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Direct and indirect excitonic emission in GaSe

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Photoluminescence spectra of undoped crystals of the layer semiconductor GaSe have been measured from 80 K up to room temperature. The direct and indirect excitonic emissions are clearly observed in the intrinsic part of the spectrum. Moreover, a detailed analysis of the luminescence intensity has been made as a function of exciting power and temperature, allowing one to ascribe some lines of the intrinsic part of emission spectrum to direct and indirect excitons bound to localized impurity levels in the energy gap of GaSe.

I. INTRODUCTION

The layer semiconductor compound GaSe contains four monatomic sheets in the sequence Se-Ga-Ga-Se. The intralayer chemical bondings of the atoms are predominantly covalent, while the interlayer forces are relatively weak. In the literature, three principal forms of GaSe structure are described, namely β, ϵ, and γ.[1] The β and ϵ structure is a $2H$ hexagonal type, while γ is a $3R$ trigonal type.

The photoluminescence (PL) of GaSe has been widely studied in recent years,[2-7] but there are considerable discrepancies between experimental findings of different authors, see, e.g., Refs. 3 and 8. This is in part due to the difficulties encountered in growing perfect single crystals and in part due to the not-well-known influence of impurities on the PL spectra. The emission spectrum of GaSe single crystals is composed of two parts, within the range from 5900 to 7900 Å. The high-energy part consists of relatively narrow lines (about 4 meV of half-width at 80 K), ascribable to the free exciton (FE) and related recombinations; the remaining part contains a group of broader lines (extrinsic luminescence) whose half-width ranges from 12 to 50 meV and which extends toward lower energies. In general, the intensity of the exciton transitions is larger in undoped than in doped crystals, where the extrinsic emission predominates.[4,5] In the present paper we report the results of the detailed analysis of the excitonic part of the spectrum, obtained by varying the sample temperature and excitation intensity. A forthcoming paper will be devoted to the study of the extrinsic spectrum.

II. EXPERIMENTAL METHODS

The GaSe single crystals have been grown by the Bridgman technique and they were found to consist of ϵ and γ modifications by x-ray analysis.[9] Samples having essentially the ϵ-type structure were chosen for the present work. All crystals investigated were cleaved along the planes of the layers, to obtain platelets of about 1-cm^2 area and 0.1 to 0.5 mm of thickness. The samples were attached to the copper cold finger of a liquid-nitrogen cryostat, the temperature of which was varied from 80 to 300 K by means of a thermoregulator having an accuracy of 1 K. The surface of the sample was irradiated along the c axis by a cw Ar-ion laser, using the 5145- and 4880-Å wavelengths. The light emitted in the backscattering geometry from the face of the sample was collected and analyzed by a Spex double monochromator (model 1401) and was detected by using an RCA C31034A photomultiplier, cooled at 240 K, followed by a lock-in amplifier. The wavelength resolution of all spectra was about 1 Å. The exciting intensity was varied within wide limits by using neutral density filters and was monitored simultaneously to the luminescence intensity.

III. EXPERIMENTAL RESULTS

The PL spectra of many samples have been investigated. Figure 1 shows particularly three spectra, at 80 K, of an undoped sample using three different exciting intensities. The relative intensities of peaks, composing the spectra, sometime varied from sample to sample, but the energy positions remained constant in all investigated crystals. For completeness, Fig. 1 reports both intrinsic and extrinsic regions of spectrum. In the present work, attention will be focused on the intrinsic part of the spectrum, i.e., lines A, B, C, and D. These lines have been analyzed by decomposing the spectra into a series of overlapping Gaussians, using as fitting parameters their amplitude, half-width, and center energy. The results of this deconvolution are reported in Table I.

