melt-grown ZnSe, the *D*-*A* pair recombination lines were not observed. This is also true in our investigation for most of the samples, except for Na-doped ZnSe annealed in excess zinc or selenium in the temperature range 300–500 °C.

The discrete pair lines observed in the Na-doped samples could be associated with one of the two broad bands *X*0-4606 and *X*0-4587. [Figures 5(c) and 6.] However, an unambiguous choice has to be made in order to identify the centers involved. In fact, the two bands *X*0-4587 and *X*0-4606 observed in the sample annealed at 500°C in zinc fall close to the peaks *R* and *Q* reported by Dean and Merz.[6] In Sec. II we mentioned the ambiguity involved in the identification of the discrete lines with *R* in the DM spectrum. This dilemma whether *X*0-4606 or *X*0-4587 is the pair band associated with the discrete lines (Fig. 6) does not, however, exist in the present investigation. The association of the pair lines with one of the bands is made easy by the results of the measurements on Li-doped ZnSe which showed only *X*0-4606 at all times and by the irradiation experiments on annealed Na-doped crystals. Neither the as-grown ZnSe : Li crystals nor the ZnSe : Li crystals annealed in the temperature range 300–900 °C exhibited a fine structure associated with the *X*0-4606 for the same excitation condition. Furthermore the electron irradiation experiments which were performed on the annealed Na-doped samples destroyed completely the fine structure as well as the band X0-4587, and only X0-4606 remained as the prominent transition. Thus it is reasonable to conclude that the broad "distant pair" band for the fine structure observed in Fig. 6 is X0-4587. This also means that the identification of the structured pair spectra with R in the DM spectrum[6] is correct. However, we did not detect the splitting of the individual pair lines in the DM spectrum within the limit of our experiments.

B. X0-4606

The band X0-4606 and the I_1^x(Li) line are commonly seen in all as-grown and annealed samples and they are prominent in samples doped with Li. The band X0-4606 is one of the three group-III-donor–$\mathrm{Li}_{\mathrm{Zn}}$ pair spectra studied in detail by Merz *et al.*[7] Since the same band is observed in annealed ZnSe : Al [Fig. 3(d)], we associate this band with $\mathrm{Al}_{\mathrm{Zn}}$-$\mathrm{Li}_{\mathrm{Zn}}$ pair recombination.

C. X0-4625

This band is detected only in the as-grown samples, and it is prominent in ZnSe : Na. Though the Na-doped samples exhibit two I_1 lines, I_1^y(Na) and I_1(Na), only I_1^y(Na) is seen along with X0-4625 in the as-grown undoped ZnSe (Fig. 1). It is therefore reasonable to associate I_1^y(Na) with X0-4625. The disappearance of the band X0-4625 and of the I_1 sodium lines in annealed samples indicates that the Na center responsible for the edge emission is removed from the crystal. This is consistent with the results of Gezci and Woods[15] who failed to detect X0-4625 [which is the band at 4630 Å (S) 10 °K in Ref. 15] after the samples were heated in liquid zinc. They suggested that the impurity responsible for the band might be leached out by molten zinc. A similar observation has been made with the exciton emission in CdS where the I_1 sodium lines were destroyed when the crystals were annealed at high temperatures; this was attributed to the high diffusion rate of Na.[28,29] It is to be expected that Na would be a fast diffusing impurity in ZnSe also. In fact, chemical analysis of a ZnSe : Na sample that contained originally 5 ppm of Na showed only 0.1 ppm of Na after the sample was heated at 930 °C in zinc or selenium for 24 h.

