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Autor(en): **Capozzi, Vito**

Objektyp: **Article**

Zeitschrift: **Helvetica Physica Acta**

Band (Jahr): **58 (1985)**

Heft 2-3

PDF erstellt am: **09.08.2024**

Persistenter Link: <https://doi.org/10.5169/seals-115598>

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Luminescence investigation of direct and indirect excitons bound to deep-neutral-acceptors in ϵ -GaSe

By Vito Capozzi, Dipartimento di Fisica, Università degli Studi di Trento, 38050 Povo, Italy and Gruppo Nazionale di Struttura della Materia del C.N.R., Trento, Italy

(1. VIII. 1984)

In honor of Emanuel Mooser's 60th birthday

Abstract. We report on our investigations of excitonic luminescence spectra of Bridgmann grown GaSe crystals from the liquid N₂ temperature up to 300 K and at weak laser excitation intensity. We measured the spontaneous luminescence due to direct and indirect excitonic recombinations. Moreover, a detailed analysis of the intensity of the lines composing the emission spectrum versus the temperature and the excitation intensity permits to detect and assign two lines of the excitonic luminescence as due to the recombination of direct as well as indirect excitons bound to localized centres in the forbidden energy gap. On the basis of recent theories on bound exciton-impurity complexes we found that both direct and indirect excitons are bound to neutral and deep acceptor centres. From the measured dissociation energy of these bound excitons we could estimate the ionization energy of the acceptor levels, which were already identified independently in GaSe by electrical transport measurements.

1. Introduction

The semiconductor Gallium Selenide, whose crystal structure resembles that of MoS₂ is a layer-type compound with a strong structural anisotropy with respect to the c -axis which is perpendicular to the layer planes. The basic sandwich layer is made up of four covalently bound sheets of hexagonal close-packed atoms, arranged in the sequence Se–Ga–Ga–Se along the crystal c -axis [1]. Three main modifications which differ in the sequence of the basic layer units have been described in the literature, named ϵ , β and γ . The ϵ and β phases are 2H hexagonal polytypes, belonging to the space group $D_{3h}^1(P\bar{6}m2)$ and $D_{6h}^4(P6_3/mmc)$, respectively, while the 3R trigonal modification γ belongs to the space group $C_{3v}^5(R3m)$ [1].

The photoluminescence (PL) of GaSe have been extensively studied by several groups in the last years [2–7], but there is a considerable degree of inconsistency in the experimental data and assignment of the PL lines (see e.g., Refs 2 and 3). This is due to the emission spectral complexity, specially below $T = 20$ K, and to the difficulties for growing good single crystals. Above 50 K the emission spectrum, besides the well-known recombination of the direct free excitons [2], contains only a few lines. The origin of these recombinations is not well understood. The interest in the studies of radiative transitions in GaSe is due to the need for a detailed interpretation of the edge luminescence spectra which is

deeply influenced by the presence of two minima of the conduction band very close energetically (see below).

So far, very few results deal with bound excitons in GaSe and the nature of the binding centers [3] and [7]. In this paper we investigate spontaneous PL spectra of the ε -GaSe and we report the results of a detailed analysis of the lines associated to the excitonic recombinations obtained as a function of the temperature and of the excitation intensity. We propose an interpretation of the observed lines which involve the radiative decay of the direct – as well as indirect – free and bound excitons. Preliminary results of this work have been reported elsewhere [8].

2. Summary of the band structure of GaSe near the optical absorption edge

For explaining our experimental results we consider the near edge band structure calculated by Schlüter [9] and more recently confirmed by Y. Depeursinge [10], using the empirical pseudopotential method. These calculations predict the presence of an indirect minimum of the conduction band (CB) at the point M (M_3^+ symmetry) of the Brillouin zone (BZ) lower than the direct minimum (Γ_3^+) located at the point Γ . Moreover, the top of the valence band (VB) lies at the center of the BZ and has the symmetry Γ_4^- . The direct and indirect gaps are very close in energy: Mercier et al. [11] report a difference of about 25 meV between these two minima.

