

Photoluminescence of GaSe.

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Summary. — The photoluminescence of a large number of pure and doped single crystals of GaSe has been investigated in the temperature range from 4.2 to 300 °K with excitation intensities varying between $4 \cdot 10^{-5}$ and $3 \cdot 10^2$ kW cm⁻². The excitation was produced by the green line of a frequency doubled Nd:YAG laser. All crystals were grown in our laboratory, most of them by the Bridgman technique and some by transport reaction with iodine. Although no emission lines were found which were specific of the particular impurity introduced in the crystal, it was possible to classify the 4.2 °K spectra according to the amount of added impurities. Above 40 °K, the spectra of all crystals are identical. This dependence on temperature of the spectra is due to the rapid quenching between 20 and 40 °K of the luminescence resulting from recombinations at trap states and to the increasing importance at high temperatures of free-exciton recombinations. The two groups of lines associated with these two recombination channels constitute the principal part of all observed spectra. The variation of the spectra with temperature, pumping power and impurity content is interpreted as the result of a balance between the two recombination channels. A model of kinetics taking into account these two channels as well as the fact that the free exciton in GaSe resonates with the indirect minima of the conduction band is discussed in detail.

1. — Introduction.

Gallium selenide is a III-VI semiconductor which crystallizes in a layer structure. Three different periodic stacking sequences of the layers have so far been observed and have been described in the literature as β -, γ - and ε -GaSe⁽¹⁻³⁾.

⁽¹⁾ K. SCHUBERT, E. DORRE and M. KLUGE: *Metallkunde*, **46**, 216 (1955).

⁽²⁾ F. JELLINEK and H. HAHN: *Naturforsch.*, **16**, 713 (1961).

⁽³⁾ Z. S. BASINSKI, D. B. DOVE and E. MOOSER: *Helv. Phys. Acta*, **34**, 373 (1961).

The corresponding periods embrace two, three and two layers respectively.

From optical absorption measurements GaSe was found to have a lowest indirect gap (^{4,6}). According to (⁶) the energy of this gap at 77 °K is 2.065 eV for the γ and ε modifications and 2.117 eV for the β type. These energies are still somewhat uncertain since they were deduced by extrapolation and by making some arbitrary assumptions concerning the phonons in GaSe (⁶). On the basis of their stimulated-emission measurements NAHORY *et al.* (⁷) suggested that GaSe is a direct-gap material.

Recent band calculations carried out independently by SCHLÜTER (⁸) and by BOURDON (⁹) confirm the existence in GaSe of a lowest indirect gap lying very close to the direct one. They also afford an interpretation of the strong polarization dependence of the optical properties observed at the fundamental edge: with light polarized in the layers (electric field normal to the crystal *c*-axis) the interband transitions are allowed only because of weak spin-orbit coupling. The corresponding absorption coefficient therefore is small ($\kappa_{\perp} \simeq 5 \cdot 10^3 \text{ cm}^{-1}$). In light polarized along the *c*-axis the transitions are allowed in the usual sense of the term and the absorption coefficient is large ($\kappa_{\parallel} \simeq 10^5 \text{ cm}^{-1}$).

Optical and magneto-optical measurements show that with the direct gap two exciton series are associated, one containing the singlet states, the other the triplet states (the spin-orbit coupling is weak enough that the exciton states can be classified according to their multiplicity (¹⁰)). The ground states of the two series are separated by 2 meV but they converge towards the same series limit which in the γ and ε modifications and at 4.2 °K locates the direct gap at 2.1277 eV. Like the indirect gap, the direct one and the associated exciton series are shifted by 50 meV towards higher energies in the β modifications. In all three polytypes the ionization energy of the exciton ground state is about 20 meV.

In the investigated crystals, γ and ε types of stacking are intimately mixed. This mixing gives rise to a decomposition of the singlet and triplet ground states into two identical series of closely spaced lines which may cover a region as wide as 4 meV. Since this fine structure depends on the actual stacking sequence realized in a crystal, the number of lines and their detailed positions vary from sample to sample.

(⁴) C. DEPEURSINGE: private communication.

(⁵) H. KAMIMURA, K. NAKAO and Y. NISHINA: *Phys. Rev. Lett.*, **22**, 1379 (1969).

(⁶) E. AULICH, J. L. BREBNER and E. MOOSER: *Phys. Stat. Sol.*, **31**, 129 (1969).

(⁷) R. E. NAHORY, K. L. SHAKLEE, R. F. LEHENY and J. C. DE WINTER: *Sol. State Comm.*, **9**, 1107 (1971).

(⁸) M. SCHLÜTER: *Nuovo Cimento*, **13 B**, 313 (1973).

(⁹) A. BOURDON: Thesis, Paris (1972), unpublished.

(¹⁰) E. MOOSER and M. SCHLÜTER: *Nuovo Cimento*, **18 B**, 164 (1973).

The low-temperature luminescence of GaSe has been investigated by a number of authors. Thus BREBNER *et al.* ⁽¹¹⁾ in 1966 have carried out electroluminescence measurements at 77 °K. The spectra obtained, which spread over about 300 meV, contain a line of 13 meV half-width at the high-energy limit and a series of broader lines extending towards lower energies. The high-energy line was attributed to free-exciton (FE) recombination. More recently AKHUNDOV *et al.* ⁽¹²⁾ have found similar spectra under the same experimental conditions. These authors have shown that the intensity of the high-energy part of the emission spectrum grows more rapidly with the intensity of the excitation current than that of the rest of the spectrum.

The photoluminescence of GaSe was studied by KARAMAN *et al.* ⁽¹³⁾, CINGOLANI *et al.* ⁽¹⁴⁾ and by COLETTI ⁽¹⁵⁾. In general at 4.2 °K the spectra reported consist of a series of relatively narrow lines (half-widths 2 to 3 meV) which are more or less resolved and which spread over a region of about 50 meV lying immediately below the FE line. Towards low energies some broader lines (half-widths 5 to 10 meV) are observed. Although governing mechanisms and participating states have not as yet been identified, some authors ⁽¹³⁻¹⁵⁾ have ascribed the narrow lines to the recombination of bound excitons. We have performed photoluminescence measurements on a large number of pure and doped crystals which have allowed us to extract significant and reproducible results from a seemingly baffling variety of experimental data.

A number of our results on photoluminescence have already been published elsewhere, in particular those describing the effect of impurities on the emission spectra at 4.2 °K ⁽¹⁶⁾ and those relating to a series of long-lifetime lines ⁽¹⁷⁾. In ref. ⁽¹⁶⁾ we have described the luminescence spectra by giving the intensity $L(h\nu)$ of the emitted light as a function of the photon energy $h\nu$. We have shown that all spectra $L(h\nu)$ obtained at 4.2 °K can be understood as superpositions $L(h\nu) = (1 - y)A(h\nu) + yC(h\nu)$, $0 \leq y < 1$, of two extreme spectra $A(h\nu)$ and $C(h\nu)$ which correspond to the purest ($y \simeq 0$) and to the most heavily doped ($y \simeq 1$) crystals, respectively. It is noteworthy that the observed spectra $L(h\nu)$ only depend on the concentration of impurities contained in the crystal and not on the chemical nature of these impurities: no recombination radiation

⁽¹¹⁾ J. L. BREBNER and E. MOOSER: *Proceedings of the International Conference on Luminescence* (1966), p. 1933.