Figure 2 shows the integrated luminescence in-

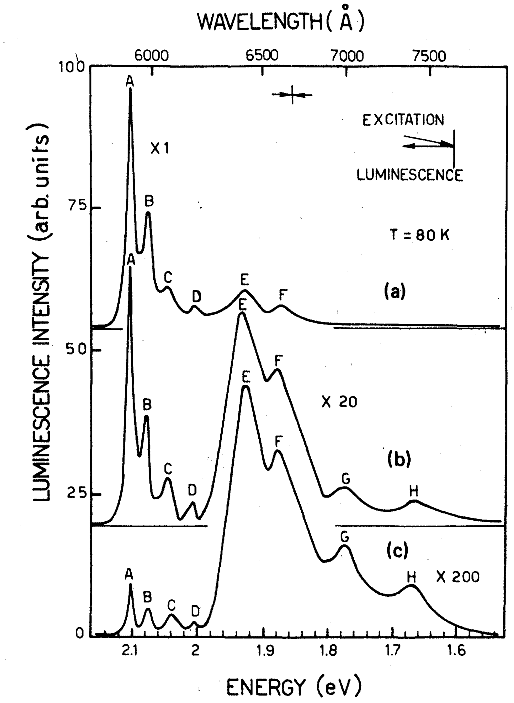

FIG. 1. Photoluminescence spectra of ϵ-GaSe at 80 K measured from the face perpendicular to the c axis, at three different exciting intensities (I): (a) 400 mW/cm^2, (b) 40 mW/cm^2, and (c) 3 mW/cm^2. The main characteristics of the lines A, B, C, and D are reported in Table I, while the remaining bands (E, F, etc.) will be described in the forthcoming second part of this work. For each spectrum, the amplification factor is indicated.

tensity (L) of the various intrinsic lines of Fig. 1 versus exciting intensity (I). The curves can be fitted by a simple power law

$$L \propto \mathrm{I}^{y},$$

where I is the excitation intensity and y is an adimensional exponential power. It is important to note that no saturation effects are observed in the investigated intensity range. The exponent y is 1.3 for lines A and B and 1 for lines C and D.

TABLE I. Excitonic characteristic lines of the photoluminescence of ϵ-GaSe at 80 K. The denomination of the lines, their wavelength, energy E, and half-width ΔE of each structure are indicated.

Denomination of lines and their wavelength (Å)	Energy E (eV)	Half-width average value ΔE (meV)
A(5910 ± 1)	2.0981	6
B(5976 ± 1)	2.0751	16
C(6092 ± 1)	2.0354	17
D(6203 ± 1)	1.9982	29

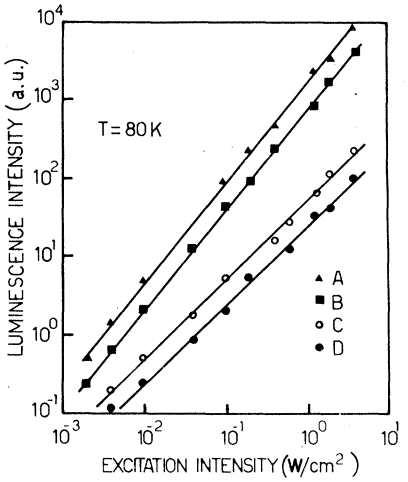

FIG. 2. Integrated emission intensity of the A, B, C, and D lines versus excitation intensity at 80 K. The experimental points were obtained by decomposing the photoluminescence spectra in a series of Gaussians.

When temperature increases, there is a strong change of PL spectra. In fact, of all structures appearing in Fig. 1 at 80 K which are still resolved up to about 180 K, only two bands are visible in Fig. 3, at 298 K, and are centered at 6213 and at 6398 Å. The temperature dependence of the intensity of lines A and C are reported in Fig. 4(a), where the results are all referred to the same exciting intensity. The behavior of A and C lines is the same in all crystals investigated and their intensity decreases linearly up to 300 K. An exponential dependence has been found instead for B and D lines as shown by the semilog plot of Fig. 4(b).