Several experimental results seem to confirm this model as reported by Thanh and Depeursinge [12] and by Abdullaev et al. [5] on the basis of their absorption measurements. The binding energy of the direct free exciton (DFE) associated to the direct conduction band (DCB) is about 20 meV [2] and therefore, DFE is resonant with the continuum free-electron states of the indirect-conduction band (ICB) minimum. An experimental evidence of this resonant state for DFE was reported by Mercier et al. [11]. The indirect free exciton (IFE) relative to the indirect conduction band minimum (ICB) was investigated by detailed absorption measurements at 2 K [12, 13] and recently by resonant luminescence at liquid Helium temperature and at 80 K [14]. The IFE ground state of the ε -GaSe found in Ref. 12 is at about 2.075 eV above VB (at $T = 2$ K) and the experimental value of the IFE binding energy is about 30 meV [12]. A scheme of this model showing the above features and relative energies is reported by Staehli and Frova [15]. The recombination model of the photoexcited electrons and holes in Gallium Selenide, proposed by Mercier and Voitchovsky [2] was confirmed experimentally [11] and [16]. When the holes thermalize at the top of VB and the electrons at the bottom of the two minima, direct and indirect radiative recombinations can both occur. This model will be here applied to understand our results.

3. Experimental techniques

The single crystals investigated were grown from the melt by the Bridgmann method. Details of the grown techniques are reported elsewhere [17]. By X-ray

analysis and by excitonic transmission spectra [18] we found that our crystals have mostly the ε -structure, but sometimes, also the γ -modification is present. In this work we investigated only the samples having the ε -modification. Their electrical conductivity was of p -type with $N_A - N_D \approx 10^{15} \text{ cm}^{-3}$ and $N_A + N_D \approx 10^{17} \text{ cm}^{-3}$, where N_A and N_D are the concentrations of acceptors and donors, respectively [17 and 19]. The ingots were cleaved along the planes of layers, obtaining slices about 0.1 mm thick. The samples were attached to a cold finger of a cryostat, the temperature of which could vary from 80 to 300 K, by means of a thermostat having an accuracy of 1 K. The crystal surface was illuminated by the 5145 Å line of a cw Argon ion laser (focalized on a spot of about 100 μm of diameter), in a direction forming a 45° angle with the c -axis. The spontaneous luminescence was collected from the illuminated front face of the sample and analyzed by a double spectrometer. The signal, detected by a cooled photomultiplier, was recorded by a multichannel analyzer, using standard photon-counting technique. The data were sent to a computer for storage and processing. The laser intensity absorbed by the crystal was varied between 10^{-3} and 10 Wcm^{-2} , by means of a set of calibrated neutral density filters.

4. Experimental results

Figure 1 shows a spontaneous photoluminescence spectrum of an ε -GaSe sample, measured at $T = 80 \text{ K}$ and at the laser intensity (J) of 1 Wcm^{-2} . The lines shown in this figure are typical of all the samples investigated in the range from 10^{-3} up to 10 Wcm^{-2} . These lines were analyzed by decomposing the spectra into a series of overlapping Gaussians (using as fitting parameters their amplitude, half-width and energy center), in such a way that their sum matches the measured spectra. This procedure was applied only to the spectra in which the structures are well defined. The result of this analysis is reported in Table I.

The integrated intensity (L) of the emission lines obtained from the above deconvolution is reported in Fig. 2 as a function of J . The experimental data shown in this figure were fitted by the simple power law (continuous lines)

$$L \sim J^s \quad (1)$$

where s is an exponent. In each sample investigated we found a superlinear dependence on J for all the lines labelled in Fig. 1. In particular the exponent s is 1.4 ± 0.1 for the emissions A and B and 1.2 ± 0.1 for C and D . Moreover, we note that there is not any saturation effect in the investigated excitation intensity range.

When the temperature (T) increases from 80 K to 300 K, there are some changes in the spectra, mostly as far as the intensities of the lines B and D are concerned. The temperature dependence of the intensity of the lines A and C are reported in Fig. 3, where the results are referred to the same indicated excitation intensity. In this figure we see a slow linear decreasing of the intensity of these two lines, when T increases up to 300 K.