The association of X0-4625 with Na is also confirmed by the results on the as-grown ZnSe doped with Al, Ga, In, or In + Na as shown in Fig. 3. Though the chemical analysis indicates that in the as-grown samples both Li and Na are present in concentrations of less than 0.1 ppm, the crystals must have had more Na than Li contamination, proved by the result that the same edge emission band X0-4631 is observed in ZnSe : In and ZnSe : In + Na [Fig. 3(c)]. Also the long-wavelength pair bands, X0-4625, X0-4621, and X0-4631, seen in as-grown ZnSe : Al, ZnSe : Ga, and ZnSe : In, respectively, disappear after the crystals are annealed in zinc at 830 °C. The short-wavelength pair bands X0-4606(Al), X0-4613(Ga), and X0-4615(In), which are associated with Li, are observed in the annealed crystals. This result is consistent with our theory that Na diffuses out of the crystal faster than Li.

Having determined that X0-4625 involves a Na acceptor and $\mathrm{Al}_{\mathrm{Zn}}$ [Fig. 3(a)] we now proceed to calculate the ionization energy of the acceptor. From the position of the distant pair peaks X0-4625, X0-4621, and X0-4631 and an estimated value $e^2/\epsilon r = 9$ meV (from Fig. 6) we calculate $E_A + E_D$ to be 148, 149, and 151 meV, respectively. When we use the E_D values for Al, Ga, and In given in Ref. 5 we obtain $E_A \simeq 117$–122 meV. From the peak position of the HES band, Y0-4619, associated with X0-4625, we estimate $E_A \simeq 125$ meV for[22] $E_g = 2.809$ eV at liquid-nitrogen temperature. These two estimates for E_A are in close agreement. However, the estimate made from the position of the HES band must be treated with caution, as there is a possibility of phonon induced broadening of the HES band.

The $E_A \simeq 117$–122 meV for the Na acceptor, when compared to $E_A \simeq 114$ meV for $\mathrm{Li}_{\mathrm{Zn}}$,[7] suggests that the Na acceptor is probably $\mathrm{Na}_{\mathrm{Zn}}$. The covalent radius of Na is 1.54 Å while that of Li is 1.33 Å in comparison to the covalent radius of 1.31 Å for zinc. Therefore, from size considerations alone one would expect $E_A(\mathrm{Na}_{\mathrm{Zn}})$ to be greater than $E_A(\mathrm{Li}_{\mathrm{Zn}})$. So we identify $\mathrm{Na}_{\mathrm{Zn}}$ as the acceptor involved in the band X0-4625 and the line I_1^y(Na). We could not, however, ascertain if I_1^y(Na) is associated with a simple $\mathrm{Na}_{\mathrm{Zn}}$ center by Zeeman analysis. The g values are relatively small in ZnSe and the exciton lines are much broader in ZnSe than in CdS, due presumably to the effect of internal strain on the Γ_8 hole states at the degenerate valence-band maximum of the cubic semiconductor.[6] In our experiments we did not observe any effect on the lines caused by magnetic fields up to 40 kG. Table III compares E_{Bx} and E_A for $\mathrm{Li}_{\mathrm{Zn}}$ and $\mathrm{Na}_{\mathrm{Zn}}$ in ZnSe.

D. X0-4587 and X0-4566

1. Preferential and random pairing

Two bands are seen in Na-doped ZnSe, X0-4587 in samples annealed at 500 °C in zinc vapor, and X0-4566 in samples annealed at 300 °C in selenium vapor. The observation that the same set of pair lines merge into these two bands suggests that the bands probably arise from the recombination between the same donor and acceptor centers. Now,

TABLE III. Shallow acceptors and exciton binding energies.

	Acceptor	E_{Bx} (meV)	E_A (meV)	E_{Bx}/E_A
ZnSe	$\mathrm{Li_{Zn}}$	9.8	114[a]	0.086
	$\mathrm{Na_{Zn}}$	9.2	117–122	0.079–0.075
	$(\mathrm{Li_{Zn}}V_{\mathrm{Se}})$	10.9	(110–130)	0.1[b]
	$(\mathrm{Na_{Zn}}V_{\mathrm{Se}})$	8.3	(80–100)	0.1[b]
	$\mathrm{I_1^{DEEP}}$	19.2	~200	0.1
CdS	$\mathrm{Li_{Zn}}$[c]	17.7	165	0.107
	$\mathrm{Na_{Zn}}$[c]	17.5	169	0.103
CdSe	$\mathrm{Li_{Zn}}$ or $\mathrm{Na_{Zn}}$	9.2	109	0.084

[a] Determined by Merz *et al.*, Ref. 7.

