PHYSICAL REVIEW B VOLUME 24, NUMBER 12 15 DECEMBER 1981

Phonon scattering at impurity pairs in ZnSe

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(Received 12 March 1981)

We have investigated in detail the phonon lines in the luminescence excitation spectra of donor-acceptor pairs in ZnSe as a function of crystal temperature and surface orientation. At low temperatures $T < 50$ K, the phonons are emitted during the donor-acceptor pair excitation or recombination process. Besides the carrier-phonon interaction of the Fröhlich type, a second interaction correlated with close donor-acceptor pairs is clearly observed. The phonon lines indicate further that the acceptor ground state is split due to interimpurity interactions. In the temperature range from 50 to 80 K, no phonon lines are detected. The lines reappear at temperatures $T > 80$ K. Selection rules for first-order Raman scattering at different surfaces are observed. At $T > 100$ K, the LO-phonon line grows relative to the TO due to resonant Raman scattering.

I. INTRODUCTION

In recent years, much work has been done on the luminescence excitation spectroscopy of donor-acceptor pairs in semiconductors. In these experiments, the crystals are irradiated with light from a tunable dye laser, and the radiative recombination of donor-acceptor pairs with a fixed pair separation R_{DA} (giving a photon of energy $\hbar\omega_l$) is measured as a function of excitation energy $\hbar\omega_p$. Peaks are observed in the spectra when the excitation energy is equal to $\hbar\omega_l$ plus an electronic transition at the donor or the acceptor, assuming that the detector energy is chosen to fulfill some conditions concerning the recombination probability or the number of pairs with separation R_{DA}.[1]

A second group of peaks in the excitation spectra occurs at energy separations to the exciting laser line equal to an optical phonon. These peaks show a pronounced dependence on the detector energy at low temperatures. In particular, small deviations of the LO-phonon energy from the LO energy of the unperturbed lattice have been observed.[2]

The aim of this paper is to investigate the one-phonon region in the excitation spectra of donor-acceptor pairs, and to find the physical processes for the generation of the phonon lines. For this purpose, excitation spectra have been taken on ZnSe samples between helium and room temperature, and for various surface orientations.

The paper is organized as follows: Sec. II contains a description of the experimental setup. In Sec. III, the experimental results will be presented. Section IV contains the discussion of the temperature ranges 1.6 K (Sec. IV A), 5 to 80 K (Sec. IV B), and for temperatures above 80 K (Sec. IV C). In Sec. V, the results are summarized.

II. EXPERIMENTAL

The ZnSe samples used in our experiment were undoped single crystals, some of which were covered by an epitaxial layer. A part of the crystals with (110), (100), and (111) surface orientations were prepared from one bulk crystal to assure the same impurity concentrations in all these samples. The (110) and (100) surfaces were cleaved planes, whereas the (111) surface was cut and mechanically polished.

The luminescence excitation spectra were taken in the back scattering configuration. The crystals were placed in an immersion cryostat for experiments at 1.6 K, or in a temperature-variable cryostat for temperatures from 5 to 300 K. The crystals were irradiated with light from a tunable Stilbene-3 dye laser. The linearly polarized components of the luminescence light were examined. The photons were analyzed in a 0.75-m double-grating spectrometer and detected by a cooled photomultiplier.

III. RESULTS

The experimental results presented in this paper are obtained from the pair band of the Li acceptor in ZnSe with a pair-band maximum at about 2.69 eV at low temperatures.[3] Luminescence excitation spectra are taken with the detector at different energies between $\hbar\omega_l = 2.72$ eV (corresponding to a donor-acceptor separation R_{DA} of 36 Å), and $\hbar\omega_l = 2.68$ eV, corresponding to infinite pair separation.