The luminescence of the lines B and D fall down exponentially versus T . This is shown in Fig. 4, where a semilogarithmic plot of the intensities of the lines B and D are reported as a function of $1/T$. The continuous lines are least square

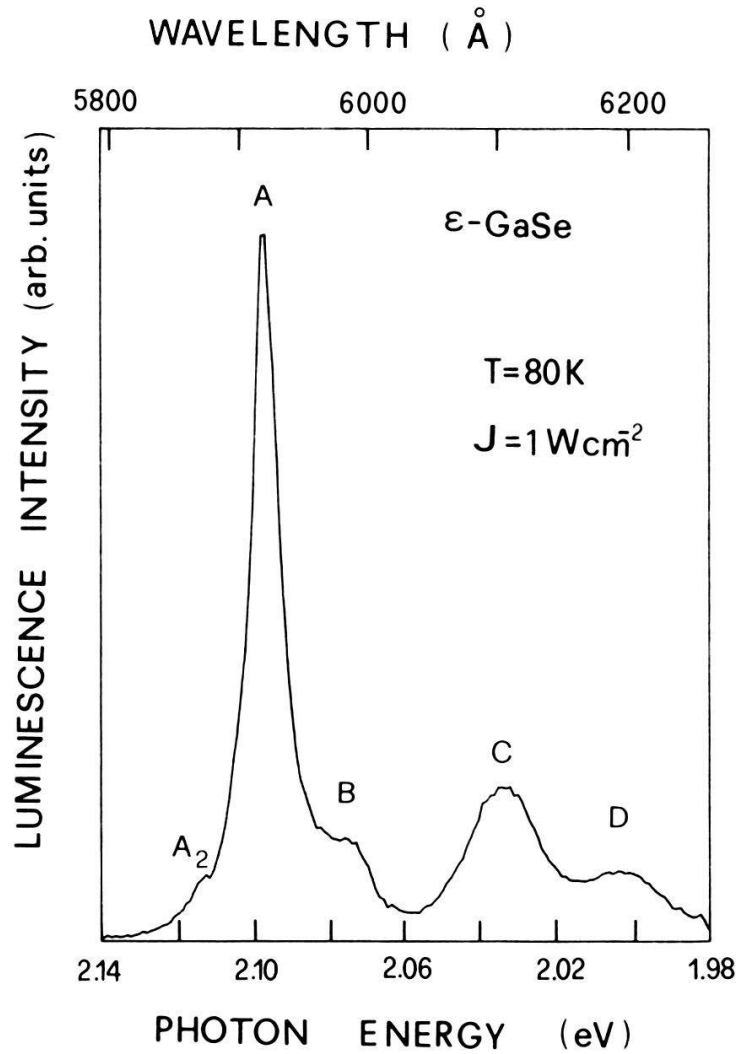


Figure 1

Spontaneous photoluminescence spectrum of a Bridgmann sample of ϵ -GaSe measured at 80 K and at the excitation intensity J indicated. Light was collected from the front surface of the crystal. The main features of the labelled lines are reported in Table I. Spectral resolution is 1 Å.

Table I
Features of the luminescence excitonic lines of ϵ -GaSe at 80 K.

Emission lines	Wavelength (Å)	Energy (eV)	Exponents of eq. (1)	Half-width average values (meV)
A	5910 ± 1	2.098	1.4 ± 0.1	8
A ₂	5868 ± 1	2.113	1.4 ± 0.1	8
B	5976 ± 1	2.075	1.4 ± 0.1	12
C	6093 ± 1	2.035	1.2 ± 0.1	24
D	6191 ± 1	2.003	1.2 ± 0.1	26