⁽¹²⁾ G. A. AKHUNDOV and A. G. BAGIROV: *Sov. Phys. Semicond.*, **4**, 805 (1970).

⁽¹³⁾ M. I. KARAMAN, V. P. MUSHINSKII, B. S. RAZBIRIN, A. N. STARUKHIN and S. S. CHEKOL: *Sov. Phys. Semicond.*, **6**, 356 (1972).

⁽¹⁴⁾ A. CINGOLANI, F. EVANGELISTI, A. MINAFRA and A. RIZZIO: *International Conference on Luminescence* (Leningrad, 1972).

⁽¹⁵⁾ F. COLETTI: Thesis, Marseille (1972).

⁽¹⁶⁾ PH. SCHMID, J. P. VOITCHOVSKY and A. MERCIER: *Phys. Stat. Sol.*, **21**, 443 (1974).

⁽¹⁷⁾ J. P. VOITCHOVSKY and A. MERCIER: *Phys. Stat. Sol.*, **18**, 545 (1973).

specific of the introduced dopant (Cu, Zn, Cd, Sn, I₂) has been detected. On the basis of a simple model of recombination kinetics we were able to explain the experimental correlation between γ and the impurity concentration. The rapid disappearance with increasing temperature of the long-lifetime lines which appear at 4.2 °K in the spectra of the purest samples could be accounted for with a recombination model involving the absorption of a phonon (¹⁷).

In the present paper we report on the remaining results of our photoluminescence measurements: all the lines characteristic of the emission spectra of GaSe are listed and their polarization properties as well as their behaviour with temperature and pumping power are described. An extension of the earlier recombination models is proposed, and the properties of the spectra are discussed in terms of this extended model.

2. - Experimental procedure.

The crystals used in the present investigations were all grown in our laboratory, most of them by the Bridgman technique, a few by transport reaction with iodine. Except for an unavoidable iodine doping the transport-reacted samples were pure. Some Bridgman grown crystals were doped intentionally by the addition of impurities (Cu, Zn, Cd, Sn) to the growth ampoules. Growth conditions and the effects of impurities upon the properties of GaSe have been described in detail in ref. (¹⁶).

By cleaving the Bridgman ingots along the plane of the layers, samples were obtained in the form of elliptical platelets of about 1 cm² area and of 0.1 to 1 mm thickness. By means of a eutectic mixture of Hg, In and Tl which is liquid at room temperature, the samples were pasted to a copper support. For measurement, support and sample were introduced into a cryostat which allows any temperature between 2 and 300 °K to be reached. In order to maintain the sample within ± 0.5 °K of a given temperature in this range the support was equipped with a heater whose input was controlled automatically. In one case we verified that the sample temperature in the excited region is identical to that of the support (¹⁷). We also ascertained that the fixation did not introduce strain into the sample which would affect its luminescence spectrum (¹⁶).

In general the photoexcitation of the samples was achieved by the green line ($\lambda = 5320$ Å) of a frequency doubled Nd:YAG laser. It should, however, be mentioned that for excitation wavelengths ranging from 4730 Å to 5620 Å no changes of the luminescence spectra were observed. The laser was operated in both the pulsed and the continuous modes. In the pulsed mode the maximum peak power density was 200 kW cm⁻² without focalization, the pulse length was 60 ns and the repetition rate 75 Hz. By focusing the beam, peak power densities of 3 MW cm⁻² could be reached at which irreversible damage to the

crystals occurred. In continuous-mode operation, the maximum power density was 0.4 W cm^{-2} . By inserting calibrated filters into the laser beam the power densities could be varied within wide limits.

As a rule the light emitted by the samples was dispersed by a 0.3 m Mc Pherson grating spectrometer and the scattered excitation radiation eliminated by an optical 3-66 Corning low-pass filter. In some experiments a SPEX 1402 double spectrometer without filter was used. The intensities of luminescence and excitation radiation were measured simultaneously, in pulsed operation by two parallel boxcar integrator systems, in continuous operation by a lock-in amplifier coupled to a mechanical chopper (luminescence radiation) and by a continuous detection system (excitation radiation). All measurements were carried out in reflexion, most of them with the exciting beam normal to the layer plane, *i.e.* parallel to the crystal *c*-axis. In order to detect polarization effects in the emitted light some measurements were made with light propagating at an angle of 45° with respect to the *c*-axis. It was possible in this geometry to separate the emitted light polarized perpendicular to the *c*-axis from that containing a polarization component along *c*.

3. - Experimental results.

3.1. Characteristic lines and polarization. - The characteristic lines composing the extreme spectra $A(h\nu)$ and $C(h\nu)$ which together form the photoluminescence spectrum $L(h\nu)$ of GaSe at 4.2°K are listed in Table I. The first among the three columns relating to each of the two extreme spectra contains the denomination of the lines, the second column gives their position in the spectrum and the third column their polarization factor which is defined as the ratio I_{\parallel}/I_{\perp} of the intensities of the emitted light polarized parallel and perpendicular to the *c*-axis. I_{\parallel}/I_{\perp} was evaluated with a refractive index of 2.8⁽¹⁸⁾ and for the particular geometry of our experiment (45° incidence). Because of this geometry and the high value of the refractive index, only values $I_{\parallel}/I_{\perp} > 1$ are significant. Values which do not satisfy this condition have been denoted 0-1 in Table I and in order to render them meaningful, polarization measurements should be performed with light propagating along the layer plane. Unfortunately in this geometry the luminescence spectra are strongly modified by reabsorption of the emitted light in the region of the indirect gap.

Also listed in Table I are the positions and polarization factors of the characteristic lines of the photoluminescence spectra at 40°K and at 77°K . At these temperatures the spectra of all crystals are identical and the distinction between two extreme spectra relating to pure and impure crystals respectively is no longer possible. Some typical photoluminescence spectra of GaSe at different

(18) J. L. BREBNER and J. A. DEVERIN: *Helv. Phys. Acta*, **38**, 250 (1965).