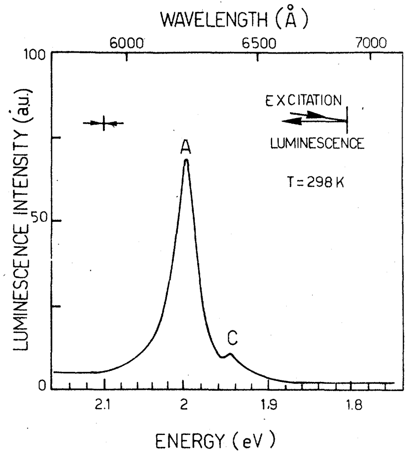

FIG. 3. Photoluminescence spectrum of an ϵ-GaSe crystal at room temperature, obtained by using an excitation intensity of 30 mW/cm^2, in the backscattering geometry along the c axis.

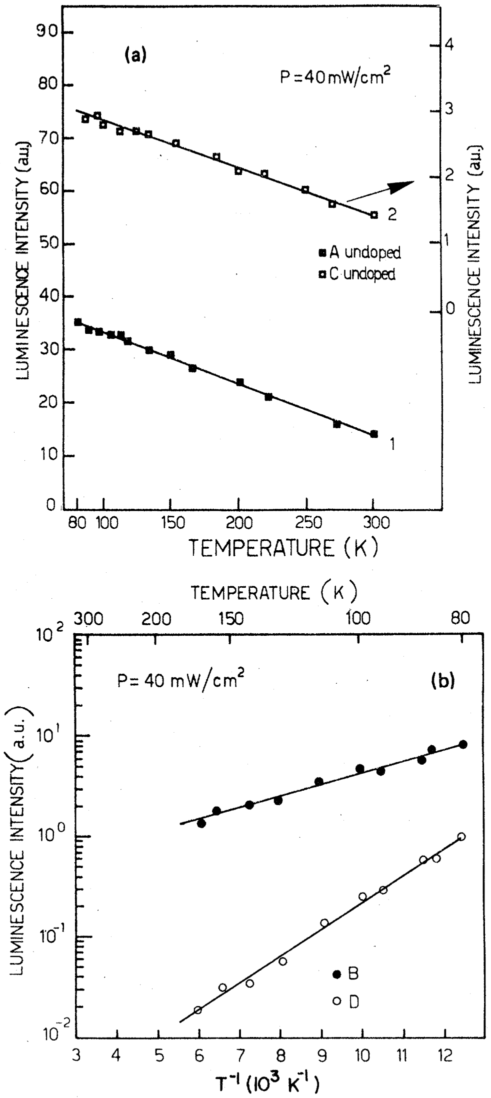

FIG. 4. (a) Temperature dependence of the luminescence intensity of the excitonic lines *A* and *C* at I=40 mW/cm^2. (b) Semilog plot of the emission intensity of the lines *B* and *D* versus reciprocal temperature $(1/T)$ at the same excitation intensity of (a). The continuous straight lines of (b) are the result of the least-squares fit of experimental points to Eq. (1) of the text, giving the exciton binding energy E_b reported in the discussion.

IV. REVIEW OF THE MODEL

In order to explain the above experimental results, we consider the band structure of GaSe calculated by Schlüter.[10] This model points out the fact that gallium selenide is an indirect semiconductor with the top of its valence band (VB), located at the center Γ of the Brillouin zone, having the Γ_4^- symmetry and the bottom of the conduction band (CB) situated at the M point (M_3^+ symmetry). Moreover, a relative minimum of the conduction band (Γ_3^+) at Γ point happens to be a few tens of meV above the minimum of M point.[10] A consequence of this structure is that the direct free exciton (FE) associated with the minimum Γ_3^+ of the CB becomes a resonant state with the continuum free-electron states of the indirect-conduction-band (ICB) minimum. Impurities and phonon scattering can strongly couple the two kinds of states and then FE in GaSe is therefore a resonant state, in the sense reported by Phillips.[13] On the basis of this model, the recombination kinetics of excited electrons and holes in GaSe proposed in Ref. 4 and confirmed by different measurements[11,12] is here applied to understanding our results.