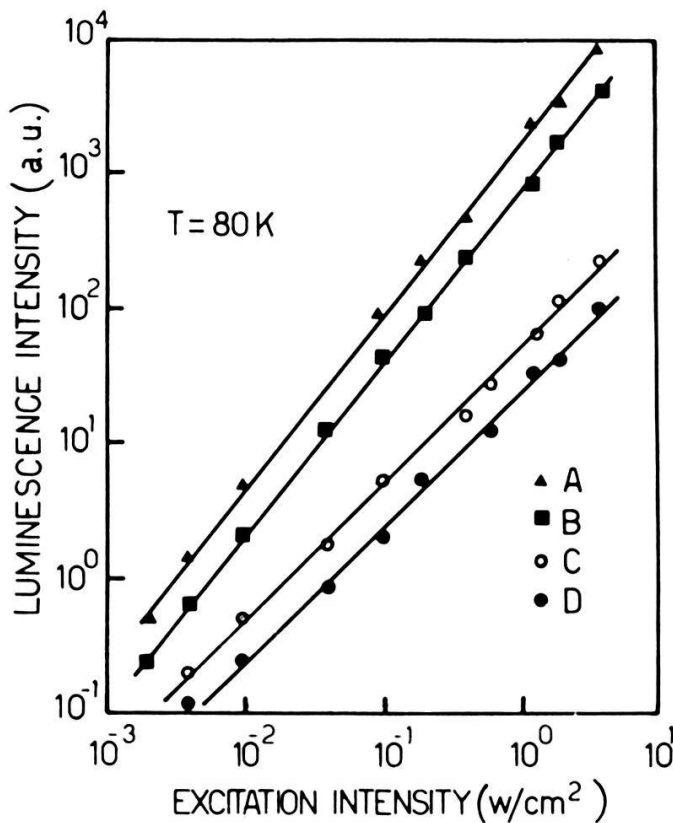


Figure 2
 Logarithmic plots of the integrated intensities L of the spontaneous emissions A, B, C and D versus excitation intensity J . Continuous lines are the least square fits of the experimental intensities (dots) to a simple power law $L \sim J^s$. Exponents found are indicated in Table I.

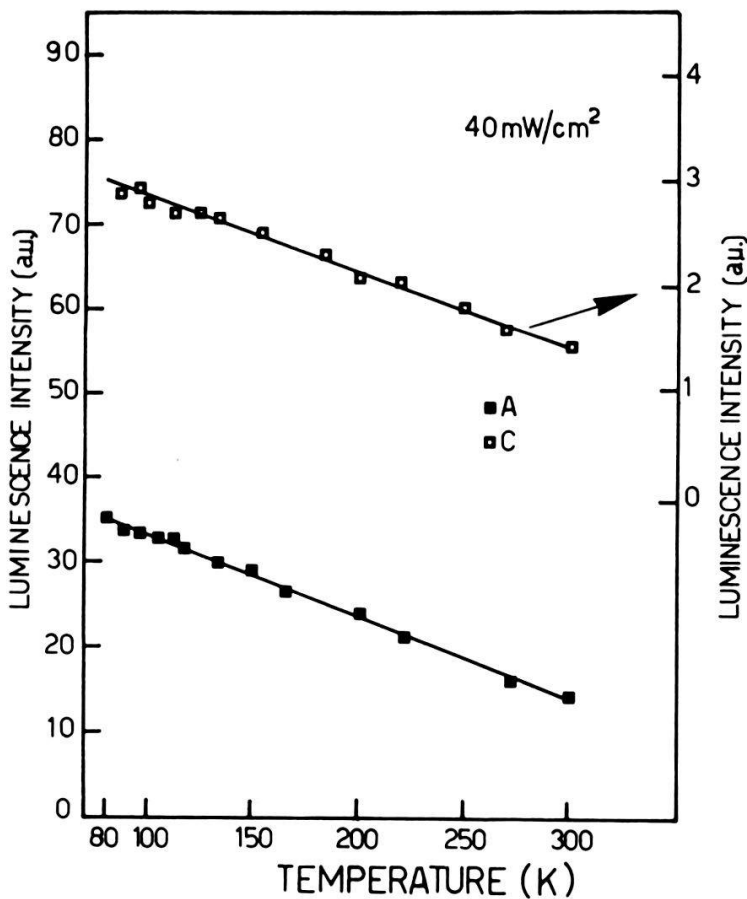


Figure 3
 Temperature dependence of the luminescence intensity of the lines A and C at the photoexcitation intensity of 40 mW cm^{-2} .

