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Donor-acceptor pair bands in ZnSe

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The donor-acceptor pair (DAP) bands have been studied in single crystals of ZnSe grown by vapor-phase epitaxy, from solutions of Ga, and In, and also by liquid-phase epitaxy. The temperature dependence of both steady-state photoluminescence and time-resolved spectra was used to identify the DAP bands R_0, Q_0, P_0 associated with Li and Na dopants. The DAP band Q_0 at 2.695 eV was already identified by Merz *et al.* as due to $\mathrm{Al}_{\mathrm{Zn}}^{+}$-$\mathrm{Li}_{\mathrm{Zn}}^{-}$. We have associated the DAP band P_0 due to transitions involving $\mathrm{Al}_{\mathrm{Zn}}^{+}$ donor and $\mathrm{Na}_{\mathrm{Zn}}^{-}$ acceptor and the DAP band R_0 due to transitions involving a shallow donor and $\mathrm{Li}_{\mathrm{Zn}}^{-}$ acceptor, respectively. This shallow donor level seems to be associated with the presence of Li in ZnSe and could be $\mathrm{Li}_{\mathrm{int}}^{+}$. From these studies we obtain the acceptor level due to $\mathrm{Na}_{\mathrm{Zn}}$, 124 ± 2 meV, and the shallow donor associated with $\mathrm{Li}_{\mathrm{int}}$ as ≈26 meV, respectively. This study suggests that compensation in ZnSe may be related to background donor impurities such as $\mathrm{Li}_{\mathrm{int}}$ rather than native defects.

I. INTRODUCTION

In wide-band II-VI semiconductors such as CdS, ZnSe, and ZnS, it has been extremely difficult to grow or fabricate good *p*-type conducting material.[1,2] In the past few years, many attempts were made to incorporate shallow acceptors in CdS and ZnSe either during bulk crystal growth,[3,4] or by ion implantation,[5,6] or by a nonequilibrium heat-treatment process.[7] The results of these experiments of dopant incorporation to date are that only highly resistive *p*-type bulk material could be fabricated. In a nonequilibrium heat-treatment process, thin *p* layers (~0.1 μm) of resistivity 10 ohm cm have been reported.[7] However, in this material, the nature of the acceptor responsible for *p*-type conductivity is not completely understood. Tentatively, monovalent species of Ga, In, and Tl were assigned as the active shallow acceptors with ionization energies in the range 100–200 meV. Identification of shallow acceptors in these thin layers, as well as in other materials, is crucial in obtaining conducting *p*-type ZnSe.

Several studies have been made to identify and understand the role of shallow acceptors in CdS and ZnSe primarily using high-resolution optical spectroscopy at low temperatures.[3,4,8–14] From these studies, it is concluded that Li and Na are the only shallow acceptors in these materials, confirming similar conclusions from electron-spin-resonance experiments.[15]

The approximate acceptor ionization energies of both Na and Li in CdS and ZnSe are, respectively,[3] 170 meV and[4,8–11] around 115 meV. Incorporation of these impurities in the range of 10^{16}–10^{17} cm^{-3} did not yield conducting *p*-type ZnSe or CdS. Respectable evidence was provided in Ref. 3 that an additional donor was introduced during Li incorporation in CdS. Although the identification of this donor was not established beyond doubt, it was suggested this donor may be due to interstitial lithium ($\mathrm{Li}_{\mathrm{int}}$) or a complex of a sulfur vacancy with lithium on a cadmium site (V_{S}-$\mathrm{Li}_{\mathrm{Cd}}$).[3] Any evidence of the existence of $\mathrm{Na}_{\mathrm{int}}$, $\mathrm{Li}_{\mathrm{int}}$, anion vacancies, or their complexes, should be taken as circumstantial since optical spectroscopy or electrical measurements have not yielded any conclusive results so far.

The first detailed studies of shallow acceptors in ZnSe using pair-spectral analysis was performed by Dean and Merz[8] (henceforth referred to as DM) in ZnSe. They observed two pair bands R_0 and Q_0, respectively, at liquid-helium temperatures. The high-energy peak R_0 at 2.708 eV and Q_0 at 2.692 were observed at moderately high excitation intensity. Both showed pairlike behavior but only R_0 was claimed to have discrete pair lines associated with it. Furthermore, only one free-electron to bound-hole transition (FB) associated with the Q_0 peak was observed at high temperature (60 °K). From the analysis of the discrete pair lines, the value of $E_A + E_D = 141$ meV was obtained. Individual impurities responsible for this specific donor and acceptor were not known; however, both were located at the same sublattice (Type-I pair spectra). Merz *et al.* later analyzed several samples purposely doped with Li and its isotope. They established beyond a doubt that the Li acceptor was indeed responsible for the pair band Q_0, and gives rise to discrete pair lines when codoped with Ga, In, and Al donors. The value of $E_A + E_D$ derived was 141 ± 2 meV. Since the donor-binding energies had already been determined by Merz and co-workers,[16] the Li-acceptor level was derived as 114 ± 2 meV. Merz *et al.* also claimed that the Li acceptor was responsible for the pair lines observed by DM and that the R_0 pair peak did not produce any pair lines. Dean,[17] however, provided an alternative explanation which claimed that the R_0 peak is due to a deeper donor than shallow group III donors and a shallower acceptor than $\mathrm{Li_{Zn}}$ is involved. The acceptor or donor could even be an axial one.

In recent years, several workers have studied the role of the Na acceptor in the observed pair band in ZnSe, particularly associating the Na acceptor with the R_0 pair band reported by DM. Na-diffused and Na-ion implanted samples were used for these studies. In this section we will review briefly the conclusions about the Na acceptor obtained by these workers and discuss their interpretation later in Sec. IV.

Chatterjee *et al.*[9] studied ZnSe samples which were fired in molten Zn either with Na or Na and Al. In Na-doped samples, they observed two pair bands at 4.2 °K peaking at 2.695 and 2.680 eV, respectively. These values of peak energy are estimated from Fig. 1 of Ref. 9, since actual values were not mentioned in the text. For this reason, these values may be in error by ±2 meV. Chatterjee *et al.*[9] assigned these two peaks to R_0 and Q_0 of Dean and Merz, though R_0 and Q_0, as reported by DM, were at 2.708 and 2.692 eV, respectively. This large difference of approximately 12 meV in observed peak positions of R_0 and Q_0 between those reported by DM and Chatterjee *et al.* cannot be simply accounted for by the difference in the intensity of the excitation source. The shift in the position of the peak is approximately 3.5 meV for a tenfold change in the excitation intensity.[8] However, such a large enough variation in excitation intensity to account for the difference of 12 meV in peak position, is not expected from the experimental conditions used by DM and by Chatterjee *et al.* This discrepancy in the peak positions of R_0 and Q_0 observed by DM and those observed by Chatterjee *et al.*[9] can be resolved by suggesting that there are three different peaks: R_0, Q_0, and P_0. The common peak Q_0 at 2.695 eV has been identified by Merz *et al.*[4] as due to the Li acceptor. Later in this paper we will discuss the origin of pair peaks P_0 and R_0.

Rosa and Streetman[10] studied Na-ion implanted ZnSe samples in which they observed a pair peak at 2.701 as estimated from Fig. 3 of Ref. 10. This peak was seen in unimplanted, Ne- and Na-implanted samples which all were appropriately annealed around 600 °C. They attributed this pair-band peak at 2.701 to the Na acceptor. This value of peak energy should correspond to a saturated value of the pair peak since the excitation intensity used seems to be high. (The excitation source used was a xenon flashlamp capable of delivering total integrated output energy of 10 J in 1.5 sec.) From the discussion above, it is rather difficult to associate the 2.701-eV peak to the original R_0 reported by DM peaking at 2.708 eV at moderate excitation intensity. However, the above peak could easily be assigned to Q_0.