Figure 1 shows the one-phonon part of the ex-

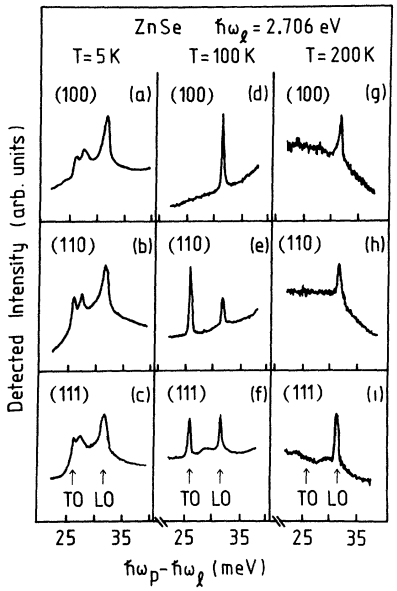

FIG. 1. Excitation spectra of ZnSe at a detector energy of $\hbar\omega_l$ = 2.706 eV for three temperatures 5, 100, and 200 K, and for the (100), (110), and (111) surface orientations. Shown is the energy region of the one-phonon lines. The energy positions of the lattice TO and LO are indicated. Exciting photons and luminescence photons are polarized parallel to each other.

citation spectra obtained at $\hbar\omega_l = 2.706$ eV for different temperatures and different surface orientations. The spectra at 5 K show three peaks,

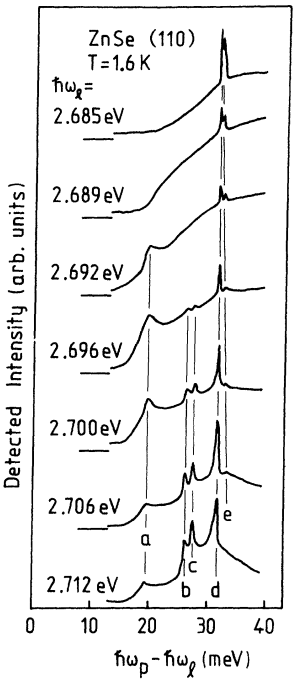

FIG. 3. Excitation spectra of a (110) surface at 1.6 K for different detector energies $\hbar\omega_l$. a corresponds to the 1S-2S transition line of the donor, probably Cl. b is the TO phonon. c is a phonon bound to impurities, see Sec. IV A. d and e are LO phonons with a donor-acceptor pair as intermediate state, as discussed in Sec. IV A. Exciting photons and luminescence photons are polarized perpendicular to each other. The spectra are normalized to the same spectral height.

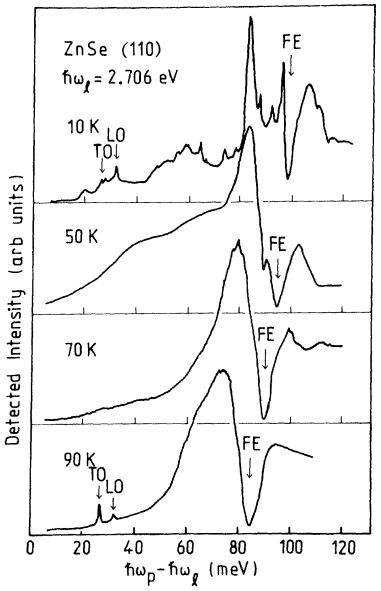

FIG. 2. Excitation spectra in the temperature region from 5 to 100 K. Exciting photons and luminescence photons are polarized parallel to each other. The spectra are normalized to the same spectral height.

two of which coincide in energy with the TO and the LO lattice phonon.[4] A third peak occurs at a separation of 27.4 meV to the exciting laser line. The spectra at 5 K show no dependence on the orientation of the crystal surface relative to the electric vector of the luminescence light.

At 100 K, the phonon lines have narrowed relative to the spectra at 5 K. Only the TO and LO phonon are observed. A pronounced dependence of the intensities of the phonon lines on the surface orientation is found. At 200 K, only the LO line is observed in the spectra for all three surface orientations.

The transition from the broad lines at 5 K to the narrow lines at 100 K is shown in more detail in Fig. 2. Here the complete spectra are recorded for different temperatures between 5 and 100 K. Besides the phonon lines, a variety of additional information is gained from the excitation spectra. In all spectra, a pronounced minimum at the free-exciton (FE) position is found. Further minima indicate bound-exciton recombination, an effective competing recombination mechanism to the donor-acceptor pair luminescence. At low tempera-

tures, the $1S$-$2P_{3/2}$ and the $1S$-$2S$ transitions of the Li acceptor appear as sharp peaks in the excitation spectra. The structures in the spectra of Fig. 2 are fully discussed in Ref. 1. Figure 2 shows that there is a temperature region between approximately 50 and 80 K where no phonon lines can be detected.