TABLE I. — *The characteristic lines of the photoluminescence spectra of GaSe at 4.2, 40 and 77 °K. The denomination of the lines, their energy $h\nu$ and their polarization I_{\parallel}/I_{\perp} factor are indicated.*

$T = 4.2\text{ °K}; A(h\nu)$			$T = 4.2\text{ °K}; C(h\nu)$			$T = 40\text{ °K}$		$T = 77\text{ °K}$	
Denomi- nation of the lines	$h\nu$ (eV)	$\frac{I_{\parallel}}{I_{\perp}}$	Denomi- nation of the lines	$h\nu$ (eV)	$\frac{I_{\parallel}}{I_{\perp}}$	$h\nu$ (eV)	$\frac{I_{\parallel}}{I_{\perp}}$	$h\nu$ (eV)	$\frac{I_{\parallel}}{I_{\perp}}$
FE: $n=3$	2.1260	4							
$n=2$	2.1235	4				2.1210	0.1	2.1140	10
$n=1$	2.1110	900				2.1090	1000	2.1030	220
	2.1090	3				2.1065	0.1	2.1015	0.1
	2.1075	3				2.1050	4	2.0980	3
	2.1060	10							
a_1	2.1050	40				2.1020	18		
a_2	2.1035	40				2.1005	18		
a_3	2.1005	60				2.0980			
a_4	2.0980	10							
			c_1	2.0955	8				
a_5	2.0940	10							
φ_1	2.0920	0.1							
a_6	2.0905	0.1							
			c_2	2.0890	3				
a_7	2.0880	2							
φ_2	2.0855	0.1							
			c_3	2.0835		2.080	12	2.075	15
φ_3	2.0800	0.1	c_4	2.0800	0.1				
			c_5	2.0770					
a_8	2.0735	0.1	c_6	2.0735					
φ_4	2.0710	0.1				2.070			
			c_7	2.0665	5				
φ_5	2.0640	0.1							
φ_6	2.0585	0.1	c_8	2.0585	5				
a_9	2.041	9	c_9	2.041		2.042		2.037	
a_{10}	2.029								
a_{11}	2.008								

temperatures and pumping power are displayed in Fig. 1 and 2. The denominations of the lines in these Figures are those of Table I.

The set of lines denoted FE in Table I, which forms a part of the 4.2 °K spectrum $A(h\nu)$, can readily be attributed to the recombination of free excitons associated with the direct gap. Indeed, their energies are in excellent agree-

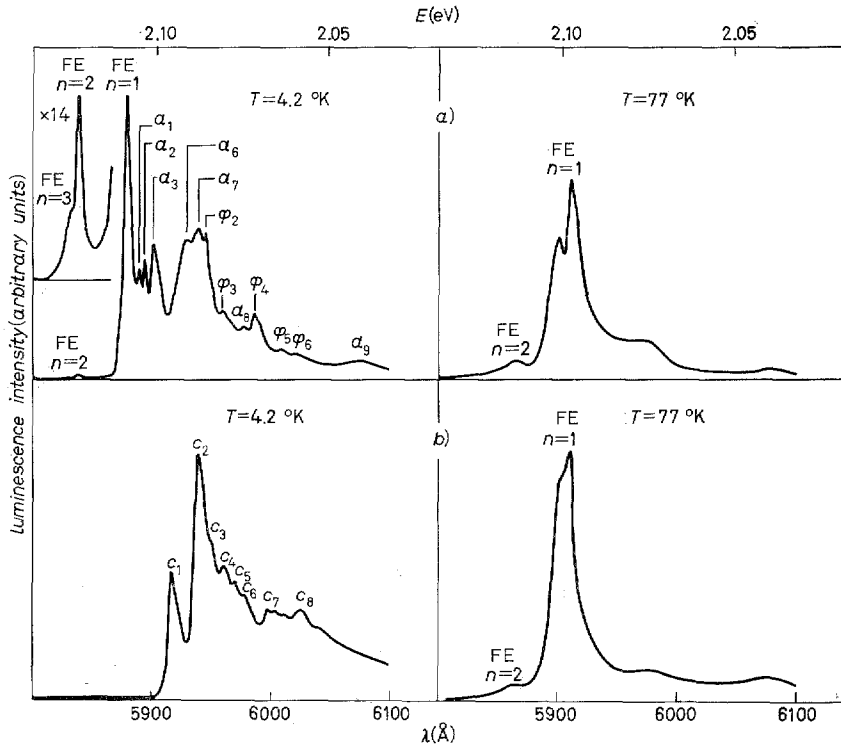


Fig. 1. — Luminescence spectra of GaSe measured at 4.2 and 77 °K with an excitation intensity of 20 kW cm⁻², a) for a relatively pure crystal (crystal II, $y = 0.33$), b) for a doped crystal (crystal IX, $y = 0.99$). The notations are those of Table I.

ment with those observed in absorption⁽⁴⁾. The different lines ascribed to the $n = 1$ exciton state are components of the fine structure which is induced by the different stacking configurations of γ -, ϵ -GaSe and which can be observed in both the triplet and the singlet ground states. As a rule, the most intense components are those located at $h\nu = 2.109$ eV and at $h\nu = 2.1075$ eV. From their small polarization factor, they are readily recognizable as triplet states. Since the geometry of our experiment is not very favourable for the observation of the singlet components (their polarization is parallel to the c -axis) only the strongest one among them was detected at $h\nu = 2.1110$ eV. Its singlet nature is clearly indicated by the large polarization factor $I_{\parallel}/I_{\perp} = 900$. Higher exciton states corresponding to the principal quantum number $n = 2$ and $n = 3$

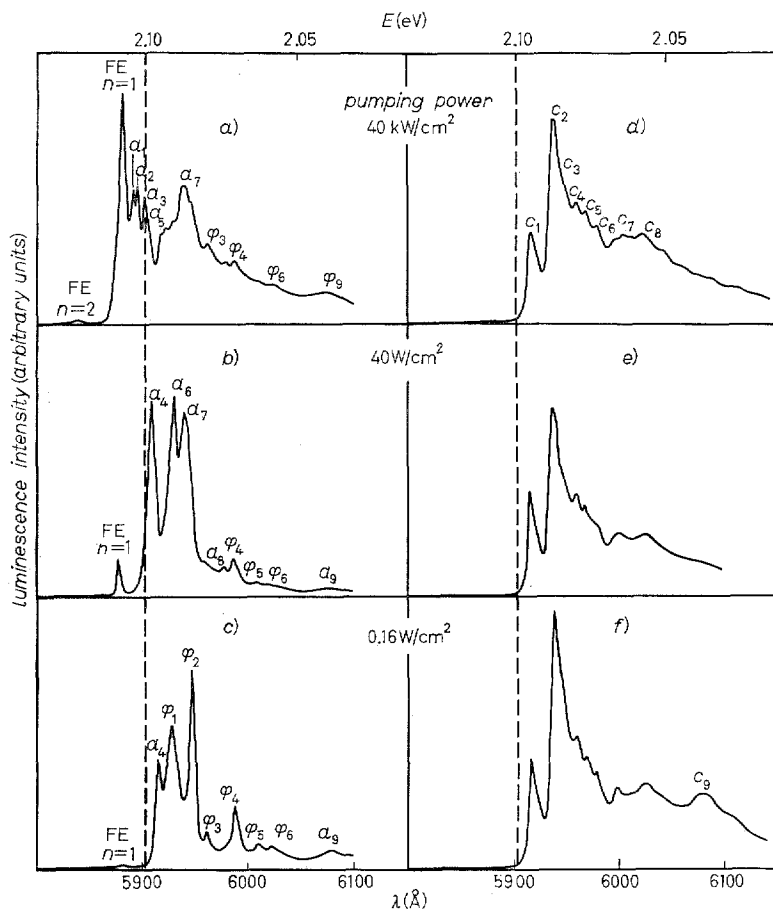


Fig. 2. - The 4.2 °K photoluminescence spectra of the crystals II and IX measured at 40 kW cm⁻², 40 and 0.16 W cm⁻². *a*), *b*) and *c*) show the evolution with excitation intensity of the extreme spectrum *A*(*hν*) (crystal II, *y* = 0.33); *d*), *e*) and *f*) show that the extreme spectrum *C*(*hν*) does not change with excitation intensity (crystal IX, *y* = 0.99). The spectra *c*) and *f*) were obtained in continuous-mode operation of the laser, the others in pulsed-mode operation. The part of the spectrum to the left of the dashed line corresponds to free-exciton recombinations (FE), the part to the right of it is due to transitions to impurity states (TR).