If holes in the excited crystals thermalize at the top of the VB and the electrons at the bottom of the ICB, the band structure described above suggests that two distinct competing channels of recombination are available near the CB minimum at the M point:

(a) Indirect recombination. This is composed of intrinsic lines due to indirect free and bound excitons and by extrinsic bands due to recombinations via impurity states. These processes are clearly dominant at low temperatures and low pumping levels.

(b) Direct recombination, which involves the resonant exciton states FE, having energies slightly higher than the ICB. These processes become more probable, if the temperature is high enough to allow electrons in the ICB to jump on the FE levels and are also favored by high pumping power and low densities of impurity levels.[4]

V. DISCUSSION

The *A* line of Fig. 1 at 2.098 eV is attributed to the well-known recombination of the free exciton and this assignment is energetically consistent with the absorption data at 77 K of the exciton ground state.[6]

The ionization energy of the exciton ground state is about 20 meV (Ref. 4) and then the direct gap of the GaSe at 80 K lies at about 2.118 eV above the top of the VB. Curve 1 of Fig. 4(a) shows that the integrated intensity of line *A* decreases slowly and linearly as function of *T*; this line is still visible at 298 K, where it is situated at 6213 Å.

The *B* line at 2.075 eV is only present in the PL spectra when *A* is well resolved and its energy position at 80 K is coincident with the C_3 line reported in Ref. 4. To understand the origin of this line, it is useful to summarize the experimental results. The emission intensity of *B* increases, with the exciting intensity, in the same way as the *A* line, in the range of I reported in Fig. 2. Moreover, the thermal quenching of the B intensity reported in Fig. 4(b) is fitted by an equation of the type

$$\mathrm{L} = \text{const}\ \exp(\Delta E/kT) \tag{1}$$

with $\Delta E = (23 \pm 1)$ meV. This is the same as the energy difference between the A and B lines observed in all the emission spectra. These results tend to indicate B as resulting from the recombination of direct bound excitons, which have been captured at impurity centers. These could be identified with the donor levels, lying 0.195 eV below the DCB, detected recently by electrical transport measurements in undoped crystals[14] which have shown a shallow donor level with a concentration of 10^{17} cm^{-3}. In fact, using Fig. 1 of Ref. 15 and the effective masses of GaSe at Γ point[16] $m_{e_\perp} = 0.17 m_0$ and $m_{h_\perp} = 0.8 m_0$, the ratio between the binding energy E_b of the exciton to the donor and donor ionization energy E_d results in $E_b/E_d = 0.115$, from which $E_b = 22.5$ meV which agrees with the energy difference between A and B lines.

The quenching of the B line with temperature can be attributed to the thermal freeing of excitons from impurities. In fact, using a simple rate-equation treatment, the following approximate dependences are obtained for the emission intensities of the A and B lines:

$$\mathrm{L}_A \sim g, \tag{2}$$

$$\mathrm{L}_B \propto g \exp(E_b/kT), \tag{3}$$

where g is the generation rate, which is proportional to the exciting intensity and T the absolute temperature. The above approximate equations are consistent with the results of Figs. 2 and 4 which show a linear dependence of both lines on I (and then on g) and a nearly constant behavior of the A-line intensity versus T, contrasted to the sharp exponential decrease of the line B with increasing temperature [Fig. 4(b)]. It should also be pointed out that the rate equations require the identification of ΔE with E_b, as it is experimentally observed.