In Fig. 3, the dependence of the phonon lines on the detector energy position is examined. The spectra are recorded at 1.6 K on a (110) surface. At 19.3 meV, the donor $1S$-$2S$ transition is found [line (a)].[5] The TO [line (b)] and the 27.4-meV line [line (c)] intensities decrease with increasing pair separation. Both lines disappear when the detector energy corresponds to the maximum of the donor-acceptor pair band.

The LO line [line (d)] is present in all spectra. One observes a narrowing of the line with decreasing $\hbar\omega_l$, i.e., with increasing pair separation. In addition, a second line [line (e)] with an energy slightly higher than the LO energy is found in the spectra. This line appears as a small peak in the spectrum with $\hbar\omega_l = 2.706$ eV, separated from line (d) by 1.3 meV. It grows with decreasing detector energy. While growing, the separation between this line and the LO line (d) decreases. At $\hbar\omega_l = 2.685$ eV, the separation between (d) and (e) has reduced to 0.25 meV. No TO phonon is observed at this detector energy. For smaller detector energies $\hbar\omega_l < 2.685$ eV, (d) and (e) are no longer resolved as separate peaks.

The experimentally determined optical-phonon energies from the high-temperature spectra ($90 \leq T \leq 250$ K) are $E_{\mathrm{TO}} = (26.0 \pm 0.5)$ meV, $E_{\mathrm{LO}} = (31.7 \pm 0.5)$ meV, and $E_{2\,\mathrm{LO}} = (63.5 \pm 0.5)$ meV. Above 150 K, a slight decrease of the 2 LO energy is observed, giving $E_{2\,\mathrm{LO}} = (63.3 \pm 0.5)$ meV at ($200 \leq T \leq 250$ K). This decrease of phonon frequencies with increasing temperature is well known to be due to anharmonic forces in the crystal lattice.[6] It should be noted that the phonon lines in the low-temperature spectra coincide precisely with the high-temperature energies within a relative experimental error of ± 0.2 meV.

IV. DISCUSSION

A. 1.6 K

Two types of contributions to the generation of the phonon lines have to be considered: first-order Raman scattering without impurity scattering, and generation of phonons during processes where impurities are involved.

A consequence of Fig. 1 is that first-order Raman scattering via deformation potential or Fröhlich interaction *without participation of impurities* does not play an important role for the generation of the one-phonon lines in the low-temperature excitation spectra. Deformation potential scattering would show a clear orientation dependence of the LO and TO intensities. Scattering via Fröhlich interaction would generate only the LO phonon but not the TO, and further the scattering cross section is zero when the polarizations of the exciting and the scattered photon are perpendicular to each other. Such a dependence on the direction of polarization was not found.

In the following we will show that all the low-temperature spectra can be understood when a donor-acceptor pair is taken as an intermediate state for the light scattering. The whole process is described as follows: An incoming photon $\hbar\omega_p$ is absorbed in the crystal by creation of a virtual electron-hole pair, the electron of which is trapped by an ionized donor, and the hole is trapped by an ionized acceptor. This first process describes the neutralization of a donor-acceptor pair, called for short "pair neutralization" in this paper. The four-particle system neutral-donor–neutral-acceptor acts as an intermediate state of lifetime $\tau(R_{DA})$ where the electron and the hole are in discrete, i.e., bound states of the donor and the acceptor. The recombination of the electron and the hole after the pair lifetime τ generates a luminescence photon $\hbar\omega_l$. This last process is called "pair recombination" for short.