Recently Rosa and Streetman[14] have analyzed the temperature dependence and shift of pair peak with excitation intensity and they conclude that the peak at 2.701 eV is indeed due to a donor-acceptor transition. The acceptor responsible for this particular band was assigned as Na on the basis of mass spectrographic analysis, secondary-ion microprobe mass spectroscopy (SIMS) and absorption-impurity analysis. They have presented quite convincing arguments to associate the peak at 2.701 eV with Na. On the contrary, we believe that their crystals had Na, but not incorporated as substitutional Na, as a shallow acceptor. This will be discussed in Sec. IV B.

Gezci and Woods[12] studied the pair bands in ZnSe and observed three bands with zero-phonon-peak energies at 2.678 eV (4630 Å), 2.686 eV (4615 Å), and 2.705 eV (4590 Å). Pair lines associated with any of these bands were not detected but all three showed shifts to higher energy when excitation was increased. The bands at 2.678 and 2.686 eV were observed in crystals annealed in Zn atmosphere and bands at 2.678 and 2.705 were seen in crystals grown in excess selenium. Comparing these results to studies of Bryant *et al.*,[18] they tentatively assigned 2.686- and 2.705-eV bands to the same acceptor and donor but associated with random and preferential pairing. They assigned the binding energies of acceptors responsible for the 2.686- and 2.678-eV bands as 112 and 122 meV. Later we shall show that these two acceptors are respectively due to Li and Na.

Swaminathan and Greene (henceforth referred to as SG) have most recently studied in detail the pair emission in melt-grown ZnSe. They observe five different pair recombination bands at 4.2 °K with zero-phonon-peak energies at 2.715, 2.702, 2.698, 2.691, and 2.680 eV. The pair band at 2.680 and 2.691 were associated with $\mathrm{Al_{Zn}}$-$\mathrm{Na_{Zn}}$ and $\mathrm{Al_{Zn}}$-$\mathrm{Li_{Zn}}$ donor-acceptor pairs, respectively. In one of the samples (spectra C in Fig. 5 of SG), discrete pair lines were observed. The value of $E_A+E_D=139$ meV was derived from the pair-line data. SG proposed that the donor is Al and the acceptor involved is Na.

An interesting part of this analysis is that although SG claimed Na as the acceptor for the discrete lines in the above spectra, the identical value of E_A+E_D is obtained in samples containing Al and Li by Merz *et al.*[4] As we will discuss later, we feel that only the $\mathrm{Li_{Zn}}$ acceptor is observed in the pair lines, and it is responsible for the Q_0 peak in ZnSe. So far, to our knowledge, pair lines associated with the Na acceptor have not been observed. Perhaps this is due to the presence of overlapping Li-related Q_0 and R_0 donor-acceptor pair (DAP) bands.

Swaminathan and Greene further contended that the 2.702- and 2.715-eV bands involve the same acceptor and donor and that the higher energy band arises from preferential pairing and the lower energy band from random pairing of the donor and acceptor centers. The donor and acceptor assigned to these transitions were the doubly ionized zinc interstitial donor and an acceptor consisting of a complex of a selenium vacancy with sodium on the zinc site (V_{Se}-$\mathrm{Na}_{\mathrm{Zn}}$).

It is clear from the brief summary of published results that various donor-acceptor pair (DAP) bands (as many as five different bands between 2.680 and 2.715 eV) were associated with Li and Na acceptors. In case of Q_0 (2.695 eV), the acceptor level due to $\mathrm{Li}_{\mathrm{Zn}}$ was unambiguously identified[4] while in all other cases the interpretation was ambiguous. This was due to several reasons: these DAP bands frequently overlap, DAP peak positions depend on the excitation intensity, and, lastly, Li and Na are background impurities in most of the bulk ZnSe studied. This is also complicated by the fact that under heat treatment Li and Na move rapidly out of the Zn site.

In order to identify the role of Li and Na acceptors in various DAP bands, we have studied the temperature dependence of the DAP bands in the region of 2.680 to 2.715 eV in ZnSe grown by vapor-phase epitaxy,[19] from solutions of Ga, In, and Bi,[20] and also by liquid-phase epitaxy.[21] Several samples were purposely doped with Li and Na while most of them had these impurities as background dopants.

In order to isolate the various overlapping DAP bands and free-electron to bound-hole (FB) transitions, we have examined the various spectra at different times after the excitation. The temperature dependence of the time resolved spectra has enabled us to identify the DAP and FB transition associated with Li and Na and clarify some of the confusion which has been in the literature.

The time resolved spectra has provided three improvements which have aided in the understanding of the shallow acceptor bands. First, the narrowing of the bands has enabled us to separate more easily two adjacent bands as well as the pair transition from the free to bound at intermediate temperatures. Second, it allows unambiguous identification of a band as pairlike or free to bound depending on whether there is a peak shift with delay time. Finally, the longer delay times enhance transitions with slower kinetics allowing them to be observed when they are sometimes not seen under dc excitation.

In our present study the time resolved spectra at low (5–30 °K) and intermediate temperatures (40–100 °K) has been particularly useful in establishing that the two pair bands (Q_0 and P_0) are due to two acceptors, rather than due to two donors. This is evident as two donors and a single acceptor ($E_{D1},E_{D2} < E_A$) would lead to a single free-to-bound transition at intermediate temperatures. In our case, we clearly observe two free-to-bound transitions, suggesting that there are two acceptors. Since the donors are shallow ($E_{D1},E_{D2} < E_{A_1},E_{A_2}$) and thermalize in the vicinity of 30 to 40 °K, it is difficult to tell whether more than one donor is involved.

II. EXPERIMENTAL PROCEDURE

Most of the ZnSe crystals used in this investigation were either grown by vapor-phase epitaxy (VPE)[19] or from solutions of In or Ga.[20] In some crystals the layer was grown by liquid-phase epitaxy using Bi as the solvent and Li or Na was used as dopants.[21] In VPE samples KI was usually used as a transport agent but in some samples NaBr was also used.

Optical measurements were made on these epitaxial layers between 5 and 120 °K using a variable temperature Janis Dewar. The excitation source was an Ar^+ ion laser emitting in the uv (3511 and 3638 Å). The spectra were taken by a $\frac{3}{4}$-m Spex double spectrometer (model No. 1401) and a cooled S-20 response photomultiplier (EM19558*Q*) was used as the detector.

For the time-resolved spectra measurement, the samples were mounted in a variable temperature cryostat which provided temperature regulation of 1 °K or better. Excitation was from a nitrogen laser operating at approximately 50-Hz repetition rate. The 3371 Å laser emission was passed through a uv-passing, visible-blocking filter to remove any stray light from the electrical discharge. The beam was then weakly focused onto the sample. The resulting luminescence was collected and focused onto the entrance slit of a $\frac{1}{2}$-meter spectrometer. A photomultiplier detected the light at the exit slit. A uv blocking filter was placed before the entrance slit to remove scattered uv laser light from entering the spectrometer.

The signal from the photomultiplier was put into a PAR 162 boxcar averager using a suitable load resistor to give the necessary signal strength and time constant. The boxcar time constant was set to average approximately 100 pulses to reduce the pulse to pulse fluctuations of the nitrogen laser and shot noise. The output of the boxcar went to a *x*-*y* recorder.

No correction has been made for the spectral response of the spectrometer-photomultiplier combination. However, a check against a standard lamp showed the response to be smooth and relatively flat in the region of our interest. It should be noted that for the weaker luminescing samples the excitation was often strong enough to distort the zero-delay spectra. However, at even the shortest delays used, the distortion has decayed to a negligible level before the first delayed measurement (2 μsec).