have also been observed (see insert Fig. 1). The spacing of lines belonging to different *n* values closely follows a hydrogenic (1/*n*²)-law. This permits the ionization energy of the exciton ground state to be evaluated as (19.5 ± 1) meV. The direct gap of GaSe thus becomes at 4.2 °K

$$E_{\text{gap}} = (2.1275 \pm 1 \cdot 10^{-3}) \text{ eV}.$$

The (1/*n*³)-law which the relative intensities of hydrogenlike exciton lines should follow is not confirmed by the present experiments. In fact the

ratio of the intensity of the line $n = 2$ to that of the line $n = 1$ is about 0.05 at 4.2 °K. A possible explanation for this observation will be discussed in Sect. 4. Here we only mention that at higher temperatures the experimental intensity ratios begin to approach the theoretical expectations.

Among the characteristic lines of the spectrum $A(h\nu)$, there is a group denoted by φ_i which have lifetimes long enough to permit them to be distinguished from the rest of the spectrum by delayed detection (¹⁷). These lines are notable for their common features: they all have the same decay time and the same behaviour with temperature and excitation intensity. Moreover, they have no preferred polarization and, while the relative intensities of the other lines may vary somewhat from one crystal to another, those of the φ_i remain the same in all of them.

In the spectrum $C(h\nu)$ the transitions associated with the free-exciton states are no longer visible (Fig. 2 right). As long as the doping of the samples is sufficiently heavy, the relative intensities of the characteristic lines c_i of this extreme spectrum practically do not vary from sample to sample. As a consequence, the spectra of the most heavily doped crystals are more reproducible than those of the purest crystals. Furthermore, none of the c_i is specific of the particular impurity added to the GaSe.

In both spectra $A(h\nu)$ and $C(h\nu)$ the lines lying above 2.058 eV have half-widths varying between 2 and 3 meV; those lying below 2.058 eV have half-widths between 5 and 10 meV.

3'2. The temperature dependence of the characteristic lines. — We have seen that at 4.2 °K the photoluminescence spectra of GaSe can be considered as superpositions of two extreme spectra which correspond to pure and doped crystals respectively. When the temperature is increased, the spectra change drastically: above about 40 °K all crystals give rise to the same spectrum independently of the amount of impurities which they contain. Moreover, at these temperatures the emission spectrum essentially consists of the free exciton lines (Table I). Figure 1, in which the 4.2 °K and the 77 °K spectra of a pure sample (*a*) are compared to the corresponding spectra of a doped one (*b*), is a good example of this behaviour which must be attributed to the different evolutions with temperature of the characteristic lines of $A(h\nu)$ and $C(h\nu)$. In fact, most of these lines belong to one or the other of two main groups of lines each of which is characterized by a specific temperature behaviour. The first contains the free-exciton lines FE and the second is formed by the lines a_s to a_8 , φ_1 to φ_6 and c_1 to c_8 . In the following this second group will be referred to as TR.

The lines a_9 to a_{11} and c_9 , which are much broader than all the other lines, will not be considered here, because their contribution to $A(h\nu)$ and $C(h\nu)$ is small. Their properties will be discussed briefly in Sect. 4.

The temperature behaviours of the two principal groups of lines are recog-

nizable from Fig. 3a) which shows that with increasing temperature the FE recombination lines become visible also in crystals, which at 4.2 °K show only a $C(h\nu)$ spectrum: above 40 °K these transitions are the same in all types of crystals and their intensity decreases linearly up to 300 °K. Contrary to this the TR recombination lines disappear rapidly between 20 and 40 °K as the temperature increases.

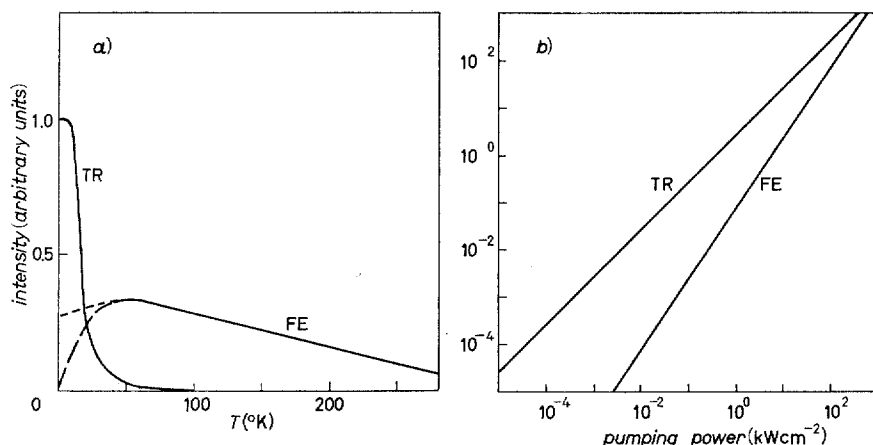


Fig. 3. — Comparison of the dependence of the intensities of the groups of lines FE and TR on temperature (a)) and on excitation intensity (b)). Except for the low-temperature part of the curve, no details are given on the effect of impurities. a) --- $A(h\nu)$, — — — $C(h\nu)$.

A closer look at the temperature dependence of the TR lines shows that within a given crystal all of them disappear at the same temperature. However, the temperature of disappearance varies from one crystal to another: it is lowest in the purest samples ($y \approx 0$) in which $A(h\nu)$ predominates and it is highest in the most impure ones ($y \simeq 1$) in which $C(h\nu)$ is preponderant. This finding is seen from Fig. 4 where the emission intensities of the TR lines of four crystals with different y values are plotted as functions of the temperature.

The temperature dependence of the lines a_1 and a_2 is similar to that of the TR lines except that they disappear at a somewhat higher temperature, *i.e.* around 60 °K. Since they are visible only in the purest crystals we were unable to establish a y -dependence of their quenching temperature. We shall see in Subsect. 3'3 that the behaviour of a_1 and a_2 with excitation intensity is identical to that of the FE transitions.