In bound states, the carriers can only transfer energy to a phonon if the energy level separations of the electron or hole states coincide accidentally with an optical-phonon energy, or if a transfer process of the excitation to another donor-acceptor pair is possible. The energy transfer from one donor-acceptor pair to a second pair depends on the density of neutral pairs and on the pair lifetime. It has been shown in an earlier publication that the energy transfer is small for pairs with separations corresponding to the high-energy side of the donor-acceptor pair band, and for the low excitation intensities used in our experiments.[1]

The condition of a lower-lying electronic state is usually not fulfilled, except in the case wherein the binding energy of the donor or the acceptor is smaller or equal to an optical phonon, as for the donors in ZnSe with $E_D \approx 26$ meV (Ref. 5) $\hbar\omega_{\mathrm{TO}} = 26.0$ meV, and $\hbar\omega_{\mathrm{LO}} = 31.7$ meV. In this case, a free electron-bound hole pair can be created when the excitation energy is $\hbar\omega_p \geq E_g - E_A$, where E_g is the band-gap energy and E_A is the acceptor binding energy. The electron can transfer to the ground state of the donor by emitting an optical phonon, and eventually in addition some acoustical phonons to account for the Coulomb energy

between donor and acceptor. Such a process yields a broad band in the excitation spectra since all pair separations are possible.[7] It does not contribute to the phonon *lines* which are studied in this paper.

Carrier-phonon scattering involving impurity pairs is possible during the processes of pair neutralization (process A), and pair recombination (process B). Both processes can be clearly distinguished. Assume an excitation spectrum is recorded for a detector energy $\hbar\omega_l$. The energy available for the neutralization of a donor-acceptor pair is reduced by the phonon energy if the phonon emission takes place during the neutralization process, giving a pair with a separation R_{DA}. However, the whole energy of the exciting photon is available for the neutralization of a donor-acceptor pair if the phonon generation occurs during the recombination process. Thus a pair with a smaller $R'_{DA} < R_{DA}$ results. The TO or LO energy are usually of the same magnitude as the Coulomb term for pairs on the high-energy side of the pair band. Thus the difference between R'_{DA} and R_{DA} is significant. For illustration, assume a detector energy $\hbar\omega_l = 2.706$ eV as in the experiment of Fig. 3. An LO-phonon line can be observed when the excitation energy is $\hbar\omega_p = \hbar\omega_l + \hbar\omega_{LO} = 2.737$ eV. This energy allows the neutralization of donor-acceptor pairs with a separation of $R'_{DA} \simeq 27$ Å when the phonon is emitted at the donor-acceptor pair recombination, and $R_{DA} \simeq 62$ Å when the phonon is emitted at pair neutralization. In our model, process A always represents donor-acceptor pairs with larger pair separations than the pairs from process B. We will assume that the interaction between carriers and phonons is of the Fröhlich type, as described in Refs. 8 and 9 (see also references cited therein). Thus only LO scattering occurs.

The relative contributions of processes A and B to the phonon scattering can be estimated as follows. We assume equilibrium conditions, and a homogeneous distribution of photons of energy $\hbar\omega_p$ in the crystal volume which is irradiated by the laser beam. The density of donor-acceptor pairs which are neutralized during process A is proportional to $nSW(R_{DA})N^*(R_{DA})$, and $nW(R'_{DA})N^*(R'_{DA})$ for process B. Here S is the phonon coupling constant which is assumed to describe equally the processes of phonon scattering during photon absorption and photon emission. $W(R_{DA})$ is the transition probability for neutralization of a donor-acceptor pair of separation R_{DA}, $N^*(R_{DA})$ is the density of ionized donor-acceptor pairs with separation R_{DA} present in the crystal volume. n is the probability of finding a photon next to one such donor-acceptor pair. n thus depends on the incident flux of photons. We have $0 < n \leq 1$. S can be estimated from the relative intensities of the LO replicas of the donor-acceptor pair band.[7,8] In a detailed calculation, S also depends on R_{DA}.[8] For the Li pair band in ZnSe, we find $S \simeq 0.6$.