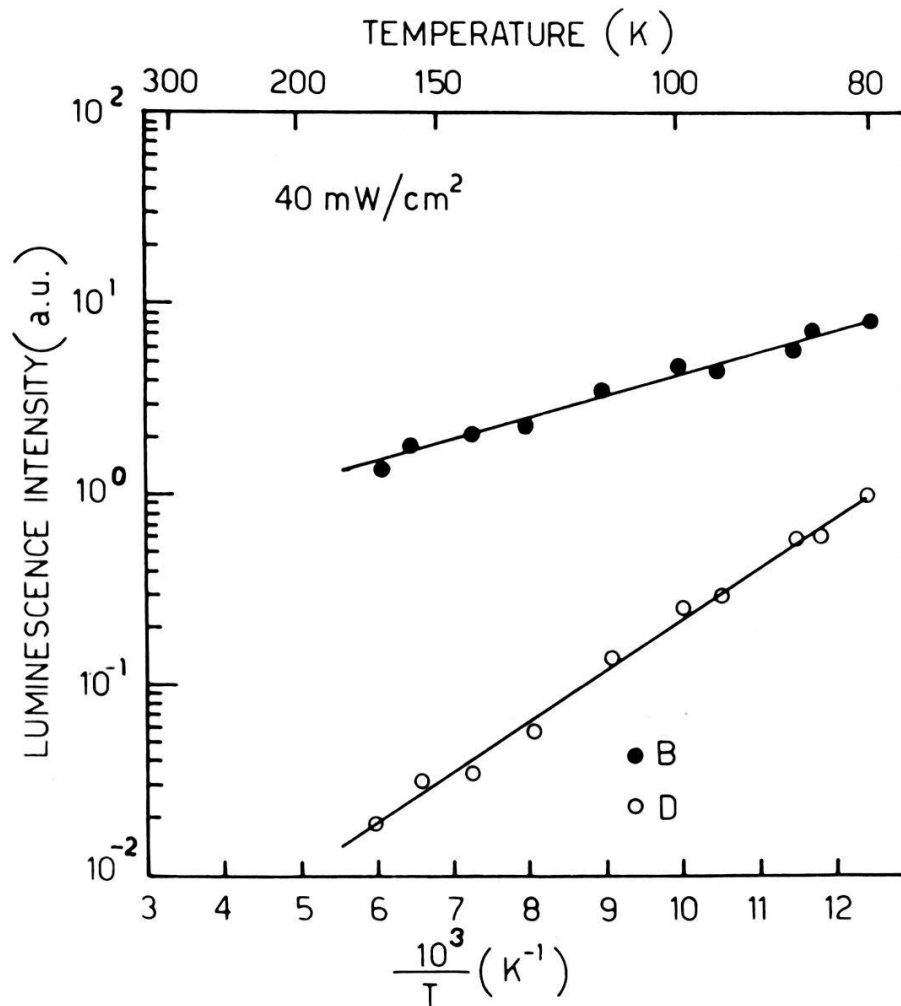


Figure 4
Semilog plot of the emission intensity of the lines *B* and *D* versus reciprocal temperature $1/T$, at the indicated excitation intensity. The continuous straight lines are the least-square fits of the experimental data (dots) to equation (2) reported in the text.

fits of the experimental intensities to the relation

$$L \propto \exp(\Delta E/kT) \quad (2)$$

where ΔE is the thermal activation energy and k the Boltzmann constant. From equation (2) we obtained the following thermal activation energies ΔE_B and ΔE_D for the lines *B* and *D* respectively:

$$\Delta E_B = 23 \pm 1 \text{ meV} \quad \text{and} \quad \Delta E_D = 35 \pm 1 \text{ meV}$$

Increasing the temperature we found that the energy position of all the lines shown in Fig. 1 move forward longer wavelengths, because the forbidden energy gap of the GaSe reduces with the temperature increasing [2].

At temperatures higher than 250 K the lines *B* and *D* are practically disappeared and the luminescence spectrum is composed only by the emissions *A* and *C*.

5. Discussion

The line *A* of Fig. 1 at 2.098 eV is due to the well known zero-phonon recombination of the direct free exciton [2]. This assignment is in agreement with the absorption measurements at 77 K of the exciton ground state [20]. The ionization energy of the DFE has been accurately determined from the hydrogenic absorption series of the excitonic states and it results $E_b^d = 20$ meV [21]. This value is in agreement with the Rydberg energy calculated considering the direct effective masses of electrons and holes measured by Ottaviani et al. [22] and reported in Table II.

Table II

Values of the effective masses of electrons at the direct $-(\Gamma)$ and indirect $-(M)$ minima of the conduction band and of holes, after Ottaviani et al. [22], in units of the free electron mass m_0 . The symbols (\parallel) and (\perp) stand for the directions parallel and perpendicular to the crystal *c*-axis.