III. RESULTS

Our aim is to study and compare the pair spectra observed in various samples grown by vapor-phase epitaxy and from solutions of In, Ga, and Bi. Some samples were doped with Na or Li. Steady-state and time-resolved spectroscopy of pair spectra along with their temperature dependence between 5 and 100 ° K are used to obtain information regarding the role of shallow acceptors.

A. Vapor-grown samples

The spectra at 5 ° K of a vapor-grown sample (A) in which NaBr and KI were used as transport agents is shown in Fig. 1. The pair spectra in this sample consists of two peaks at 2.692 eV (Q_0) and 2.680 eV (P_0), respectively, and their associated phonon replicas. The prominent bound-exciton emission at 2.7931 eV with $E_{BX} = 8.4$ meV is observed. The excitonic band gap is taken to be 2.8015 eV.[4] This bound-exciton transition is commonly observed in Na-doped ZnSe and believed to be due to an excitonic transition at neutral Na_{Zn} acceptors.[4,9,13]

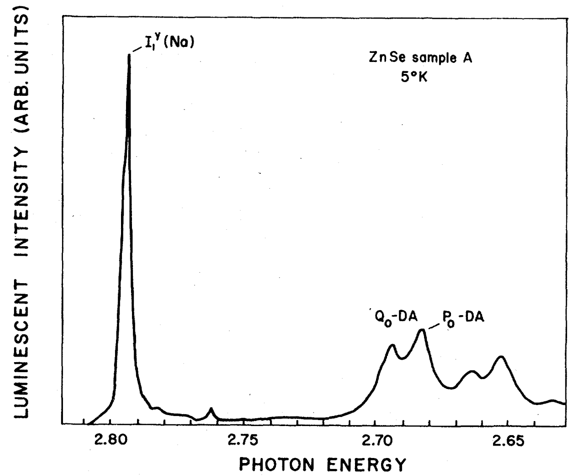

FIG. 1. Photoluminescence spectra at 5 ° K of a Na-doped vapor-grown ZnSe sample (A) where KI and NaBr were used as transport agents. The bound-exciton line at 2.7931 eV [I_1^Y(Na)] and both Q_0 and P_0 donor-acceptor pair (DAP) bands are observed.

In order to understand the role of shallow acceptors and donors, we studied the temperature dependence of the time-resolved spectra. Figure 2 shows the time-resolved spectra taken at 20 and 60 ° K at various time delays after the excitation pulse. In Fig. 2(a), at 20 ° K, the peak positions shift to lower energy with increasing time delay, a characteristic of the donor-acceptor pair transition. From time delay of 2 to 25 μsec, a shift of 6 Å (−3.5 meV) is observed in the Q_0 peak. In Fig. 2(b), at 60 ° K, the peak positions marked P_0(FB) no longer shift with time delay, suggesting that a free-electron to bound-hole (FB) transition is dominating. Q_0(FB) is clearly seen at 2-μsec delay, while at 25-μsec delay P_0(FB) is much stronger than Q_0(FB). This relative change of intensity is possibly related to the fact (i) the holes tunnel

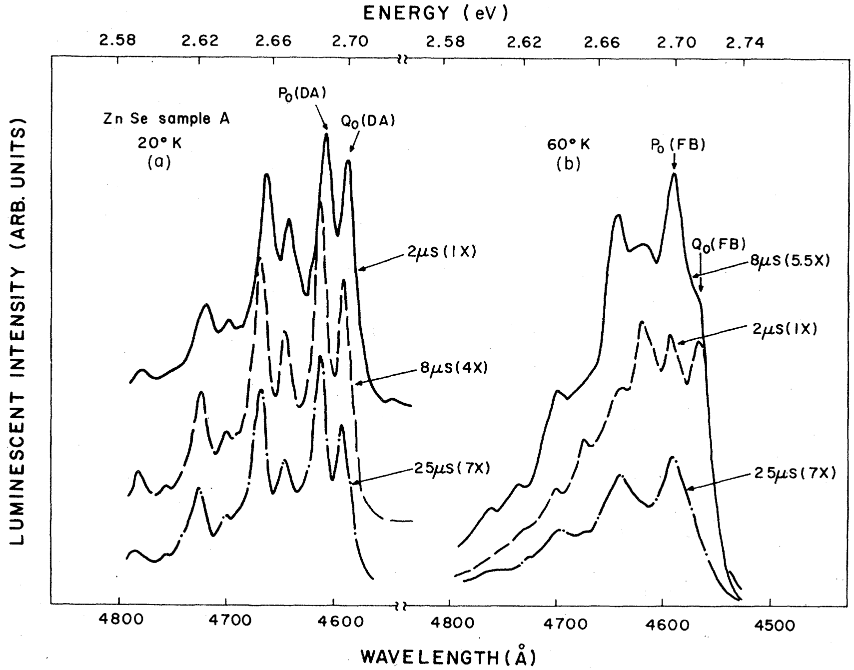

FIG. 2. Time-delayed photoluminescence spectra from vapor-grown ZnSe epi-layers (NaBr and KI transport agents). Figure 2(a) is donor-acceptor pair emission (DA) at 20 ° K for Li(Q_0) and Na(P_0) acceptors. The shift to longer wavelengths (lower energy) with increasing delay time is characteristic of DAP emission. The same bands at 60 ° K (b) are now due to free electrons to holes bound at the acceptors (FB). The separate peaks are from the two shallow acceptors: Li(Q_0); and Na(P_0). These bands do not shift with delay time as expected for free to bound emissions. The unmarked longer wavelength peaks are phonon replicas of P_0 and Q_0 in both (a) and (b).

to the deeper acceptor given time to do so and (ii) the relative hole occupancy itself varies, especially at higher temperatures. However, in the temperature dependence of the spectra taken under steady-state excitation the identification of FB transitions is somewhat difficult to interpret since the donor-acceptor pair (DAP) band and the FB contributions from P_0 and Q_0 overlap. However, when the temperature dependence of the spectra taken at a fixed delay time is taken, this confusion could be resolved as shown in Fig. 3. In this figure we have plotted the spectra taken at 8-μsec delay at various temperatures. At 20 °K [Fig. 3(a)] the peaks are Q_0 and P_0 and their phonon replicas are observed. At 30 °K, FB emission due to Q_0 and P_0 starts contributing, especially the contribution of Q_0(FB), which is clearly visible.

There is a significant contribution from the FB transition at 30 °K due to partial thermalization of the shallow donor E_D at 30 °K. This contribution from the FB transition, relative to the DAP transition, increases as we increase the delay time as depicted in Fig. 4 and can be explained on the basis of two effects. First, there is a decrease in the spectral overlap of Q_0(DAP) and Q_0(FB) transitions because the DAP peak shifts to lower energies with increasing delay.[22,23] Second, as we increase the delay, the slower electron-hole recombination rate at distant pairs dominates. This reduced recombination rate increases the relative number of electrons thermalized as compared to those trapped on the donors and the contribution from the FB transition increases. In Fig. 4 this relative enhancement of FB is clearly depicted. Furthermore, the presence of both FB and DAP at these low temperatures (<30 °K) often makes it difficult to interpret the data when steady-state excitation is used.

There is an unfortunate overlap of P_0(FB) with Q_0(DAP) peak. However, at higher temperatures, e.g., 60 °K, FB transitions dominate and the presence of two separate FB transitions are clearly seen. Figure 2(b) illustrates this vividly, where Q_0 and P_0 FB transitions can be unambiguously observed.