[b] For these cases, E_A was estimated assuming $E_{Bx}/E_A \sim 0.1$.

[c] Determined by Henry *et al.*, Ref. 19.

Bryant *et al.*,[16] who studied the effects of electron irradiation damage on the edge emission of CdS, suggested that the pair at 5149 Å, seen in samples fired in excess sulphur, and the pair band at 5174 Å, seen in samples fired in excess cadmium, involve the same acceptor and donor; the shorter-wavelength band is due to preferential pairing (association of closer pairs) the longer-wavelength band to random pairing. They were able to advance this suggestion as the result of their observation that when irradiated with electrons the band at 5149 Å shifted to longer wavelengths, while the band at 5174 Å shifted to shorter wavelengths. This behavior according to their theory indicated preferential pairing for the band at 5149 Å and random pairing for the band at 5174 Å.

Though in the present investigation the electron irradiation experiments on ZnSe did not produce any wavelength shift for X0-4566 and X0-4587, we tentatively propose that X0-4566 is associated with preferential pairing and that X0-4587 is associated with random pairing between the donors and acceptors for the following reasons: (i) the same fine structure is observed for both bands which indicates that they involve the same centers; (ii) the shorter wavelength band is observed in samples annealed in excess nonmetal which is consistent with results of previous investigations in[16] CdS; (iii) some degree of association between oppositely charged centers is to be expected when samples are annealed at low temperatures.[30] It is also interesting to note that the energy difference between the two bands, $\Delta E \sim 12$ meV, is of the same order of magnitude as that observed for the preferentially and randomly paired bands in CdS.

2. *Acceptor and donor centers for X0-4587*

Since we have proposed that the same donor and acceptor are involved in X0-4587 and X0-4566, from now on we will focus our attention on X0-4587. It is recognized that X0-4587 is probably the same band observed by Chatterjee *et al.*,[12] Rosa and Streetman,[13] and Dean and Merz.[6] Based on the observations that this band responded to Na doping[12,13] and that the bound exciton line I_1^y(Na) is associated with X0-4625 (Sec. VC) it is reasonably to assume that the bound exciton line associated with X0-4587 is I_1(Na). Since there is strong evidence that the line I_1^y(Na) results from $\mathrm{Na_{Zn}}$ (Sec. VC), the acceptor responsible for the I_1(Na) and X0-4587 luminescence might be a Na acceptor other than $\mathrm{Na_{Zn}}$.

A common factor in the present study and in the earlier investigations[6,13] is that X0-4587 is detected only after the samples are annealed in zinc atmosphere at 300–500 °C. In addition, Rosa and Streetman[13] observed in Na-implanted ZnSe that the pair band appeared strong only after the specimen had been annealed, and the distribution of native defects introduced by radiation damage thus affected. Their result together with our observation that the band is destroyed after the samples are irradiated with 1.0-MeV electrons suggest the role of native defects in X0-4587. Now, any model that we propose for the chemical identity of the centers involved in the I_1(Na) and X0-4587 luminescence should take into account the following: (i) native defects due to excess zinc are involved; (ii) the individual pair lines appeared as a doublet in DM spectrum.[6]