Effective mass components	\perp	\parallel
m_e^d	0.17	0.3
m_e^i	0.5	1.6
m_h	0.8	0.2

The peak A_2 at 2.113 eV on the high energy tail of the line *A* is due to the radiative recombination of the DFE from the excited state $n = 2$, which can be thermally populated at 80 K. In fact, the energy difference between the lines A_2 and *A* is 15 meV, i.e. $\frac{3}{4}$ of the direct exciton Rydberg.

The line *B* at 2.075 eV is associated to DFE luminescence. To understand the origin of this line, it is useful to summarize our experimental results. The emission intensity of *B* depends superlinearly on the laser excitation intensity exactly as that of the line *A*, in the range of *J* reported in Fig. 2. Moreover, the intensity of this line decreases exponentially with the temperature (see Fig. 3). As reported above, a thermal activation energy $\Delta E_B = 23 \pm 1$ meV is obtained from equation (2). This is the same value as the energy difference between the lines *A* and *B* (see Table I).

These results suggest that the emission *B* is due to the radiative recombination of direct bound excitons which have been captured by impurities or defects present in our GaSe crystals.

In semiconductors excitons can bind to ionized or neutral impurities which can be acceptor or donor centres. The binding energy of an exciton in the exciton-impurity complex depends on the ionization energy of the binding centre (not on its nature) and on the ratio $\sigma = m_e/m_h$ of electron to hole effective masses. This problem was extensively studied in the last years and for a review see i.e. U. Schröder [23].

In Gallium Selenide the carrier effective masses are anisotropic. At the point Γ of the BZ we must consider the electron and hole masses for the directions either parallel (\parallel) or perpendicular (\perp) to the *c*-axis.

At the *M* point of BZ the anisotropy is larger and there are 3 minima of the ICB along the 3 principal axis of the crystal and then three values of the effective

electron masses. In Table II we report the experimental values of the above carrier masses obtained from electrical transport measurements [22]. In particular, the electron and hole effective masses at point Γ of BZ reported in Table II have been recently confirmed by optical measurements by le Toullec et al. [21].

As reported for other semiconductors, e.g. CdS, ZnO and GaSb [24], the appropriate electron and effective masses which we considered for comparing our results with the theory on exciton-impurity complex, are the geometric mean of the tensor components reported in Table II. Then, we obtained the following mean values in units of the free electron mass:

$$m_h = (m_h(\parallel) \cdot m_h(\perp) \cdot m_h(\perp))^{1/3} = 0.50 \quad \text{for the holes,}$$

$$m_e^d = (m_e^d(\parallel) \cdot m_e^d(\perp) \cdot m_e^d(\perp))^{1/3} = 0.20 \quad \text{for the electrons}$$

in the direct minimum of the conduction band (DCB), and

$$m_e^i = (m_e^i(\parallel) \cdot m_e^i(\perp) \cdot m_e^i(\perp))^{1/3} = 0.74 \quad \text{for the electrons}$$

in the indirect minimum ICB. For the meaning of symbols see Table II.

We have, then, two ratios σ of electrons to hole masses, relatively to the direct and indirect parts.

$$\sigma^d = m_e^d/m_h = 0.41$$

and

$$\sigma^i = m_e^i/m_h = 1.47.$$

An exciton can be bound to an ionized or neutral impurity center. In general these impurities or defects behave as donor or acceptor levels localized into the energy gap of a semiconductor. There are four kinds of bound-exciton states classified as follows, according to the charged state of the binding center: neutral donor (D^0, X), neutral acceptor (A^0, X), ionized donor (D^+, X), and ionized acceptor (A^-, X). The temperature dependence of the luminescence intensity gives information on the type of binding centre, because the thermally dissociated particle is an exciton for the complex (D^0, X) and (A^0, X), while it is a hole (or an electron) for (D^+, X) and (A^-, X), respectively [25].

The theory on the bound exciton-complexes shows that the thermal activation energy ΔE of the luminescence intensity of bound excitons is equal to the optical binding energy E_b (i.e. the energy difference between the free and bound exciton recombination lines) for (D^0, X) and (A^0, X), whereas it is not so for (D^+, X) or (A^-, X). In the last two cases ΔE is only a few percent of the optical binding energy [25]. In our case, since the optical binding energy of the line B is equal to the thermal activation energy ΔE_B , we deduce that the bound state responsible for the recombination B is attributed to an exciton neutral-complex, which can be (A^0, X) or (D^0, X).