B. Solution-grown Ga-doped ZnSe

All the ZnSe:Ga samples were grown from Ga solution. The particular sample reported here (B) was grown from Ga solution with an excess of Zn mole fraction to enhance the pair emission in comparison to self-activated emission.[20] In Fig. 5, the structure at 2.797 and 2.792 eV at 5 °K, is due to bound excitonic transitions at neutral Ga donors and Li acceptors, respectively. The Li acceptor seems to be present in most of the samples that are treated or grown in excess Zn atmosphere. Under steady-state excitation, using 10 mW of focused radiation from an

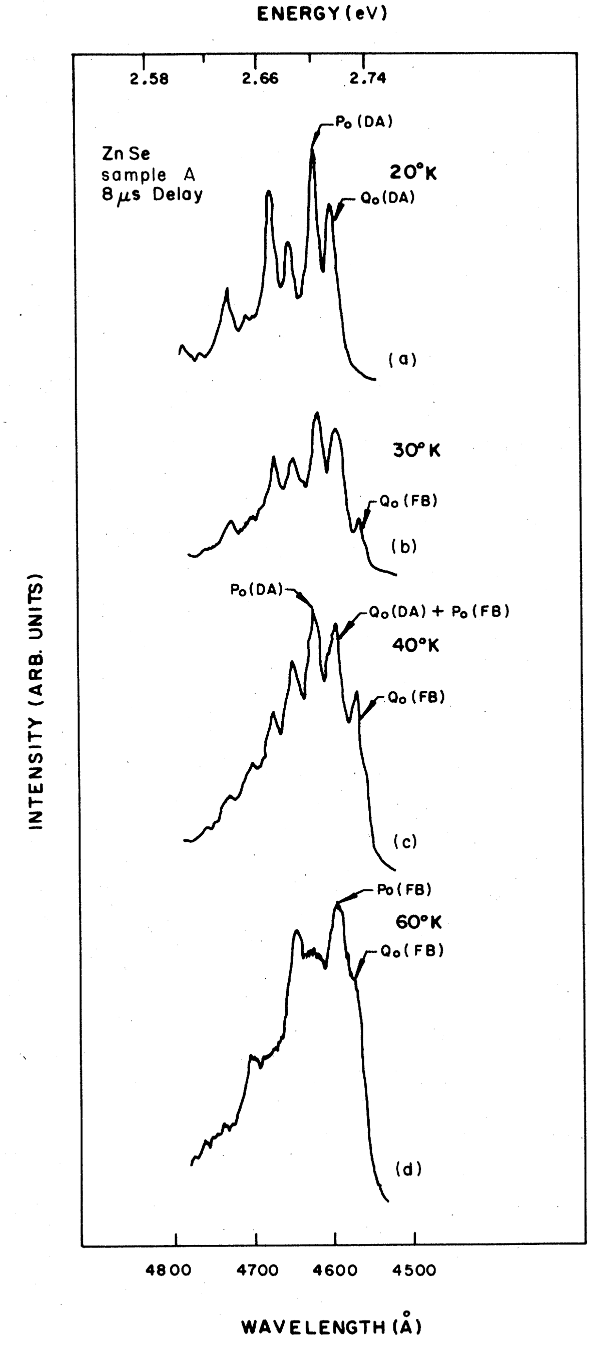

FIG. 3. Same crystal as shown in Fig. 2 (Na-doped, vapor-grown ZnSe epi-layer) at a fixed delay time (8 μsec) and four temperatures. As the temperature increases the two pair bands, Q_0(Na acceptor) and P_0(Li acceptor), begin to show a free bound (FB) peak as well as the pair peak (DA) [compare (a) and (b)]. At higher temperatures the FB to DA continues to increase until at 60° it is predominately FB. Unfortunately, Q_0(DA) and P_0(FB) have the same wavelength and cannot be separated at the intermediate temperatures where both exist.

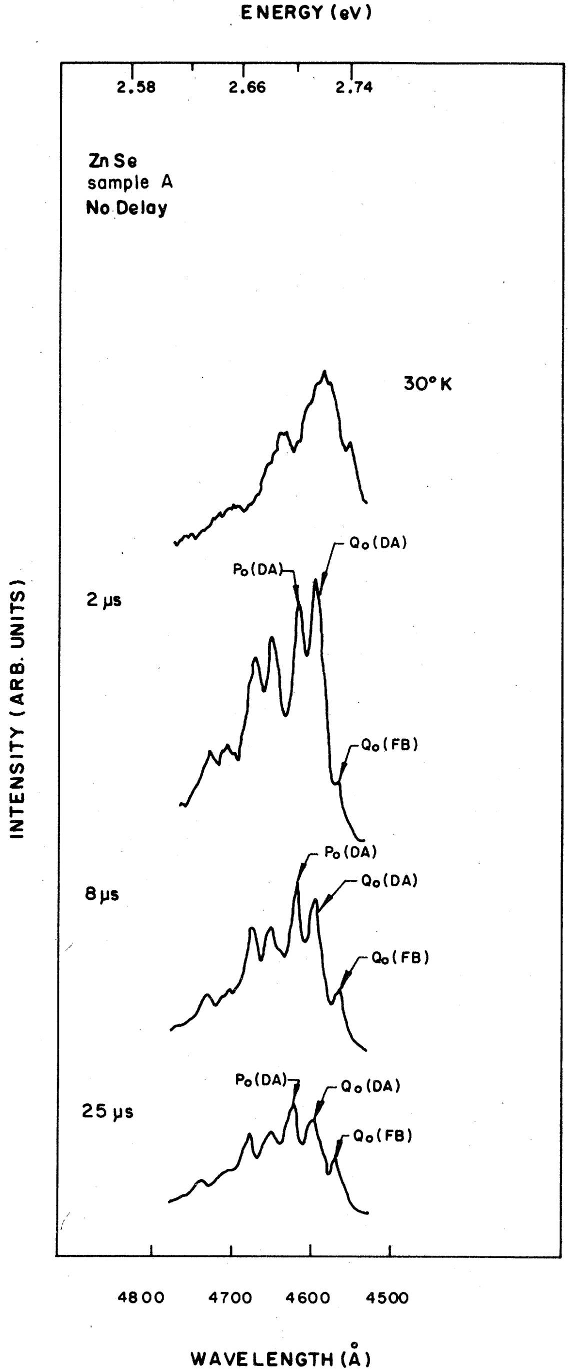

FIG. 4. Same crystal as shown in Figs. 2 and 3 at fixed temperature and four delay times. The undelayed spectra shows very broad peaks due to the high-carrier generation rate during excitation. In the three delayed spectra both of the pair peaks, P_0(Na) and Q_0(Li), can be seen as well as one free to bound peak, Q_0(Li). P_0(FB) overlaps Q_0(DA) and may give some contribution to the Q_0(DA) peak. The changing relative intensities are due to the different decay kinetics of the three different transitions.

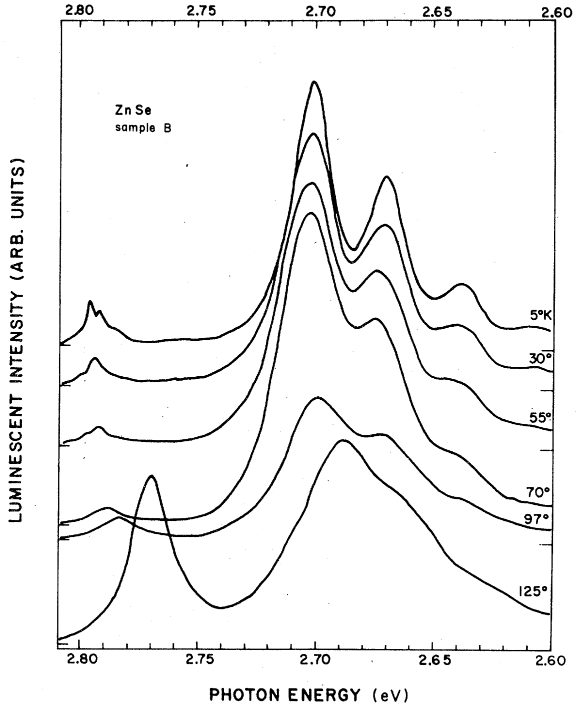

FIG. 5. Temperature dependence of a solution-grown sample (B) where only Q_0(DA) is observed. The important observation is that at 55 °K the peak Q_0 has moved to higher energies while E_g decreases. This suggests, as discussed in the text, that around 55 °K the emission is FB rather than DA consistent with the data in Fig. 3.