The C line at 2.035 eV is present only in crystals where the direct FE peak is well resolved, as happens in high-quality samples. It was suggested in Ref. 5 that this emission results from a transition between localized impurity levels, or, as reported in Ref. 8, it is interpreted as a phonon replica of the indirect bound exciton. But the weak-temperature quenching of the C line, similar to that of the A line [Fig. 4(a)] and its intensity dependence (Fig. 2) suggest that this line at 2.035 eV is due to the radiative decay of the indirect free exciton (IFE) in the transition $M_3^+ \rightarrow \Gamma_4^-$, with emission of an A_1' phonon as predicted by the selection rules. This assignment is consistent with the luminescence and absorption measurements reported in Ref. 17, in which indirect exciton absorption is observed also at room temperature.

The irreducible representations corresponding to the Γ and M points of the conduction band of the ϵ-GaSe are isomorphous[18]; thus indirect transitions involve phonons which are fully symmetric at M. In fact, the symmetry group of ϵ-GaSe at the M point is C_{2v} and the fully symmetric phonon modes have the representation A' in this group.[19] The A' mode is compatible with the representation A_1' of D_{3h} (symmetry group at Γ point of the ϵ-GaSe); then the most probable indirect transition is associated with the A_1' mode at Γ. This phonon of 15 meV has been measured by Raman scattering[20] and by neutron scattering.[21] This same phonon was also found in absorption measurements.[22] Thus, from the energy position of the C line and the phonon energy given above, the value of about 2.050 eV for the IFE is estimated. As far as its binding energy is concerned, we take the value of 43 meV reported in Ref. 17, which is also in agreement with the Rydberg constant $R = (m_\perp e^4/2\hbar^2 \epsilon_\perp \epsilon_\parallel)$ calculated by Baldereschi *et al.*[23] at the M minimum of the CB, where $m_\perp$, $m_\parallel$, and $\epsilon_\perp$, $\epsilon_\parallel$ are the reduced effective masses of the exciton[16] and dielectric-constant tensor components, respectively.

The above attribution is also consistent with the results reported in Ref. 11, in which the minimum M of the indirect gap lies at 5924 Å (2.093 eV) at $T = 77$ K. In fact, from the above energy position of the IFE and taking into account the above-mentioned binding energy, one finds 2.093 eV for the indirect gap. From these values the energy difference between the direct gap and the indirect one is about 25 meV, consistent with Ref. 11.

Lines C and D constitute a pair similar to A and B, as is evident from the dependences of Figs. 2 and 4. Moreover, D appears only in the spectra when the C line is also present.

The thermal quenching of the D-line intensity, reported in Fig. 4(b), is fitted by Eq. (1) giving $\Delta E = (52 \pm 2)$ meV. This is in agreement with the sum of the energy difference between the C and D lines and the energy of the phonon A_1', discussed above and involved in the C transition. The identification of the line C with an indirect free-exciton recombination, immediately suggests that the line D can be ascribed to the recombination of a zero-phonon line of indirect bound excitons (IBE), resulting from the capture by impurity centers below the M_3^+ minimum. In fact, in an indirect semiconductor containing impurities or structural defect beyond the normal allowed phonon-assisted transitions, additional no-phonon processes occur, since the momentum can be conserved in an optical transition through the impurities.

If we carry out the same analysis done for the B line (from which ΔE results to be equal to E_b) and use the indirect effective masses $m_{e_x}=m_{e_y}=0.5m_0$ and $m_{h_\perp}=0.8m_0$ (Ref. 16), we get $m_e/m_h=0.625$ and, from Fig. 1 of Ref. 15, a ratio $E_b/E_d=0.125$. Taking into account the value of E_b deduced from thermal quenching of line D, the donor energy E_d is now $E_d=52$ meV/0.125 = 416 meV. This level can be identified with the deep impurity donor level at 0.421 eV found by electrical transport measurements of Ref. 24.

Summing up, we can conclude that the above-mentioned model of band structure of GaSe accounts very well for all experimental data obtained in the present work. These results are also consistent with impurity levels of undoped GaSe deduced independently by electrical transport measurements. I would like to point out that the interpretation of some lines of the intrinsic spectrum as bound excitons helps to solve many of the contradiciting interpretations of previous photonluminescence measurements of GaSe.

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