The theory on the excitons bound to neutral-donors and -acceptors have been recently developed by Ungier et al. [26]. To investigate in more details the binding centres we have used the results of these calculations which are shown in Fig. 1 of Ref. [26]. This figure reports the binding energy $W(A^0, X)/2E_A$ of the exciton-neutral-acceptor complex (A^0, X), in units of twice the acceptor Rydberg E_A , as a function of the mass ratio σ defined above. A similar curve is reported in

this same figure for the binding energy $W(D^0, X)/2E_D$ of the exciton-neutral-donor complex (D^0, X) in units of the donor Rydberg.

Using $\sigma^d = 0.41$ and the curve *A* of Fig. 1 of Ref. [26] we obtain $W^d(A^0, X)/2E_{A_1} = 4.7 \times 10^{-2}$ from which we can estimate the ionization energy E_{A_1} of the acceptor centres that bind the direct excitons in GaSe. The optical binding energy of the direct bound exciton (DBE) is $W^d = 23$ meV from which we obtain $E_{A_1} = 244$ meV above the valence band. This acceptor level is in agreement with the deep acceptor centres detected by Augelli et al. [27] by means of electrical transport measurements. In fact these authors found an acceptor level at 235 ± 6 meV above VB with a concentration of about 10^{16} cm^{-3} .

In the same way, we can estimate from the curve *D* of Fig. 1 of Ref. [26] the ionization energy E_D of the donor centres of the complex (D^0, X) . In such a case we obtained for E_D an energy larger than the energy gap which has not any physical meaning. On the other hand, our crystal have a *p*-type conductivity and in GaSe crystals grown by the Bridgmann technique, only acceptor centres have been detected at $T = 80$ K by electrical transport measurements [19] and [28]. As for the line *B* we propose it is due to the recombination of direct excitons bound to neutral acceptor centres localized at about 0.24 eV above VB.

The quenching of the intensity of the line *B* with the temperature is clearly due to the thermal dissociation of the direct excitons from the binding impurities. In fact, using a simple rate equation treatment, the following approximate dependences are obtained for the luminescence intensities of the lines *A* and *B*.

$$L_A = \text{const } G \quad (3)$$

$$L_B \propto G \exp(E_b/kT) \quad (4)$$

where G is the generation rate of the excitons which is proportional to J . The above approximate equations are consistent with the results of Figs. 3 and 4 which show a nearly constant behaviour of the intensity of *A* versus T , contrasted to the exponential quenching of L_B when T increases (see Fig. 4). The slow damping of the intensity of the free excitonic luminescence is due to the increasing of its non radiative recombination probability with the temperature [29]. The superlinear dependence on J of the lines reported in Fig. 2 can be due to the non-radiative transitions of the photoexcited carriers which are quite strong in GaSe at very low excitation intensity. In fact at higher laser intensity (10^3 Wcm^{-2}), the excitonic luminescence intensity becomes linear on J [30].

The emission *C* at 2.035 eV appears only in crystals where the peak *A* is well resolved, as happens in high-quality samples. It was suggested in Ref. [6] that this line results from an inter-impurity radiative transition. However, the weak temperature quenching of the *C* line intensity, similar to that of the line *A* (see Fig. 3) and its laser intensity dependence (Fig. 2) do not support this interpretation. In our opinion, the line *C* is due to the radiative recombination of the indirect free exciton (IFE) in the transition $M_3^+ \rightarrow \Gamma_4^-$, with emission of a $M_1(\text{Ag})$ symmetry phonon, as predicted by the selection rules [9]. This assignment is in agreement with the absorption and emission measurements reported by Depeursinge [13] and by Abdullaev et al. [5], respectively.