Ar^+ ion laser, the pair-band peaks at 2.701 eV. Comparing this with the data of DM, this corresponds to pair peak Q_0, consistent with the presence of the Li acceptor.[4] The temperature dependence of the steady-state excitation is given in Fig. 5. From 5 to 30 °K, the peak position hardly shifts. However, the pair band slightly increases in width. At 55 °K the width of the Q_0 pair band has increased and its position has shifted to higher energy by approximately 2 meV. One should note the peak at 2.694 at 30 °K shifts to a lower energy value of 2.692 at 55 °K. This shift to lower energy represents a decrease in the band gap. When we account for this band gap change in the shift in pair-band-peak position, the change in the peak position of Q_0 band from 30 to 55 °K corresponds to a minimum of 4 meV shift to higher energy.

This small change of 4 meV in the peak position can be understood if we simply express the emission energy for DAP and FB transitions as given below:

$$E(\mathrm{DAP}) = E_g - (E_A + E_D) + \frac{e^2}{\epsilon R} , \tag{1}$$

$$E(\mathrm{FB}) = E_g - E_A , \tag{2}$$

where E_g, E_A, and E_D and $e^2/\epsilon R$ are, respectively, the band gap, acceptor ionization, donor ionization, and Coulombic energies. For the DAP peak position, the estimated Coulombic energy $e^2/\epsilon R \sim 18$ meV (see Ref. 4). Using $E_D = 26$ meV, $-E_D + e^2/\epsilon R$ is then approximately -8 meV. This suggests that the peak energy of the DAP transition increases by 8 meV when the transformation to the FB transition occurs. Thus, a shift in peak position of 4 meV to higher energy is consistent with the change in the recombination process from DAP to the FB transition. Above 55 °K, FB seems to dominate and the peaks at 2.79 and 2.70 eV both follow the change in the band gap. It should be noted that the integrated intensity of the DAP and FB band did not significantly change until 70 °K. However, at 97 °K it decreased approximately by a factor of 2 and at 125 °K, it has decreased by about a factor of 8. This decrease is associated with the thermalization of the hole at the Li acceptor.[8,9]

The time-resolved spectra in this sample show results similar to those obtained on the earlier sample *A*. Using time-resolved spectral measurements, we can easily establish that indeed the emission is pairlike at lower temperatures. At about 60 °K, again, the emission characteristics change to FB, as in the case of *A*. Only one FB transition is observed in this sample, as expected from low-temperature DAP data.

C. Liquid-phase epitaxy (LPE) layers

1. "Undoped" layer

In this particular sample (*C*), the layer was grown from Bi melt[23] on a commercially available ZnSe substrate[24] with no intentional Li or Na dopants added. The prominent bound excitons due to Al, Na, and Li are clearly observed in Fig. 6 at 5 °K. The Li exciton with binding energy of 9.3 meV is observed as a triplet, as reported by Merz *et al.*,[4] and the Na exciton with binding energy of 8.7 meV. A new exciton with binding energy of 7.8 meV is also observed. We do not know the origin of this center at present. The as-grown sample again shows two peaks Q_0 and P_0, though the P_0 peak is the weaker of the two. Under steady-state conditions and low-excitation intensity, the peak positions Q_0 and P_0 are at 2.694 and 2.682 eV, respectively. Time-resolved spectra (Fig. 7) also show two pair peaks at 10 °K. At zero delay, (not shown in Fig. 7) only the Q_0 peak at 2.702 eV is observed. With the delay, P_0 is clearly visible as shown in Fig. 7(a). The shift to lower energy with increasing delay was observed for both the peaks. In this sample both Q_0 and P_0 are narrower than usually observed in the time-delay mode, suggesting lower doping or less strain in this sample. This is also reflected in the bound-exciton emission. The temperature dependence of the spectra is similar to sample *A*,

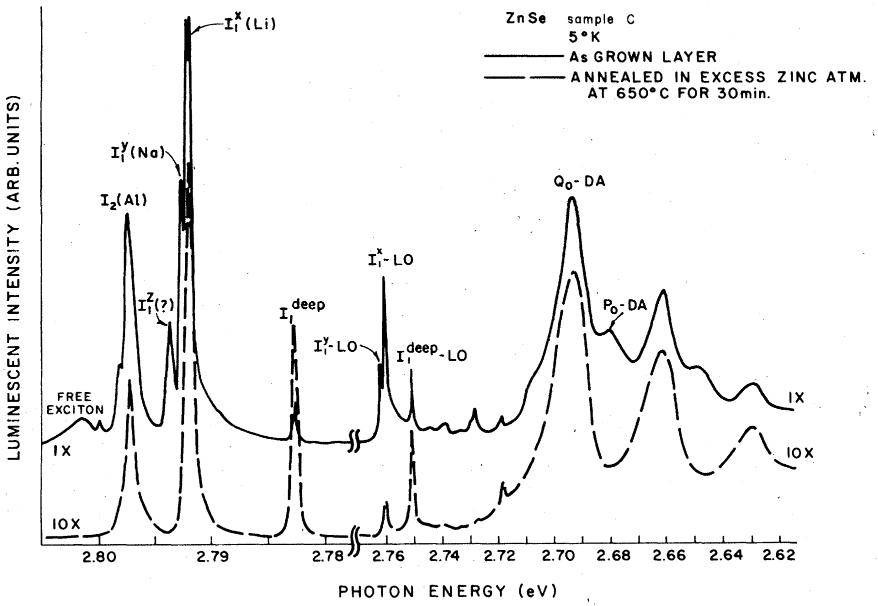

FIG. 6. Bound-exciton (BE) emission and pair bands in a not intentionally doped ZnSe sample grown by liquid-phase epitaxy. In this particular sample we observe BE, I_1^y(Na), I_1^x(Li) as well as I_1^z, as well as Q_0 and P_0. When this sample is annealed at 650 °C for 30 min, the relative intensity of both I_1^y(Na) and P_0(DA) decrease with respect to I_1^x(Li) and Q_0.