The strong polarization dependence of the singlet ground state of the exciton permits determination of the temperature shift of this state and greatly facilitates evaluation of that of the first excited state ($n = 2$). As seen from Fig. 5 the two shifts are in fact identical and we assume them to be a measure

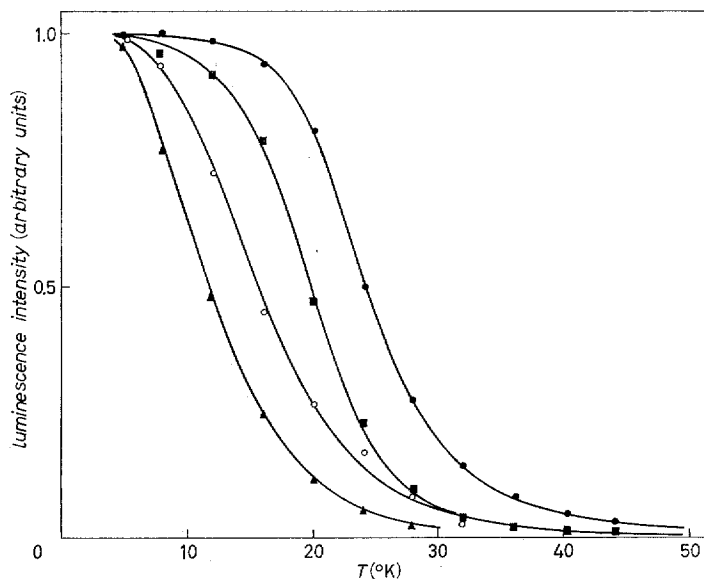


Fig. 4. - Temperature dependence of the intensity of the characteristic lines TR in 4 different crystals. The solid lines are calculated on the basis of the model discussed in Sect. 4. For each crystal, the y value which measures its impurity content is as follows: \blacktriangle VI $y = 0.17$, \circ II $y = 0.33$, \blacksquare XVII $y = 0.93$, \bullet IX $y = 0.99$.

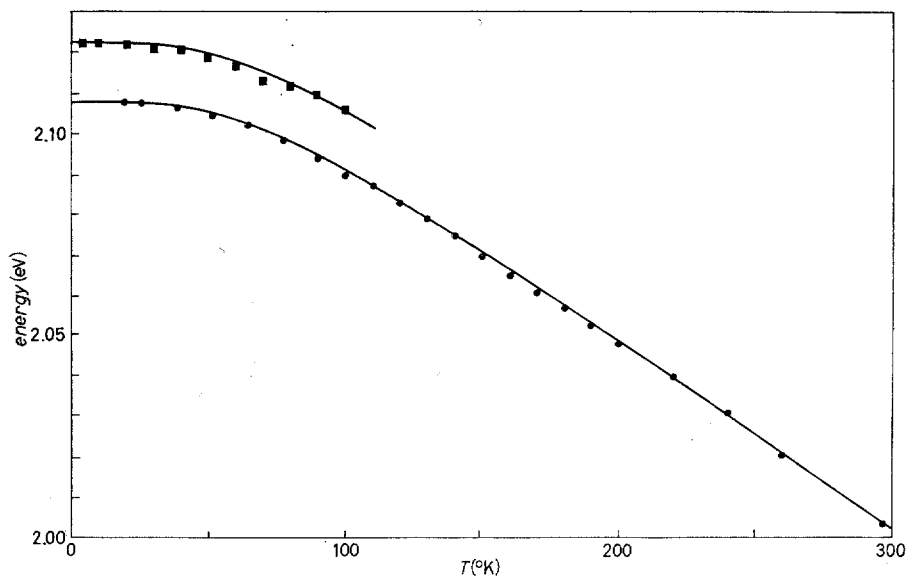


Fig. 5. - Temperature dependence of the energy position of the ground state ($n=1$, \bullet) and of the first excited state ($n=2$, \blacksquare) of the free exciton (FE). The curves represent the variation of the width of the direct gap with temperature as evaluated from electron-phonon scattering. The linear part of the curve has a slope of $0.47 \text{ meV}/^\circ\text{K}$. — theoretical curve.

of the change with temperature of the width of the direct gap. The effect of the thermal lattice expansion upon the relative positions of the band edges in GaSe is small⁽¹⁹⁾. The change of gap width therefore is essentially determined by electron-phonon interaction. On the basis of the deformation potential derived from Schlüter's⁽⁸⁾ band calculations and with the effective electron and hole masses $m_e^* = 0.3 m$ and $m_h^* = 0.5 m$ deduced from a critical discussion of the electrical and optical properties of GaSe⁽²⁰⁾, SCHMID has calculated the temperature dependence of the gap width resulting from the electron-phonon interaction⁽¹⁹⁾: by fitting the curve (solid line in Fig. 5) to the experimental results an energy $E_{ph} = 17$ meV was obtained for the homopolar optical phonon responsible for the interaction⁽²¹⁾. This value coincides with that reported by WIETING and VERBLE⁽²²⁾ for the transversal optical phonon which corresponds to the counterphase vibration along c of the partners of the bound Ga pairs. This phonon was shown by SCHMID and VOITCHOVSKY⁽²¹⁾ to give rise to a strong electron-phonon interaction which determines the charge carrier mobilities in GaSe.

3'3. Dependence of the characteristic lines on excitation intensity. — The use for excitation purposes of a laser in pulsed- and continuous-mode operation allowed us to carry out measurements at 4.2 °K with excitation intensities ranging from $4 \cdot 10^{-5}$ to $3 \cdot 10^2$ kW cm⁻² without focalization and up to 3 MW cm⁻² with focalization. Like their behaviour with temperature their dependence on the excitation intensity allows the characteristic lines to be partitioned into different groups. The first of them comprises the lines a_1 and a_2 as well as all the FE lines. They show a superlinear behaviour, their intensities varying like the p -th power of the excitation intensity where, depending on the crystal, $1.4 \leq p \leq 1.6$. The second group is formed by the lines TR which are visible only below 40 °K. At low excitation their intensities increase linearly with the excitation intensity and, depending on the crystal as well as on the particular line considered, they begin to saturate at values of the excitation intensity larger than about 1 kW cm⁻². The behaviour with the excitation intensity of the FE and TR lines is represented schematically in Fig. 3b).

Because of the temperature behaviour of the FE lines their dependence on the excitation intensity is visible in the 4.2 °K spectrum $A(h\nu)$ of pure crystals as well as in the high-temperature spectrum of any crystal independently of its purity. As far as the behaviour of the lines TR is concerned one has to distin-

⁽¹⁹⁾ PH. SCHMID: *Nuovo Cimento*, 21 B, 258 (1974).

⁽²⁰⁾ G. OTTAVIANI, C. CANALI, F. NAVA, PH. SCHMID, E. MOOSER, R. MINDER and I. ZSCHOKKE: *Sol. State Comm.*, **14**, 933 (1974).

⁽²¹⁾ PH. SCHMID and J. P. VOITCHOVSKY: *Phys. Stat. Sol.*, **65**, No. 1, in press.