The recombination of the neutralized pairs occurs without participation of phonons, or with the emission of one or more phonons. Neglecting terms with two or more phonons, we get for process A the balance for pair neutralization and pair recombination

$$nSW(R_{DA})N^*(R_{DA}) = W(R_{DA})N^0(R_{DA}) + SW(R_{DA})N^0(R_{DA}), \quad (1)$$

and for process B

$$nW(R'_{DA})N^*(R'_{DA}) = W(R'_{DA})N^0(R'_{DA}) + SW(R'_{DA})N^0(R'_{DA}) . \quad (2)$$

Here $N^0(R_{DA})$ is the concentration of neutral pairs with separation R_{DA}.

The intensity I_A of process A is expressed by the term $W(R_{DA})N^0(R_{DA})$, and for I_B of process B we have $SW(R'_{DA})N^0(R'_{DA})$. Using the total density of impurity pairs $N(R_{DA}) = N^*(R_{DA}) + N^0(R_{DA})$, we get for the ratio I_A/I_B

$$\frac{I_A}{I_B} = \gamma \frac{W(R_{DA})N(R_{DA})}{W(R'_{DA})N(R'_{DA})} \quad (3)$$

with

$$\gamma = \frac{n+1+S}{nS+1+S} . \quad (4)$$

With $S = 0.6$ and $0 < n \leq 1$ we get a value $1 < \gamma \leq 1.2$. Thus the relative contributions of processes A and B to the phonon scattering is given by the ratio of the transition probabilities, and the ratio of the densities of donor-acceptor pairs with separation R_{DA} and R'_{DA}, respectively, multiplied by a factor γ which enhances slightly the contribution of process A over the contribution of B.

Both processes A and B yield sharp LO lines and thus should be indistinguishable. There is, however, an effect that has to be considered: it has been found in GaP (Ref. 10) and in CdTe (Ref. 11) that the acceptor ground state is split by an energy $\Delta(R_{DA})$ into two levels due to inter-impurity interactions for close donor-acceptor pairs.[12] The splitting $\Delta(R_{DA})$ depends on the pair separation and decreases with increasing R_{DA}.

We will discuss here the influence of the acceptor state splitting on the process B. The discussion of process A is similar.

In our model, the holes are trapped into one of the two states during the pair neutralization process. Since both states are initially empty, the

relative occupation depends on the cross section for trapping an electron to the donor ground state plus a hole to the upper acceptor state, relative to an electron in the donor state plus a hole in the lower acceptor state.[13] Before the recombination process, which is characterized by a very long pair lifetime $\tau(R'_{DA})$ with respect to times for electronic transitions at an impurity, the holes will redistribute among the two acceptor ground-state sublevels, according to the thermal equilibrium. The pair recombination after the pair lifetime $\tau(R'_{DA})$ takes place between the electron at the donor and the holes in the acceptor sublevels. The recombination from the higher-lying acceptor sublevel can be neglected for splittings $\Delta \geq 0.3$ meV since at 1.6 K the upper level is occupied only by < 0.1 of the holes. This value of 0.1 reduces rapidly to <0.001 at $\Delta = 1$ meV.

Luminescence photons of energy $\hbar\omega_l$ are emitted for two excitation energies $\hbar\omega_p^{(1)}$ and $\hbar\omega_p^{(2)}$, representing two different processes. At $\hbar\omega_p^{(1)} = \hbar\omega_l + \hbar\omega_{LO}$, pairs with separations R'_{DA} are neutralized with the holes in the lower-lying acceptor sublevel. Accompanied by the emission of a phonon, the neutral pairs recombine after the lifetime τ and emit a photon of energy $\hbar\omega_l$. At $\hbar\omega_p^{(2)} = \hbar\omega_l + \hbar\omega_{LO} + \Delta(R'_{DA})$, donor-acceptor pairs of the same pair separation R'_{DA} are neutralized with the hole in the higher-lying acceptor sublevel. At perfect thermalization, the holes relax to the lower-lying sublevel, and the pair recombination accompanied by a phonon emission yields also a photon of energy $\hbar\omega_l$.