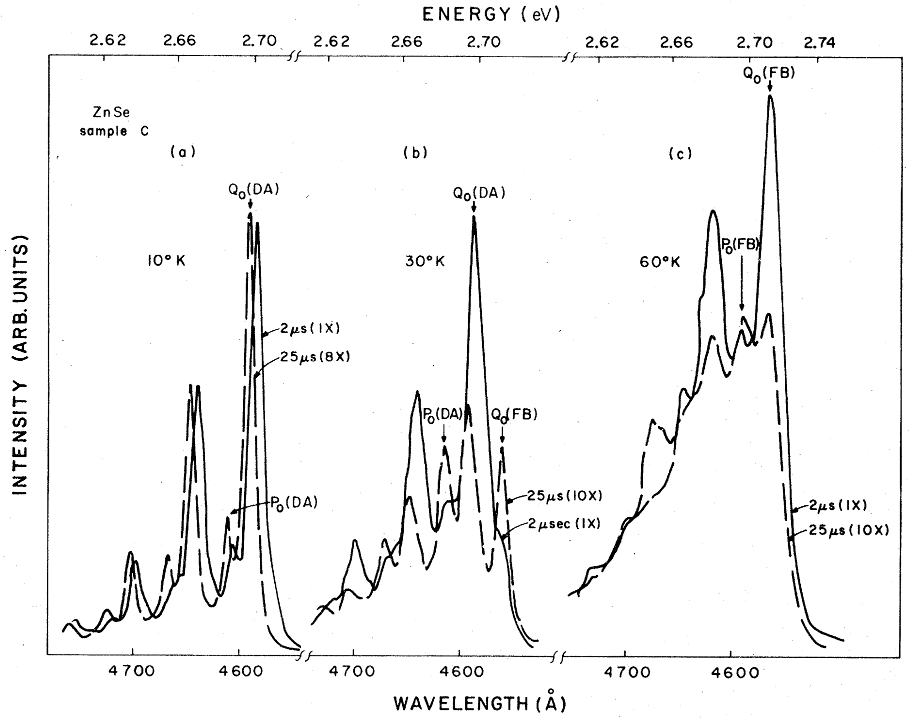

FIG. 7. Bi solution-grown epitaxial layer of ZnSe (no intentional doping). In this crystal the P_0(Na) peak intensities relative to the Q_0(Li) are very much less than in the NaBr transported crystal (Figs. 2, 3, and 4). The much narrower peaks indicate less strain in the crystal. The identification of a peak as donor-acceptor (DA) or free to bound (FB) can be made on the presence or absence of peak shifts with delay time.

but some of the fine points are more pronounced.

At 20 °K there is no evidence of a FB transition. At 30 °K, we observe all the DA peaks which are shifting with time delay [Fig. 7(b)] but we also observe a FB peak at 2.710 eV which does not shift with time delay. The enhancement of Q_0(FB) with time delay is again observed, similar to ZnSe:Ga. This again becomes quite clear in data taken at 40 and 60 °K. At 60 °K the FB emission dominates as shown in Fig. 7(c), and we observe two FB peaks due to two acceptors. The temperature dependence of the peak position at various delays is plotted in Fig. 8. The peak Q_0 and P_0 shift to a higher energy value at approximately 40 °K, due to the contribution of the FB. After 40 °K, the peak shift corresponds to that of the temperature dependence of ZnSe energy band gap.[25] This enhancement of P_0 contribution compared to Q_0 contribution with delayed time is observed both in DAP and FB transitions emission, as shown in Figs. 7(a) and 7(c). This is consistent with the data on vapor-grown sample, reported earlier.

When this sample is annealed at 600 °C for 30 minutes, as shown in Fig. 6, both the bound-exciton spectral characteristics and DAP bands change. The bound-exciton line marked I_1^y and associated with the presence of Na[4,13] is drastically reduced in intensity. Furthermore, the intensity of the DAP band P_0 is also reduced. This correlation suggests that the same acceptor, probably Na, is responsible for the bound-excitonic line I_1^y and the DAP band P_0. This heat treatment also decreases the intensity of Li-related spectra with respect to other spectra present. This is consistent with the results of SG, who also observed that I_1^y(Na) and the intensity of the band 2.680 eV (P_0) decreased under Zn annealing.

2. *Li-doped ZnSe*

When Li is purposely incorporated in LPE layers or solution grown platelets (D) we observed a lower energy emission band. This deep band which is broad compared to the $\mathrm{Li_{Zn}}$ DAP band peaks at 2.620 eV and is probably related to a Li complex is shown in Fig. 9. This sample also shows the R_0 band peaking at 2.708 eV, while the DAP band at 2.695 eV is not resolved in this spectrum.

3. *Na-doped ZnSe*

The Na-doped LPE layer (E) DAP peak occurs at 2.67 eV and is shown in Fig. 9. When compared to P_0 peak, this peak is broadened and shifted to lower energy by approximately 13 meV. The cause of this broadening is probably the high concentration of

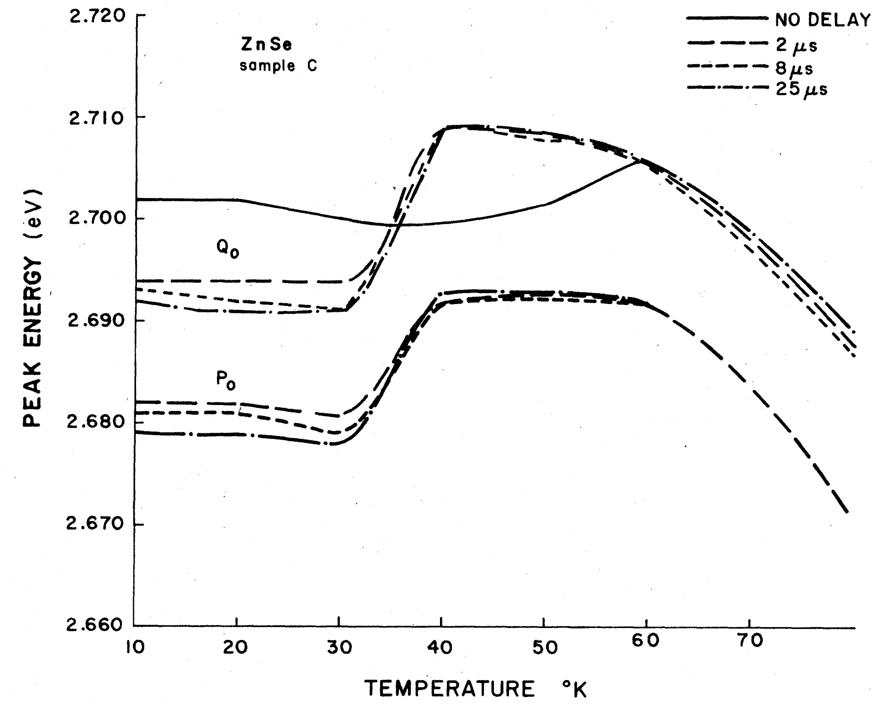

FIG. 8. Temperature dependence of peak energy of the dominant luminescence associated with the Q_0 and P_0 bands. The shift at 40 °K to higher energies is due to the emission becoming predominantly free to bound. The anomalous behavior of the no delay peak is due to distortions in the spectra caused by the very high carrier density during excitation. The shift at 60 °K to lower energies follows the lowering of the band-gap energy with increasing temperature.

Na_{Zn} acceptors, and merger of phonon replicas leads to a decrease in the observed peak energy.

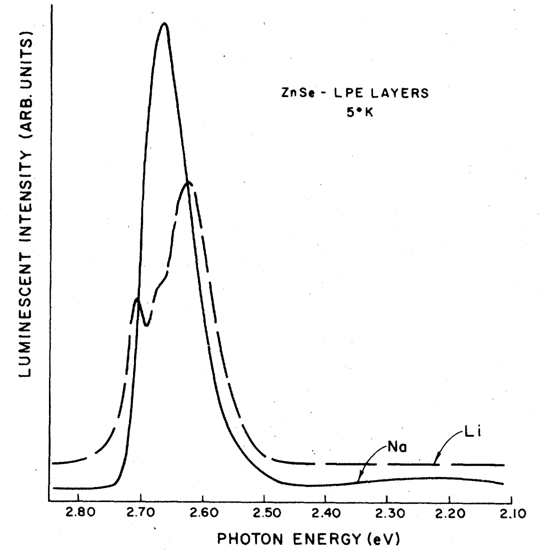

FIG. 9. Photoluminescent spectra of two samples intentionally doped with Na (solid line) and Li (dashed line). The Na-related spectra is an envelope of Q_0 while in Li-doped samples peaks corresponding to R_0 and a new band around 2.6 eV is observed. The origin of this is not clear.