⁽²²⁾ T. J. WIETING and J. L. VERBLE: *Phys. Rev. B*, **5**, 1473 (1972).

guish between that of the lines c_1 to c_8 on the one hand and that of the lines φ_1 to φ_6 and a_3 to a_8 on the other hand. This follows readily from Fig. 2 in which two series of spectra are plotted corresponding to $y = 0.33$ and $y = 0.99$ respectively. As seen from this Figure all lines c_1 to c_8 behave in the same way: their intensities increase linearly with the excitation intensity over the whole range of intensities covered by the experiment. In contrast to this, the intensities of the lines φ_1 to φ_6 and a_3 to a_8 saturate more or less rapidly as the excitation intensity increases.

In order to analyse the behaviour of each line of the spectrum $A(h\nu)$ separately, we have reconstructed $A(h\nu)$ corresponding to different values of the excitation intensity by superposing series of Gaussians of adequate height, width and position. Each Gaussian was taken to represent the emission intensity of an optical transition, *i.e.* of the characteristic line whose spectral position coincides with the maximum of the Gaussian. The choice of Gaussian lines was conditioned by the inhomogeneous character of the transitions, but it should be noted that the result of the present analysis is not critically affected by the detailed line shape. The dependence of the intensity of the characteristic lines composing the spectrum of a pure crystal on excitation intensity at 4.2 °K is represented in Fig. 6. As can be noticed, the intensities of the a_1 , a_2 and FE lines increase superlinearly with the excitation intensity. The intensity of the φ_i is first linear and then saturates above 1 kW cm⁻². Of all the observed lines the φ_i have probably the best established properties: their long lifetime permits them to be separated from the rest of the spectrum by delayed detection⁽¹⁷⁾. The behaviour of a_6 stands for all the lines a_4 to a_8 . Their intensities increase linearly until near 10 kW cm⁻² they begin to saturate. The lines a_3 and a_9 to a_{11} finally give rise to an intensity *vs.* excitation intensity plot which is essentially linear over the whole investigated range.

At very high excitation intensities, *i.e.* between 600 kW cm⁻² and 3 MW cm⁻², there appears in pure crystals a broad line whose maximum at 4.2 °K is located at 2.087 eV and which completely hides the lines of the group TR. The distance on the energy scale of this line from the direct band edge is equal to twice the ionization energy of the exciton. Moreover, the variation of its intensity with excitation intensity is quadratic with respect to that of the free-exciton lines and this line has therefore been attributed to an exciton-exciton scattering process⁽²³⁻²⁵⁾.

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⁽²⁵⁾ J. BILLE, F. ST. V. BOJNICIC-KNINSKI, A. MERCIER and J. P. VOITCHOVSKY: *Swiss Conf. Phys. Soc.* (Neuchâtel, 1973).

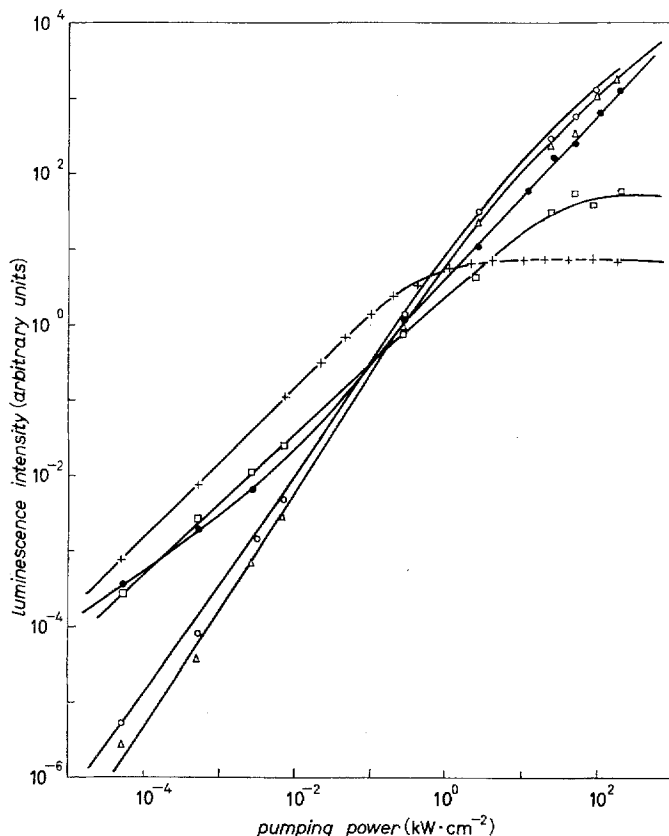


Fig. 6. — Dependence in a pure crystal at 4.2 °K of the intensity of the lines a_1 to a_3 , a_6 , a_9 to a_{11} and φ_1 to φ_6 on excitation intensity. The experimental points were obtained by decomposing the spectra of crystal II into a series of Gaussians. \circ FE; Δ a_1, a_2 ; $+$ φ_1 to φ_6 ; \square a_6 , \bullet a_3, a_9, a_{10}, a_{11} .

4. — Discussion of the results and conclusions.

The main results which emerge from the present experiments can be summarized as follows:

a) The emission spectrum of GaSe basically consists of two sets of lines, *i.e.* of those FE at high energy which are present at all temperatures and whose intensities vary superlinearly with the excitation intensity and those TR at low energy which disappear between 20 and 40 °K and whose intensities vary superlinearly with the excitation intensity (Fig. 3).

b) The TR lines depend on the purity of the crystal but are independent of the type of doping: the purer the crystal the lower the excitation intensity at which their intensities begin to saturate.

c) The simultaneous disappearance of the TR lines with increasing temperature is accompanied by an increase in the intensity of the FE lines.

In order to account for the above results let us consider the band structure of GaSe. It is characterized by a valence band whose maximum (I_4^-) is located at the centre Γ of the Brillouin zone, by a conduction band with a number (3 or 6) of equivalent absolute minima away from Γ and by a relative minimum (I_3^+) at Γ a few meV above the relative minima. In the light of new experimental data⁽⁴⁾ the difference of 50 meV between absolute and subsidiary minima reported in ref. (6) seems too large and a value of (25 ÷ 30) meV seems more probable. As a consequence, the direct exciton states associated with the band extrema at $\Gamma(k=0)$ are degenerate with electron-hole states of non-zero wave vector. Under these circumstances they can more properly be described as resonant states similar to those discussed in detail by BASSANI, IADONISI and PREZIOSI^(26,27) for the case of impurities.

The basic properties of resonant excitons were described by PHILLIPS⁽²⁸⁾ and can be summarized as follows: the wave function consists of two parts, *i.e.* a localized function which goes to zero as the electron-hole distance increases and a running-wave part made up of free Bloch states. The peculiarity in this case lies in the fact that the localized function has zero momentum while the running-wave part has a finite wave vector \mathbf{k}_i . We can write

$$(1) \quad \Psi_{\text{RFE}} = A(t) F_{ni}(|\mathbf{r}_e - \mathbf{r}_h|) \psi_e(\mathbf{0}, \mathbf{r}_e) \psi_v^*(\mathbf{0}, \mathbf{r}_h) + B(t) \psi_e(\mathbf{k}_i, \mathbf{r}_e) \psi_v^*(\mathbf{0}, \mathbf{r}_h),$$

where $F_{ni}(|\mathbf{r}_e - \mathbf{r}_h|)$ is the envelope function in the effective-mass approximation and where the spin co-ordinates are implicitly contained in \mathbf{r}_e and \mathbf{r}_h . The first term on the right-hand side of eq. (1) represents the free-exciton state which is obtained from the relative minimum of the conduction band at $\mathbf{k} = 0$. The second term is the contribution to the wave function from the continuum above the absolute minima and a summation over the equivalent \mathbf{k}_i values is implied. The time-dependent coefficients $A(t)$ and $B(t)$ give the relative weights of the two contributions and represent the probability amplitudes of the localized and of the dissociated states respectively.