The native defects which are introduced by annealing in excess zinc are zinc interstitials Zn_i and selenium vacancies V_{Se}. These defects are known to behave as singly or doubly ionized donors.[31,32] At 500 °C (which is 0.43 T_m, where T_m is the melting point in degrees Kelvin) there will be sufficient diffusion of impurities to bring forth some degree of association between them. For example, associates like $(\mathrm{Na_{Zn}}V_{\mathrm{Se}})'$ may form according to the equilibrium reaction, $\mathrm{Na}'_{\mathrm{Zn}} + V_{\mathrm{Se}}^{\times} \rightleftharpoons (\mathrm{Na_{Zn}}\,V_{\mathrm{Se}})'$, the complex behaving like an acceptor.[33] If this is the acceptor involved in X0-4587, then the doubling of the pair lines in

DM spectrum is easily explained. The acceptor, $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})'$, is an axial defect with a symmetry (C_{3v}); lower than the T_d symmetry of $\mathrm{Na}_{\mathrm{Zn}}$. This lowering of symmetry would lift the degeneracy of the T_d center, and this may be responsible for the splitting of the pair lines. If we associate the I_1(Na) line with $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})'$ then we obtain from $E_{Bx}[I_1(\mathrm{Na})]$ an acceptor ionization energy of ~80 meV using $E_{Bx}/E_A = 0.1$.[34] This value of E_A is close to the estimate of 70 meV for the acceptor in DM spectrum. The concentration of $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})'$ will decrease with increasing temperature of annealing. The diffusion rates of the complex will also be smaller than those of the simple center $\mathrm{Na}_{\mathrm{Zn}}$. This is the reason why X0-4587 associated with $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})'$ is observed while X0-4625 associated with $\mathrm{Na}_{\mathrm{Zn}}$ (Sec. V C) is not observed in samples annealed in the temperature range 300–500 °C. Thus, these above mentioned considerations strongly suggest that the acceptor involved in X0-4587 is $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})$ with $E_A \simeq 80$ meV.

We now proceed to determine the identity of the donor involved in X0-4587. The estimate of $E_D \simeq 70$ meV for this donor,[6] in comparison to $E_D \simeq 30$ meV for the shallow donors in ZnSe,[5,18] indicates that neither the group-III donors nor the alkali metal-interstitial donors are involved in this pair band. A possible candidate for the deep donor responsible for X0-4587 is one of the native double donors V_{Se} or Zn_i. This suggestion is also consistent with the proposal that the band X0-4566 is due to preferential pairing between the donors and the acceptors (Sec. V D) for the following reasons: (i) The enthalpy of association between Zn_i'' (or V_{Se}'') and $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})'$ would be twice that expected if only a singly ionized donor were involved. Therefore, a high degree of preferential pairing will occur between these centers. In fact, this is the reason why the pair lines are detected for only X0-4566 and X0-4587 and for none of the other bands as preferential pairing will increase the intensity of pair lines in comparison to random pairing.[35] Also, preferential pairing will be more predominant at 300 °C than at 500 °C, confirming our hypothesis that X0-4566 seen in samples annealed at 300 °C is due to preferential pairing. (ii) A pair recombination band identified as due to double native-donor–substitutional-acceptor lithium pairs in CdS is believed to be a preferential pair band.[36]

The results of the electron irradiation experiments strongly suggest that the doncr involved in X0-4587 is Zn_i. Watkins[37] studied the effects of electron irradiation damage in ZnSe using EPR measurements and suggested that irradiation with 1.0–1.5-MeV electrons in the temperature range 20–300 °K produced damage only in the zinc sublattice. The disappearance of the pair bands X0-4566 and X0-4587 after electron irradiation might be explained if the native defects produced by the radiation damage interacted with the donor or acceptor centers responsible for the pair recombination so as to eliminate at least one of them. For example, if the donor involved in the pair bands is Zn_i, it could interact with the zinc vacancies or the excess Zn_i created by electron irradiation to form complex centers like close Frenkel pairs and thus not be available for pair luminescence.