IV. DISCUSSION AND CONCLUSIONS

A. ZnSe:Li

1. Origin of Q_0

In all the samples we have studied, the observed pair peak at 2.696 eV (Q_0) is attributed to the presence of Li, confirming earlier conclusions of Merz *et al.*[4] In several samples, we have observed discrete pair lines corresponding to Al_{Zn} donor and Li_{Zn} acceptor and these samples have shown a DAP peak at 2.696 eV. Also, a bound exciton (BE) with a binding energy of 9.3 meV is always present with the 2.696-eV band. This BE has been associated with the Li acceptor.[4] The band, Q_0, is also observed in Li-doped layers if Li incorporation is kept at a minimum (probably $<10^{17}$ cm^{-3}). Thus, there is no doubt that the 2.696-eV band is associated with the Li acceptor.

Swaminathan and Greene[13] studied a sample under zinc annealing and reported a discrete pair-line spectra in their Fig. 6. They analyzed the data in their Fig. 7 and obtained a value of $E_A + E_D = 139$ meV.

These pair lines were associated with the distant pair band peaking at 2.702 eV (referred to as X_0-4587 in Ref. 13), and the acceptor responsible for this emission was attributed to $\mathrm{Na_{Zn}}$ based on doping experiments. For $\mathrm{Al_{Zn}}$ donor and $\mathrm{Li_{Zn}}$ acceptor, Merz *et al.*[4] obtained a value of $E_A+E_D=140\pm1$ meV, suggesting that Swaminathan and Greene were indeed observing the pair lines due to $\mathrm{Li_{Zn}}$ rather than $\mathrm{Na_{Zn}}$ acceptors. Comparing data of SG with that presented in Merz *et al.* (Fig. 1 of Ref. 4), we strongly feel that the Q_0 peak at 2.692 eV (labelled as X_0-4606 by SG) is indeed responsible for the pair lines in Fig. 6 of SG, i.e., $\mathrm{Li_{Zn}}$ is responsible for discrete pair lines in this sample rather than $\mathrm{Na_{Zn}}$, as claimed by SG. This pair peak also dominates in crystals where Li has been purposely introduced.[4,13] We observe similar results in LPE layers of ZnSe doped with Li. However, if the concentration of Li is high, we do not observed discrete pair lines, but two additional peaks at 2.708 and 2.620 eV appear, as shown in Fig. 9 for a Li-doped LPE layer. These Li-doped samples appear much darker in appearance.

2. Origin of R_0

The peak at 2.708 is the peak referred to as R_0 by Dean and Merz.[8] From the temperature dependence of the spectra DM observed that only Q_0 gave rise to a FB peak while R_0 did not. This is expected if R_0 involves a shallow donor E_D^x and same acceptor as in Q_0, which we know now is $\mathrm{Li_{Zn}}$. As the temperature is raised, the bound electrons at E_D^x and the Al donor will thermalize within a small interval of temperature, and will give rise to the same FB transition involving the acceptor $\mathrm{Li_{Zn}}$ as observed by DM. In fact, the temperature dependence of the Q_0 peak, reported in Fig. 5, is similar to that observed by DM in sample where R_0 and Q_0 were both present. Recently, Tews *et al.*[26] have studied excitation spectra on different DAP bands and have also concluded that the acceptor involved in the R_0 pair band is substitutional Li. From the above data, it is concluded that the transition in DAP band R_0 involves the Li acceptor and a different shallow donor E_D^x of ionization energy comparable to other known hydrogenic donors exists in ZnSe.[16]

In order to identify this new donor E_D^x, several observations are made from the published data on R_0 and Q_0 DAP bands. They are (i) R_0 most occurs with Q_0, (ii) there seems to be a considerable variation in the peak positions of R_0, reported by various workers; this variation has normally been attributed to preferential and random pairing of donors and acceptors[12,13]; (iii) discrete pair lines from DAP band Q_0 have been clearly identified while the observation of pair lines in R_0 has not yet been understood,[4,8] (iv) the half width of the R_0 emission band is larger than that of the Q_0 band,[8] (v) the variation of peak position with excitation intensity of R_0 is almost twice that observed for Q_0, and (vi) in the original DM spectra[8] a doubling of individual pair lines was observed (see Fig. 5 or Ref. 4). All of these characteristics of R_0-DAP spectra, except the last one, can be accounted for qualitatively if we postulate that the particular donor in question is associated with the highly mobile impurity Li and is possibly related to $\mathrm{Li_{int}}$. We now discuss the aforesaid properties of R_0-DAP spectra in detail.

The observation (i) suggests that the dopant responsible for the Q_0 band is also responsible for R_0 band, i.e., E_D^x donor is related to Li impurity. A possible explanation could be that E_D^x is $\mathrm{Li_{int}}$, which is expected to be a shallow donor. This shallow donor attributed to $\mathrm{Li_{int}}$ could also be related to a complex of V_{Se}-$\mathrm{Li_{Zn}}$,[3] which will be a singly charged donor if V_{Se} is a doubly charged donor.

The R_0-DAP peak typically occurs at about 12–14 meV higher energy than Q_0-DAP peak. This difference in the peak positions of R_0 and Q_0 yields $E_D^x\approx14-16$ meV, since the aluminum-donor (E_D^x) energy responsible for Q_0-DAP peak is 26.3 meV.[4] As it will become clear from the discussion below, this estimate is erroneous since the Coulombic term in Eq. (1) for Q_0- and R_0-DAP spectra differ considerably.

Additional but somewhat more accurate value of E_D^x could be obtained from the comparison of original DM pair line spectra and $\mathrm{Al_{Zn}}$-$\mathrm{Li_{Zn}}$ DAP spectra as depicted in Fig. 6 of Ref. 4. From this comparison of the positions of discrete pair lines, we conclude $E_D^x\approx E_D^{\mathrm{Al}}\pm0.5$ meV, i.e., $E_D^x\approx26\pm1$ meV.[27] This close value of E_D^x and E_D^{Al} when compared with the observed difference in the peak positions of R_0 and Q_0 can be explained qualitatively if we propose that the donor E_D^x is due to $\mathrm{Li_{int}}$. Due to a high mobility of $\mathrm{Li_{int}}$ at temperatures as low as 200 °C, we expect moderate association in the distribution of donor and acceptors. This association, commonly referred to as preferential pairing,[18] increases the value of the Coulombic energy term $e^2/\epsilon R$ at the peak position of the DAP spectra. This enhanced value of $e^2/\epsilon R$ shifts DAP peak to a higher energy than what is expected for the impurities which are less mobile at low temperatures. In fact, depending on the thermal history of the sample, R_0-DAP peak varies from 2.705 to 2.715 eV. However, in conventional DAP spectra (e.g., Q_0) where two substitutional impurities are involved, we expect negligible preferential pairing due to low mobilities of substitutional dopants at low temperatures. The observations (iv) and (v), respectively, are related to the differences in the half widths of R_0- and Q_0-DAP bands and to the difference in the rate of change of peak position with increasing excitation intensity. Both of these observations can be explained if we believe that R_0-DAP band involves relatively "close" donor-acceptor pairs while Q_0

DAP involve distant pairs. The apparent half width in a DAP spectra at larger distances is expected to be small since change in the Coulombic term, $\Delta(e^2/\epsilon R)$, decreases with increasing R values, i.e., larger R corresponds to narrower peak, as noted in the case of Q_0. Similarly, with increasing intensity this change $\Delta(e^2/\epsilon R)$ is expected to be smaller for larger values of R. Since R_0 DAP involves close pairs, it is expected to have larger half width and faster rate of change of peak position, consistent with the observation of DM.