Coming back to the phonon scattering processes A and B, we expect to find an LO phonon in our excitation spectra with the energy of the lattice phonon, i.e., at an excitation energy $\hbar\omega_p = \hbar\omega_l + \hbar\omega_{LO}$ due to scattering at distance pairs (process A) where $\Delta(R_{DA})$ is negligibly small. From close pairs (process B), we expect an LO-phonon line at $\hbar\omega_p = \hbar\omega_l + \hbar\omega_{LO}$ when the lower-lying acceptor ground state sublevel was involved in the pair neutralization process, or an LO-phonon line at $\hbar\omega_p = \hbar\omega_l + \hbar\omega_{LO} + \Delta(R'_{DA})$ when the higher-lying acceptor ground-state sublevel was involved.

The experimental results are shown in Fig. 3. One observes the two LO-phonon lines [(d) and (e)] with a splitting that decreases with increasing pair separation. Further, the change in the relative intensities between lines (d) and (e) is clearly seen.

Both processes A and B are necessary for the description of the experimental results. At large detector energies $\hbar\omega_l$, the contributions of process B to the phonon lines is small due to the small density of impurity pairs with small pair separations [see Eq. (2)]. For close pairs, we have large $\Delta(R_{DA})$, i.e., complete thermalization of the holes into the lower-lying acceptor sublevel. As a consequence, the relative contributions from process B to the lines (d) and (e) are constant and express the relative strengths of the involved transition matrix elements between the donor ground state and the two acceptor substates. In Fig. 3, however, the intensity ratio between (d) and (e) changes even for large Δ. Line (d) at large $\hbar\omega_l$ is thus mainly due to process A.

For small detector energies, process A is negligible due to the vanishing density of pairs with very large R_{DA}. The lines (d) and (e) at small $\hbar\omega_l$ thus describe the contributions from process B.

For very close pairs, the crystal is locally perturbed by the impurity pair. The interaction of carriers with optical phonons at close donor-acceptor pairs is influenced by the polarization of the crystal due to the impurity pair. First-order Raman scattering of free carriers in such a system with reduced symmetry, however, does not lead to efficient phonon lines since the scattering volume is very small. The scattering volume can be approximated by two spheres with radii equal to the Bohr radii of the donor electron r_e and the acceptor hole r_h, separated by R_{DA}, and multiplied by the number of donor-acceptor pairs in the crystal volume which is seen by the light beam. In ZnSe, we have $r_e \approx 30$ Å, $r_h \approx 12$ Å for the Li acceptor, and a concentration of impurities $C_i \lesssim 10^{17}$ cm^{-3}. Assuming that *all* of the form neutral donor-acceptor pairs with separation R_{DA}, we obtain an upper limit for the scattering volume of $(4\pi/3)(r_e^3 + r_h^3)C_i \Phi l \approx 0.01\ \Phi l$ with Φ the beam diameter and l the light penetration depth. The Raman intensity at the impurity pairs will thus be $<1\%$ of the scattering intensity of the crystal volume and thus can be neglected.

We will now consider a close donor-acceptor pair as an intermediate state for the phonon scattering process. The Raman scattering tensor can be separated into two terms $\partial\chi_{ij}/\partial Q$ and $(\partial\chi_{ij}/\partial\epsilon)\epsilon$ where χ_{ij} is the polarizability tensor, Q are the vibrational coordinates, and ϵ is the electric field generated by dipolar vibrations.[6,14] The term $(\partial\chi_{ij}/\partial\epsilon)\epsilon$ represents electro-optical scattering. ϵ consists of local and macroscopic fields, e.g., in ionic or uniaxial crystals. In our system of a close donor-acceptor pair, ϵ is influenced by the electric field of the impurity pair. It has been found that strong contributions to the scattering of both longitudinal and transverse phonons can result from electro-optical scattering.[6,14] We believe that this type of interaction generates the TO line in the excitation spectra,

plus an LO line which superimposes with the LO from Fröhlich scattering. The broadness of the lines is caused by "many"-particle interactions within the donor-acceptor complex.