The irreducible representations corresponding to the Γ and M points of the conduction band of ϵ -GaSe are isomorphous [31], then, the above phonon-assisted indirect transition involves phonons which are fully-symmetric at the M

point, where the symmetry group of the ϵ -GaSe is C_{2v} [9] and the fully symmetric phonon modes have the representation A_g in this group [32]. The A_g modes at the point M are compatible with the representations A'_1 and E' of D_{3h} (symmetry group at Γ point of ϵ -GaSe) along the direction Σ of the BZ. Therefore, the indirect transition $M_3^+ \rightarrow \Gamma_4^-$ can involve only phonons having the representation A'_1 or E' at the point Γ . From the polarization geometry of our measurements we deduced that only the mode E' could be observed. The dispersion curves of the phonon modes in ϵ -GaSe, connecting the points Γ and M along the direction Σ of the BZ, report only one representation E' [33]. This vibration mode (of LO-type) has an energy of about 27 meV and has been detected both by Raman scattering [34] and neutron scattering [33]. From the energy position of the peak C and that of the phonon E' just discussed, we can get an estimate of about 2.062 eV (above VB) for the ground state of the IFE at $T = 80$ K. As reported by the experimental results of Mercier et al. [11], at $T = 80$ K the indirect minimum of CB is located at about 2.092 eV above the VB. Then, the binding energy of IFE results of 30 meV. This value is the same Rydberg energy found by Depeursinge [12] and [13] from accurate absorption measurements on the indirect features of GaSe.

The lines C and D constitute a pair similar to A and B . This is evident from the dependences versus J and T of Figs. 2, 3 and 4. Moreover, the line D is present only in the spectra where the line C appears. The thermal quenching of the intensity of the emission D (see Fig. 4) gives an activation energy $\Delta E_D = 35 \pm 1$ meV, as reported in Section IV. This is in agreement with the energy difference between the peaks C and D (see Table I). The identification of the line C with the radiative decay of the indirect free exciton, immediately suggests that the line D can be attributed to the recombination of indirect bound excitons (assisted by the phonon E' discussed above) and resulting from the capture by defect or impurity centres associated to the indirect gap of GaSe. We note that the measured optical binding energy of the indirect bound exciton W^i is $\approx \Delta E_D$, then through the same analysis done above for the line B we deduce that the bound state responsible of the radiative recombination D is due to an exciton-neutral-complex, which can be (A^0, X) or (D^0, X) .

Using $\sigma^i = 1.47$ and the curve A of Fig. 1 of Ref. [26] we obtain $W^i(A^0, X)/2E_{A2} = 3.2 \times 10^{-2}$ from which we can estimate the ionization energy E_{A2} of the neutral acceptor centres to which the indirect excitons are bound. From the optical binding energy $W^i(A^0, X)$ of IBE (see Table I) we obtain $E_{A2} = 500$ meV above VB. This level can be identified with the deep acceptor centres at 0.46 eV above VB (having a concentration $\approx 10^{13} \text{ cm}^{-3}$) found by means of electrical transport measurements in our crystals [19]. Deep acceptor levels located between 0.4 and 0.5 eV were also detected in GaSe crystals grown in other laboratories [35].

Following the same analysis done above for the line B , we propose that the line D is due to the radiative recombination of indirect excitons bound to neutral-deep-acceptor centres.

Conclusions

We investigated spontaneous luminescence from excitonic recombinations in the layer semiconductor GaSe from $T = 80$ K to 300 K. We worked at weak laser

excitation intensities (J) at which the excitons form a dilute and therefore an ideal gas. The direct and indirect free excitonic luminescence is clearly observed. Moreover, the spectral positions of the luminescence lines, as well as the dependence of their intensity on T and J , permitted us to identify two lines as the radiative decay of direct and indirect excitons bound to defect centres localized in the forbidden energy gap. From recent theories [26] on exciton-impurity complexes, we found that in our crystals direct and indirect excitons can bind to deep-neutral-acceptor centres. The measured optical bonding energy (dissociation energy) of these bound excitons permits to estimate the ionization energy of the deep-acceptor centres; they are in agreement with the acceptor levels identified independently in GaSe by transport electrical measurements [19] and [35]. We think that these acceptor centres are not associated to some particular chemical impurities, but to somewhat extended regions of defects. They may well correspond to dislocations or stacking faults which are quite easily produced in GaSe because of the weakness of the interlayer bonds.

We would like to point out that the interpretation of some lines of the excitonic spectrum, as due to recombination of bound excitons, helps to solve many of contradicting interpretations of previous photoluminescence measurements.

Acknowledgments

I am grateful to F. Lévy for the very good quality of crystals provided and to K. Maschke and J. L. Staehli for the stimulating and helpful discussions. It is a pleasure to express my deep gratitude to Prof. E. Mooser for continuous support, discussion and encouragement that I received during a many-years long and fruitful interaction in the field of optical properties of semiconductors.

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