The last of the observation regarding doubling of pair lines in R_0 DAP is yet to be explained. In fact, the understanding of the origin of discrete pair lines in R_0 could establish unambiguously whether $\mathrm{Li_{int}}$ is the donor responsible for the level E_D^x. It is somewhat hard to establish since in most of the samples discrete pair lines from R_0 are difficult to resolve. If $\mathrm{Li_{int}}$ is the donor, it should give rise to either type-II or -III spectra.[28] DM have analyzed the spectra to be type-I, thus, further work is needed to resolve the origin of discrete pair lines in R_0-DAP spectra.

B. ZnSe:Na

In all Na-doped samples, a pair peak at 2.680 eV occurs. As we discussed earlier, this peak is related to Na doping, as also was reported by Chatterjee *et al.*[9] and by SG.[13] In Na-doped samples we have not seen any other associated spectra besides this. Also, discrete donor-acceptor pair lines were not observed in Na-doped samples. This could be due to intermixing of pair lines associated with Li and Na acceptors, since Li is always present as a background impurity and Li DAP is always observed in bulk crystals. In heavily Na-doped samples the DAP band is broad and again the discrete pair-line spectra is not observable. Na-doped layers differed from Li-doped layers in several aspects: (i) No other spectra, which possibly could be associated with $\mathrm{Na_{int}}$, are discernible. (ii) When Au contacts were used to assess electrical conductivity in Li-doped samples, the current was unstable while in Na-doped samples the current remained constant. This is possibly due to the presence of $\mathrm{Li_{int}}$.[3] (iii) As shown in Fig. 6, the Na peak at P_0 and I_1^y(Na) disappear after the sample is annealed in Zn atmosphere at 650 °C for 30 min, while Q_0 and I_1^y(Li) remain fairly constant. This suggests that Na moves out of the zinc site much more easily than Li. This may explain why frequently Na-doped or Na-implanted samples have shown strong Li-DAP spectra.[10,13] Swaminathan and Greene had also observed that Na-related BE spectra and DAP band decreased on annealing. In fact, the discrete pair-line spectra observed by SG in Figs. 6 and 7 yield a value of the acceptor level which has been identified as $\mathrm{Li_{Zn}}$. This impurity exchange between Li and Na has also created some confusion in identifying the acceptor dopant in ZnSe.

From our studies and those of SG,[13] the DAP band P_0 is attributed to Na and by comparison of its peak position with Li-DAP band Q_0, we estimate the Na-acceptor level to be 124 ± 2 meV.

C. Preferential and random pairing

In all the samples we have studied, we observe only three DAP bands, R_0, Q_0, and P_0. We feel that these transitions are simply related to the presence of usually two acceptors, $\mathrm{Li_{Zn}}$ and $\mathrm{Na_{Zn}}$, and donors like $\mathrm{Al_{Zn}}$ and Li related donors (e.g., $\mathrm{Li_{int}}$). The various transitions are depicted in Fig. 10. From the time-resolved spectra it is rather clear that free-to-bound transitions also frequently contribute at low temperatures and especially at excitation energies significantly greater than E_g, and thereby complicate the situation. Consistent with our data, Gezci and Woods have also observed only three peaks.

However, there have been studies where two DAP bands which are frequently observed in the same sample have been interpreted as due to random and preferential pairing of donor and acceptor impurities.[13,18] For example, in the studies of Swaminathan and Greene,[13] the 2.714 and 2.702 eV bands were interpreted as preferential and random paired DAP bands associated with Li. Similarly Gezci and Woods[12] associated 2.705- and 2.686-eV DAP bands with preferential and random-pair bands associated with the same donor and acceptor dopants. We feel that the 2.704 band in case of SG[13] and the 2.705-eV band in case of Gezci and Woods are associated with $\mathrm{Li_{int}}$ donor while the common acceptor is Li. The

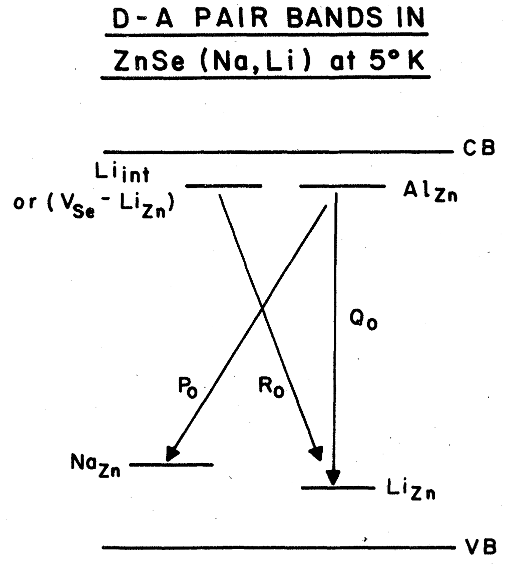

FIG. 10. Summary of the identification of various donor-acceptor pair transitions associated with Li and Na doping.

variations of the peak positions as reported by various authors could be due to the use of different excitation intensities as well as due to moderate association in case of Li_{int}. Since R_0(Li_{int} donor) and Q_0 (Al_{Zn} donor) are associated with the same acceptor Li_{Zn}[26] and are frequently observed in the same sample, this preferential and random pairing model had some basis. In fact, we have noted a considerable variation in the position of R_0 (2.707 ±0.003 eV), which indeed may be due to some preferential pairing, and was discussed earlier. However, we must be cautious associating random and preferential pairing whenever two peaks are observed and only two impurities are expected to be present. In the example above, R_0 DAP has some preferential pairing while Q_0 DAP does not. This is entirely due to high mobility of Li_{int}. Thus in a slow cooled sample, preferential pairing would be expected. However, in a regular donor-acceptor pair band where two substitutional impurities are involved, we do not expect preferential pairing. This is the case, for example, for the Na_{Zn} acceptor related DAP band P_0.

D. *p*-type ZnSe

Why do Li and Na acceptors, which are fairly shallow, not give *p*-type ZnSe? From the present study we can conclude that in Li-doped samples, Li_{int} (or other associated complexes) are shallow donors and prevent *p*-type conductivity, consistent with Henry *et al.*[3] However, if we can incorporate enough Na, the material is indeed *p*-type.[29] In such a sample we estimate the position of Fermi level to be less than 0.5 eV from the valence-band edge.

As a final comment to obtain *p*-type ZnSe, acceptors other than Li and Na are likely to succeed. In a recent study we have successfully incorporated P and N which yield *p*-type ZnSe layers. Our preliminary luminescent studies suggest that both P and N are shallow acceptors of $E_A \sim 85$ meV. This is a contradiction to studies made on P-doped ZnSe by EPR studies[30,31] where P_{Se} was attributed to a deep donor of 0.7 eV. Studies are currently being made to identify unambiguously the acceptor energy levels associated with N and P impurities. Furthermore, background Li_{int} concentration together with the concentration of any deep centers which can act as donors have to be reduced to a minimum to achieve better *p*-type conductivity.

In summary, by a careful study of donor-acceptor pair transitions in ZnSe using temperature dependence of the time-resolved spectra, we have identified the shallow-acceptor level due to Na as 124 ± 2 meV. Another shallow donor of ionization energy $\sim 26 \pm 1$ meV, which indeed may play a role in compensation, has been associated with lithium and possibly is Li_{int}. Use of well-controlled growth process like liquid-phase epitaxy and careful characterization give us a renewed hope that *p*-type ZnSe is possible. It seems that both good *p*-type and *n*-type conductivities in ZnSe are limited by extrinsic impurities rather than vacancies or self interstitials. A similar conclusion in ZnTe has been reached by Dean and coworkers.[32]

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