E. X0-4595

This band is seen occasionally in Li-doped samples annealed at 900 °C in zinc atmospheres. The exciton line associated with the band is the I_1(Li) line [Fig. 2(d)]. Based on the arguments in Sec. V D we suggest that the acceptor involved in the I_1(Li) and X0-4595 luminescence is $(\mathrm{Li}_{\mathrm{Zn}}V_{\mathrm{Se}})'$. From the peak energy of this band and from $e^2/\epsilon r = 9$ meV (from Fig. 6) we estimate $E_A + E_D = 130$ meV. From the exciton binding energy of I_1(Li) we obtain $E_A \simeq 109$ meV using $E_{Bx}/E_A = 0.1$. This gives $E_D \simeq 21$ meV. The magnitude of E_D suggests that the donor responsible for X0-4595 is probably a group-III donor. These estimates for E_D and E_A are also comparable to those obtained by Iida[11] for the ionization energies of the donor and acceptor centers for the band that he observed at 4588 Å (Sec. II B).

VI. CONCLUSIONS

Five different pair recombination bands with their zero-phonon peak wavelengths at 4566, 4587, 4595, 4606, and 4625 Å are seen in melt-grown cubic ZnSe at 4.2 °K.

The bands at 4566, 4587, and 4595 Å are observed only in annealed crystals; the band at 4625 Å is seen only in as-grown crystals; whereas the band at 4606 Å is observed in annealed and as-grown crystals.

The bands at 4606 and 4625 Å are associated with $\mathrm{Al}_{\mathrm{Zn}}$-$\mathrm{Li}_{\mathrm{Zn}}$ and $\mathrm{Al}_{\mathrm{Zn}}$-$\mathrm{Na}_{\mathrm{Zn}}$ pairs, respectively. The ionization energy of $\mathrm{Na}_{\mathrm{Zn}}$ is estimated to be 122 meV.

From the analysis of the fine structure associated with the bands at 4587 and 4566 Å and from the results of electron irradiation experiments it is suggested that these two bands involve the same donor and acceptor, and that the shorter-wavelength band arises from preferential pairing and the longer-wavelength band from random pairing of the donor and acceptor centers.

The donor and acceptor involved in the bands at 4587 or 4566 Å are tentatively assigned to be doubly ionized Zn_i and singly ionized $(\mathrm{Na}_{\mathrm{Zn}}V_{\mathrm{Se}})$. The ionization energy of the acceptor complex is estimated from the corresponding bound-exciton line to be ~80 meV.

The band at 4595 Å is tentatively assigned to $\mathrm{Al}_{\mathrm{Zn}}$-$(\mathrm{Li}_{\mathrm{Zn}}V_{\mathrm{Se}})$ pairs. The ionization energy of the acceptor complex is estimated from the corresponding bound exciton line to be 110–130 meV.

ACKNOWLEDGMENTS

The authors would like to thank D. Locker and J. Meese of the AF Avionics Laboratory for their extremely competent assistance in the electron irradiation experiments and Dr. W. Frederick and Dr. G. E. Kuhl of the AF Materials Laboratory for their interest in this work.

---

*Work supported in part by the National Research Council, National Academy of Sciences (U.S.A.).

[1] See review articles by D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Status Solidi 9, 645 (1965); 12, 3 (1965); also, R. E. Halsted, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), Chap. 8, p. 385.

[2] See review article by P. J. Dean, in *Progress in Solid State Chemistry*, edited by J. O. McCaldin and G. Somorjai (Pergamon, New York, 1973), Vol. 8, p. 1.

[3] K. Colbow, Phys. Rev. 141, 742 (1966).

[4] D. G. Thomas, R. Dingle, and J. D. Cuthbert, in *II-VI Semicondudting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 863.

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

[6] P. J. Dean and J. L. Merz, Phys. Rev. 178, 1310 (1969).

[7] J. L. Merz, K. Nassau, and J. W. Shiever, Phys. Rev. B 8, 1444 (1973).

[8] D. C. Reynolds, L. S. Pedrotti, and O. W. Larson, J. Appl. Phys. Suppl. 32, 2250 (1961).