By substituting (1) into the time-dependent Schrödinger equation the time evolution of the system is obtained and one can show that the electron and hole system resonates between the two component states. In particular, if at a given time $t=0$ the state is localized ($A(0)=1$, $B(0)=0$), it becomes completely dissociated ($A(t_0)=0$, $B(t_0)=1$) after a time

$$(2a) \quad t_0 = (\pi/2) \cdot (\hbar/M_{\text{int}}),$$

(26) F. BASSANI, G. IADONISI and B. PREZIOSI: *Phys. Rev.*, **186**, 735 (1969).

(27) F. BASSANI, G. IADONISI and B. PREZIOSI: *Progr. Rep. Phys.*, to be published.

(28) J. C. PHILLIPS: *Solid State Phys.*, **18**, 56 (1966).

where

$$(2b) \quad M_{\text{int}} = (\psi_c(\mathbf{k}_i, \mathbf{r}_e) \psi_e^*(\mathbf{0}, \mathbf{r}_h) | \mathcal{H}_s | F_n(|\mathbf{r}_e - \mathbf{r}_h|) \psi_c(\mathbf{0}, \mathbf{r}_e) \psi_e^*(\mathbf{0}, \mathbf{r}_h)),$$

\mathcal{H}_s is the Hamiltonian which describes the scattering of electrons, *e.g.* by impurities or by lattice vibrations. The same time t_0 is required to localize the electron and hole in an exciton state if they are originally dissociated at \mathbf{k}_i and $\mathbf{k} = \mathbf{0}$ respectively.

The resonant nature of the exciton should produce an asymmetric line shape in absorption⁽²⁹⁾. However, if the time t_0 is large, this asymmetry cannot be observed, the line shape is practically that of the normal exciton and the line width is essentially determined by electron-phonon interaction. An argument in favour of the resonant nature of the exciton must rather be sought in the existence in GaSe of photocurrent⁽³⁰⁾ and photovoltage⁽³¹⁾ peaks at the exciton absorption frequency. Both these peaks can easily be understood if the exciton has a finite probability of dissociation.

The above concepts together with the model of recombination kinetics outlined in Fig. 7 afford an explanation of the seemingly strange behaviour of the FE and TR lines. In addition to the resonant exciton (RFE), Fig. 7 shows the presence in the gap of a series of bound states, *i.e.* two donor levels (*D1*, *D2*) associated with the direct and the indirect minima respectively and a series of acceptor levels (*A*) with different ionization energies. The lower-lying donor state *D2* is taken to be representative of all localized states associated with the indirect minima. As seen from Fig. 7, electron-hole recombination can take place essentially via two competing channels the first of which involves the resonant exciton state (RFE) and the second the donor state *D1* and the acceptor states *A*.

The electrons which are produced in the pumping process are rapidly ($\approx 10^{-13}$ s) thermalized to the lowest minimum of the conduction band and to the available localized donor states in the gap. Since the resonant exciton states (RFE) have energies only slightly higher than those of the indirect minima, they can also be partly occupied under appropriate conditions such as high pumping power, low impurity content or sufficiently high temperature. When the resonant exciton states are occupied, radiative recombinations occur not only from the states $n = 1$, but also from the states $n = 2$ and $n = 3$ (see insert Fig. 1) and the FE lines are thus accounted for. It should be noted that the temperature dependence of the relative intensities of the FE lines corresponding to different n values is stronger than expected from the Boltzman distribution, corrected by the $1/n^3$ transition probability. This indicates that

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⁽³⁰⁾ A. H. M. KIPPERMAN: Thesis, Eindhoven (1971).

⁽³¹⁾ A. MERCIER and J. P. VOITCHOVSKY: unpublished results.

in spite of their higher energies the excited resonant states of FE can be populated directly from the conduction band.

Under different conditions, namely low pumping power, high impurity content or very low temperature, the donor-acceptor recombination channel is greatly favoured and as a result one observes the TR emission lines. In practice, there is a dynamical balance between the two channels, one being

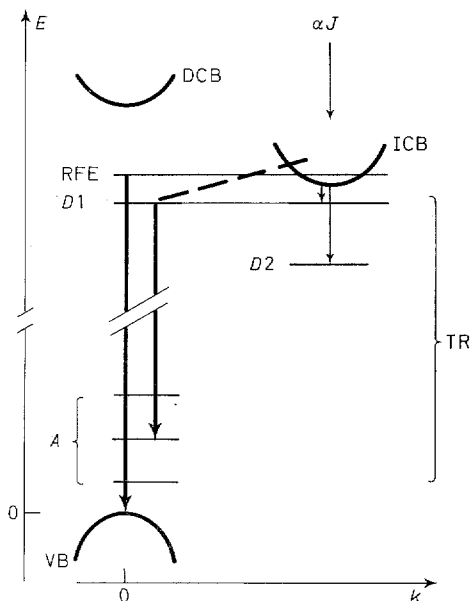


Fig. 7. - Schematic representation of the proposed recombination kinetics. The direct (DCB) and indirect (ICB) conduction band minima and the top of the valence band (VB) are shown in their relative positions. The resonant exciton state (RFE) and the donor ($D1$, $D2$) and acceptor (A) states are also indicated. The big vertical arrows represent the radiative transitions associated with the FE and TR lines, while the oblique arrow (dashed) stands for a phonon-assisted transition. The small vertical arrows represent the thermalization of the excited electrons. αJ is the number of electrons pumped, J is the pumping power and α is a number smaller than unity.

favoured with respect to the other by appropriate modifications of the pumping power, the impurity content and the temperature. High temperatures are particularly effective in favouring the FE recombinations: above 40 °K the FE lines dominate all spectra regardless of the other conditions.

It should be noted that a third recombination channel exists, involving the lowest electron traps ($D2$ in Fig. 7) associated with the indirect minima and the acceptor states. The corresponding indirect transitions are expected to give rise to broad emission bands and might thus account for the lines a_9 to a_{11} and c_9 . Since the $D2$ levels are quite deep, their occupation does not depend

appreciably on temperature and the recombination channel involving them does not compete with the others.