The electro-optical scattering will come mainly from process A, since for process B the number of pairs with a very small R_{DA} is also very small. Electro-optical scattering is not seen for large R_{DA} due to the decreasing strength of the Coulomb field between donor and acceptor with increasing pair separation. Thus no splitting of the TO line due to an acceptor ground-state splitting results. The above argument of a small scattering volume near the impurities is not valid for a process with an intermediate state at a donor-acceptor pair. In this case, *all* phonon scattering occurs in the vicinity of the donor-acceptor pair since the electron-hole pair is unstable.

In ZnTe and CdTe, additional lines in the vicinity of the optical phonons but different in energy from the lattice LO and TO have been observed in the excitation spectra of donor-acceptor pairs.[2,11,15] In ZnSe, such a phonon line occurs at 27.4 meV, (see Fig. 1). It has a constant energy position when R_{DA} is varied, and it increases in intensity with decreasing R_{DA}.

It has been found that an exciton can interact with a phonon to form an exciton-phonon bound state.[16] Similar considerations lead to a photon bound to a donor-acceptor pair, or bound to a single impurity atom.[8] Theory shows that *each* impurity can trap an LO phonon due to dielectric effects.[17] LO phonons bound to neutral donors in GaP (Ref. 16) and to acceptors in ZnTe (Ref. 2) were found with energies below the lattice LO energy. From the close relationship between ZnTe and ZnSe we conclude that the 27.4-meV line observed in our spectra is an LO-phonon bound to a neutral donor-acceptor pair. The phonon line intensity decreases with increasing temperature analogous to the decrease of the pair-band luminescence. The line is only observed for close pairs.

B. 5 to 80 K

The free-to-bound transition (eA^0) band of the Li acceptor in ZnSe appears at approximately 20 K in our luminescence spectra. It is not observed at lower temperatures due to the high donor concentration in our samples. At 40 K, the bound-to-bound and the free-to-bound band have equal intensities. Thus for temperatures $\gtrsim 50$ K, the spectra in Fig. 2 at $\hbar\omega_1 = 2.706$ eV represent excitation spectra of free-to-bound transitions.

No phonon lines are found in the excitation spectra between 50 and 70 K. Two effects are mainly responsible for the lack of the phonon lines: (1) the phonon scattering process involving donor-acceptor pairs is completely masked by the free-to-bound transition. The (eA^0) transition gives a luminescence signal much larger than the pair-band luminescence at the detector energy of 2.706 eV; (2) at a high temperature of $\gtrsim 50$ K, many acoustical phonons are thermally excited in the crystal. Thus the phonon scattering of the electron in the conduction band involves optical as well as acoustical phonons. The time available for the phonon scattering process is of the order of nanoseconds, i.e., the time constant of a free-to-bound transition. Thus the electrons thermalize and give a strong (eA^0) signal with a broad distribution in energy.

C. $T > 80$ K

The excitation spectra at temperatures $T > 80$ K show sharp and relatively intense phonon lines [see Figs. 1 (d)–(i)]. These phonon lines come from first-order Raman scattering of lattice TO and LO phonons. The orientation dependence is clearly seen in Fig. 1(d)–1(f) taken at 100 K. It represents the usual selection rules for scattering via deformation potential plus a small contribution from Fröhlich scattering. The Fröhlich scattering is seen at the (110)-oriented sample at 100 K [Fig. 1(e)] where a small peak of the LO phonon appears. It is also seen when the detector polarization is changed. The luminescence background in the high-temperature spectra is much reduced with respect to the lower-temperature spectra due to the absence of efficient impurity related luminescence at high temperatures. The experimental counting rate at the LO energy position in the excitation spectrum of e.g., the (111)-oriented sample is 10500 counts/sec at 5 K, and 1900 counts/sec at 100 K. Thus the first-order Raman lines cannot be observed in our samples at low temperatures, but they appear at high temperatures due to the reduction of the impurity related luminescence background.