[9] The precise peak wavelength positions observed for the edge emission bands by different investigators depend strongly on the method and the intensity of the excitation used. Therefore, care must be exercised in comparing results. We choose to designate the zero-phonon wavelengths of the bands for 500-W Hg-arc excitation, like, X0-4606 for LES bands seen at 4.2 °K and Y0-4619 for HES bands seen at 77 °K. In comparing our results with those cited in Refs. 6 and 7 where an Ar^+ laser was used as an excitation source we have estimated the corresponding wavelengths appropriate to HG-arc excitation using Fig. 6. Where the bands have been previously reported we have indicated the notation used by the different authors in parentheses.

[10] W. Y. Liang and A. D. Yoffe, Philos. Mag. 16, 1153 (1967).

[11] S. Iida, J. Phys. Soc. Jpn. 25, 177 (1968).

[12] P. K. Chatterjee, A. J. Rosa, and B. G. Streetman, J. Lumin. 8, 176 (1973).

[13] A. J. Rosa and B. G. Streetman, J. Lumin. 10, 211 (1975).

[14] J. C. Bouley, P. Blanconnier, A. Herman, Ph. Ged, P. Henoc, and J. P. Noblanc, J. Appl. Phys. 46, 3549 (1975).

[15] S. Gezci and J. Woods, J. Lumin. 10, 267 (1975).

[16] F. J. Bryant, W. E. Hagston, and C. J. Radford, Proc. R. Soc. A 323, 127 (1971).

[17] L. C. Greene and C. R. Geesner, J. Appl. Phys. 38, 3662 (1967).

[18] V. Swaminathan and L. C. Greene, Bull. Am. Phys. Soc. 20, 1513 (1975).

[19] C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. B 4, 2453 (1971).

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

[21] W. L. Roth, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), Chap. 3, p. 127.

[22] G. E. Hite, D. T. F. Marple, M. Aven, and B. Segall, Phys. Rev. 156, 850 (1967).

[23] S. Roberts and D. T. F. Marple, quoted in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), Chap. 7, p. 335.

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

[25] L. C. Greene and V. Swaminathan, Bull. Am. Phys. Soc. 21, 429 (1976).

[26] D. L. Kingston, L. C. Greene, and L. W. Croft, J. Appl. Phys. 39, 5949 (1968).

[27] L. C. Greene and H. A. Wilson, J. Appl. Phys. 42, 2758 (1971).

[28] A. M. Sargent, Bell Telephone Laboratories, New Jersey (unpublished).

[29] H. Woodbury, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 244.

[30] H. Reiss, C. S. Fuller, and F. J. Morin, Bell Syst. Tech. J. 35, 535 (1956).

[31] F. T. J. Smith, Solid State Commun. 1, 1757 (1969).

[32] M. M. Henneberg and D. A. Stevenson, Phys. Status Solidi B 48, 255 (1971).

[33] The charge on the defects is indicated following the notation of Kroger and Vink. A prime represents a negative charge, a dot represents a positive charge and a cross represents a neutral state. See *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 3, p. 307.

[34] Halsted and Aven [Phys. Rev. Lett. 14, 64 (1965)] have demonstrated that in many II-VI compounds the binding energy E_{Bx} of an exciton bound to a neutral acceptor is related to the ionization energy of the acceptor E_A by $E_{Bx}/E_A \simeq 0.1$. This ratio is found to be applicable even for deep acceptors having ionization energies as great as 0.8 eV. Henry *et al*. (Ref. 19) verfied this relation in CdS and CdSe for simple substitutional Li and Na acceptors as well as for a P acceptor complex. In

ZnSe also this relation is found to be applicable for Li_{Zn} and Na_{Zn} (Sec. V C). See also Table III.

[35] R. E. Halsted, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (Wiley, New York, 1967), Chap. 8, p. 385.

[36] C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. Lett. 24, 820 (1970).

[37] G. D. Watkins, Phys. Rev. Lett. 33, 223 (1974).