The energetic positions of the levels in Fig. 7 were chosen in agreement with the following features of the luminescence spectrum. At very low temperature (4.2 °K) and very low excitation intensity, the transitions through $D1$ are more favourable than those through RFE for all the crystals considered (Fig. 2c) and 2f)) since the probability of occupation of the RFE state is then too small. In this case the spectra of pure crystals are dominated by the lines a_4 and φ_1 to φ_6 (Fig. 2c)) while they are dominated by the transitions c_1 to c_6 in the case of doped crystals (Fig. 2f)). As the excitation intensity is increased at constant temperature, the spectra $A(h\nu)$ and $C(h\nu)$ evolve differently. In $A(h\nu)$, the FE transitions become visible and at high excitation intensities have an intensity comparable to that of the TR transitions (Fig. 2a) and 2b)). This phenomenon has two causes. Firstly, as the number of electrons increases, so does the probability for an electron contained in the indirect minimum to occupy the state RFE. This results in an occupancy of the resonant states which varies superlinearly with the excitation intensity and thus accounts for the super-linear behaviour of the FE lines (Fig. 3b)). Secondly, this probability becomes appreciable only if the number of electrons present in the indirect band is sufficiently high. This situation arises in the purest crystals since in this case the competitive transitions through $D1$ are saturated at high excitation intensities (Fig. 6) on account of the small number of impurity states. For highly doped crystals, the TR transitions do not saturate and consequently the probability of FE transitions is not sufficiently high for them to be detected (Fig. 2d), 2e), 2f)). Although they fall within the same energy range, the characteristic TR lines are not exactly the same for pure and doped crystals. The differences are very likely due to the influence of the impurity concentration upon the states giving rise to the TR lines (¹⁶).

As the temperature increases, the transitions originating from the states FE become much more important for all crystals than those from $D1$. This behaviour results from the change with temperature of the Fermi distribution of the electrons in the indirect band and from the thermalization of electrons from the donor state $D1$ into the conduction band minima. The quenching of the TR lines with temperature is well explained by the recombination kinetics outlined in Fig. 7 which involves the absorption of phonons. The corresponding calculations are similar to those reported in ref. (¹⁷). The results are shown in Fig. 4 as continuous lines through the experimental points. The phonons used in fitting the curves are the three lowest optical phonons at 2.4, 7.4 and 16.7 meV as deduced from Raman-scattering measurements (²²). The curves corresponding to increasingly impure crystals were calculated with decreasing lifetimes of the state $D1$. The increase of the quenching temperature with y can therefore be attributed to a decrease of this lifetime. This result is compatible with the fact that the only observed long-lifetime transitions φ_1

to φ_6 belong to the extreme spectrum $A(h\nu)$, i.e. to $y \approx 0$. Furthermore, since the lifetime of the state $D1$ is the inverse of the transition probability from this state to all possible final states and since the number of final states A depends on the number of impurities⁽¹⁶⁾, it seems reasonable that the lifetime of $D1$ decreases with increasing impurity content. In the present model, it is necessary to consider one donor state $D1$ only to account for the disappearance at the same temperature of all TR lines of a given crystal. The variety of acceptor states A accounts for the different lines.

In addition to the fact that the present model for impurity levels affords a qualitative interpretation of most of the experimental data, there is a number of arguments justifying it:

The half-width of the TR lines associated with the levels $D1$ and A is the same as that of the FE lines. This indicates that, in agreement with our assumptions, they are indeed direct transitions.

The great number of states $D1$ and A , their low ionization energy as well as their independence of the chemical nature of the impurities show that they are due to structural defects, the number of which increases with impurity content⁽¹⁶⁾.

The high electrical compensation observed in all crystals⁽¹⁶⁾ is compatible with the simultaneous presence of donor ($D1$ and $D2$) and acceptor (A) states, which might be arranged in closely spaced pairs. The recombination of electron-hole pairs bound to these centres would then give rise to the TR luminescence lines.

Since several authors^(13,15) have suggested that some of the many lines in the luminescence spectrum of GaSe are phonon replica, the question arises whether there are any among the TR lines. It does indeed appear that the long-lifetime lines φ_1 to φ_6 can be divided in two groups; corresponding members of which are separated by 19 meV. Moreover, in electroluminescence spectra obtained at 4.2 °K, two series of lines with similar relative intensities have been observed⁽³²⁾, whose corresponding members are separated by 20 meV. The phonon closest to these energies is the 17 meV (at $k = 0$) homopolar optical phonon reported in ref. (23) which is responsible for the temperature dependence of the direct gap and of the Hall mobility of holes⁽²¹⁾.

The recombination of bound excitons, resulting from the capture of free excitons by impurity centres calls for the following remark: the only lines which we attribute to this process—they were not accounted for by the preceding scheme—are the lines a_1 and a_2 . Their dependence on excitation intensity is the same as that of the FE lines and they appear only in the spectra in which the FE are important. Because of their high polarization parallel to c (Table I),

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we attribute them to bound excitons in the singlet state. The corresponding binding energies of 6 meV and 7.5 meV respectively are indeed those expected for an exciton bound to a neutral acceptor (or donor) having an ionization energy of about 30 meV⁽³³⁾. This energy agrees well with that obtained from electrical measurements for the acceptor level of the pure crystals⁽¹⁶⁾. Furthermore, the quenching of the lines a_1 and a_2 with temperature can be attributed to the thermal dissociation of exciton and impurity. In view of these new results our previous suggestion⁽³⁴⁾ that these lines should be attributed to electron-exciton scattering now appears unlikely. Finally we mention that if the proposed recombination model should prove to be valid, then the indirect-gap energy lies between 2.1005 and 2.106 eV at 4.2 °K.

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● RIASSUNTO (*)

Si sono fatte ricerche sulla fotoluminescenza di un gran numero di cristalli puri e drogati di GaSe nell'arco di temperature che va da 4.2 a 300 °K con intensità di eccitazione variabili fra $4 \cdot 10^{-5}$ e $3 \cdot 10^2$ kW cm⁻². Si produceva l'eccitazione con la linea verde di un laser a frequenza raddoppiata Nd:YAG. Si erano coltivati in laboratorio tutti i cristalli, per molti dei quali si era usata la tecnica di accrescimento di Bridgman, mentre per altri la reazione di trasporto con iodio. Benchè non si siano trovate righe di emissione caratteristiche della particolare impurità introdotta nel cristallo, si sono potuti classificare gli spettri a 4.2 °K secondo la quantità di impurità aggiunte. Oltre 40 °K si sono trovati spettri identici per tutti i cristalli. La dipendenza degli spettri dalla temperatura dovuta al rapido spegnimento, fra 20 e 40 °K, della luminescenza, risultante dalla ricombinazione negli stati trappola e alla crescente importanza alle alte temperature delle ricombinazioni di eccitoni liberi. I due gruppi di righe connessi con questi due canali di ricombinazione costituiscono la parte principale di tutti gli spettri osservati. Si è interpretata la variazione degli spettri con la temperatura, la pressione e la concentrazione di impurità come risultato di un equilibrio fra i due canali di ricombinazione. Si discute nei dettagli un modello di teoria cinetica che tenga conto di questi due canali come del fatto che nel GaSe gli eccitoni liberi entrano in risonanza con i minimi indiretti della banda di conduzione.

(*) Traduzione a cura della Redazione.