Only the LO line is found in the excitation spectra at 200 K (see Fig. 1). This effect is due to the decrease of the ZnSe band gap with increasing temperature,[18] and thus a shift of $\hbar\omega_l + \hbar\omega_{\text{phonon}}$ towards the band gap. The two major consequences are an enhancement of the absorption coefficient, and the occurence of resonant Raman scattering. The absorption coefficient in ZnSe increases over more than three orders of magnitude at the band-gap energy.[19] The strong absorption reduces the penetration depth of the light in the crystal, and thus the scattering volume for phonon scattering. Therefore, the *observed*

Raman intensity decreases in our spectra with increasing crystal temperature. The effect of a variation of the absorption coefficient can be approximated by the expression

$$I \propto \frac{I_0}{\alpha_i + \alpha_s} \{1 - \exp[-(\alpha_i + \alpha_s)L]\}, \quad (5)$$

where I_0 is the Raman intensity, I is the observed Raman intensity, L is the crystal thickness, and α_i and α_s are the absorption coefficients of the incoming and the scattered light.[20] Taking $L = 1$ mm sample thickness in our experiment and the absorption coefficients from Ref. 19, we obtain a reduction of the observed Raman signal by a factor of 100 between 100 K and approximately 160 K.

Resonant Raman scattering results in an approximately equal enhancement of the permitted LO and TO scattering cross section.[21] In addition, a very strong resonant enhancement over more than 3 orders of magnitude of the "forbidden" Fröhlich-induced LO scattering has been reported.[21] For allowed Raman scattering, the resonance in the scattering cross section can be described as being proportional to $(\omega - \omega_0)^{-1/2}$ where ω_0 is the resonance frequency. For Fröhlich-induced LO scattering, the Raman cross section has components which are proportional to $(\omega - \omega_0)^{-3/2}$.

The resonance behavior is illustrated in Fig. 4 where a strong enhancement of the LO line with respect to the TO line is observed with increasing $\hbar\omega_l$.

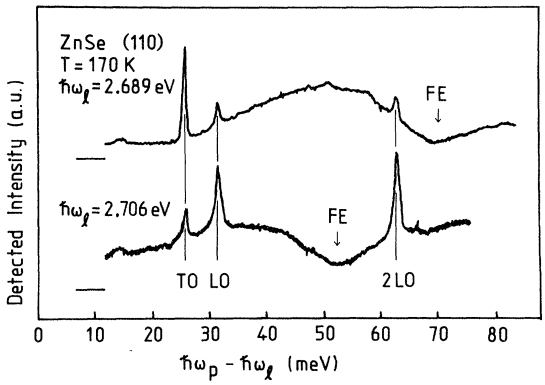

FIG. 4. Excitation spectra of a (110) surface at 170 K for different detector energies $\hbar\omega_l$. The position of the TO, LO, 2 LO, and the free exciton FE are indicated. The curves are normalized to the same spectral height.

V. SUMMARY

We have investigated in this paper the processes which lead to the phonon lines in the excitation spectra of ZnSe. At low temperatures, two effects are found: carrier-phonon interaction with the donor-acceptor pair as an intermediate state yields sharp LO lines. The LO lines are split due to an acceptor ground state splitting as a consequence of interimpurity interactions. For very close pairs, electro-optical scattering of TO and LO phonons occurs at the axial Coulomb field between donor and acceptor.

In the temperature region from 50 to 80 K, no phonon lines are found in the spectra. At these temperatures, the free-to-bound transition dominates over the donor-acceptor pair recombination. Scattering of acoustical phonons distributes the exciting photon energy over a large energy range.

At higher temperatures >80 K, the first-order Raman lines emerge from the decreasing luminescence background. A clear dependence of the line intensities on the crystal orientation corresponding to the Raman selection rules is found. At temperatures >150 K, the effect of resonant Raman scattering becomes important. The excitation energy for a phonon $\hbar\omega_l + \hbar\omega_{\text{phonon}}$ moves towards the ZnSe band-gap energy. Only the LO line is observed at 200 K at all surface orientations.

ACKNOWLEDGMENTS

We would like to thank J. Stolz, MPI Stuttgart, and Y. Marfaing, CNRS Bellevue, for helpful discussions, and W. Heinz, MPI Stuttgart, and J.-F. Rommeluere, CNRS Bellevue, for expert technical assistance. The excellent ZnSe crystals were grown in part by R. N. Bhargava and B. J. Fitzpatrick, Philips Laboratories.

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