Resonant exciton in GaSe†

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Experimental evidence is given for the occurrence in GaS_xSe_{1-x} ($0 \leq x \leq 0.2$) of a resonance between the free exciton associated with the direct band gap on the one hand and states near the indirect-conduction-band minimum on the other hand. This evidence includes the temperature dependence of the luminescence spectrum of GaS_xSe_{1-x} for excitation energies lying above and below the exciton ground state, the excitation spectra of two characteristic luminescence lines, and the shape of the absorption line of the free exciton. The experimental results are in excellent agreement with a model of recombination kinetics proposed earlier for GaSe as well as with Fano's theory of the line shape of resonant states.

I. INTRODUCTION

GaSe is an indirect-gap semiconductor.[1,2] The top of its valence band lies at Γ and the bottom of the conduction band at M. A relative minimum of the conduction band at Γ is situated a few tens of meV above the minimum at M. The band structure of the mixed crystals GaS_xSe_{1-x} ($0 \leq x \leq 1$) is similar but direct and indirect gaps as well as the difference between them increase with increasing x.

Near 4.2 °K the luminescence spectrum of GaSe containing 10^{18} cm^{-3} impurities is characterized by two groups of lines,[3,4] one originating from the recombination of the free exciton at Γ and the other from donor states coupled with the M-point minimum of the conduction band. In order to explain the behavior of these two groups of lines, Voitchovsky and Mercier[4] have proposed a model for the recombination kinetics of excited electrons and holes in GaSe. This model, which postulates a resonance between the free-exciton states and states near the M-point minimum of the conduction band, is now confirmed by (i) a study of the temperature behavior of the luminescence spectra of mixed crystals GaS_xSe_{1-x} for $0 \leq x \leq 0,2$; (ii) the measurement of the excitation spectra of two luminescence lines of GaSe, each belonging to one of the two groups of lines mentioned above; (iii) the determination of the luminescence spectra of GaSe at different temperatures with excitation energies equal to the conduction-band minimum (resonant excitation); and (iv) the discussion of the shape of the absorption lines of the exciton in GaSe in terms of Fano's[5] theory of resonant states.

II. EXPERIMENTAL PROCEDURE

The investigated crystals were grown by the Bridgeman technique under conditions similar to those described earlier[3] for GaSe. In order to assure the homogeneity of the mixed crystals, the luminescence spectra of samples cut near both ends of an ingot were determined. Only ingots for which the two spectra were identical were retained for the present investigation.

The samples were soldered to a copper support by means of Hg-Tl-In eutectic and the support fixed in a helium cryostat permitting sample temperatures between 4.2 and 300 °K.

For the study of the temperature dependence of the luminescence spectra of mixed crystals, the green line ($\lambda = 0.532$ μm) of a pulsed frequency doubled YAlG:Nd laser was used. The same line was employed to excite a dye cell (Rhodamine 6 G), which served as monochromatic source for photon energies varying between 2.0 and 2.2 eV. The excitation spectra and the spectra corresponding to resonant excitation were measured with this source. The peak power of the excitation pulses was 100 kW/cm^2, their duration 100 nsec, and their repetition rate 75 sec^{-1}.

The excitation radiation was incident along the crystal c axis, and the luminescence spectra were detected in reflection. The spectra were measured on a SPEX 1402 double spectrometer by means of a photomultiplier and a two-channel boxcar integrator.[6]

III. THE MODEL

The model of recombination kinetics proposed for[4] GaSe and applied here also to the mixed crystals is reproduced in Fig. 1 in which the top of the valence band VB and the direct DCB and indirect ICB minima of the conduction band are shown. FE denotes the direct free exciton, and D_1 is a donor state associated with ICB. The values of direct and indirect gap on the energy scale are marked by DG and IG, respectively.

As seen from Fig. 1, the exciton states near $\vec{k} = 0$ are degenerate with ICB states near $\vec{k} = \vec{k}_i$. Impurity and phonon scattering and, in the mixed crystals, scattering by compositional disorder, strongly couple the two kinds of states, and the exciton in GaS_xSe_{1-x} therefore is resonant in the sense given to this term by Phillips.[7]

If we assume the holes in the excited crystal to

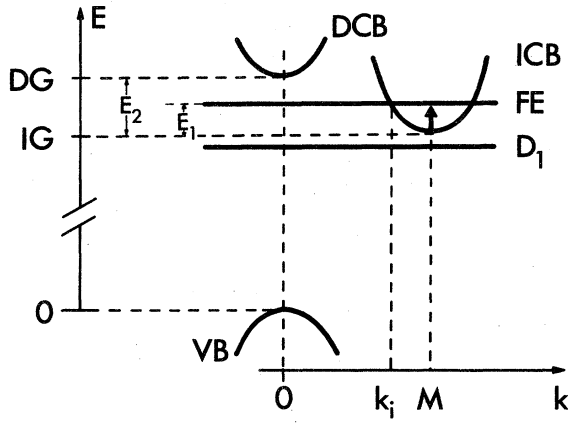

FIG. 1. Model of recombination kinetics. VB is the valence band, DCB and ICB are the direct and indirect conduction bands, respectively, FE is a free-exciton level associated with DCB, and D_1 is a representative donor level associated with ICB.

thermalize at the top of VB and the electrons at the bottom of ICB, the model affords two distinct modes of electron-hole recombination. The first is dominant at low temperatures and results from the possibility that thermalization can take the electrons below ICB into donor states D_1 from which they can recombine with the holes either at VB or in acceptor states (not shown in Fig. 1) immediately above it. This recombination gives rise to the luminescence lines constituting a first low-energy group of lines in GaSe.[4]

The second mode of recombination becomes important at temperatures high enough for the electrons in ICB to acquire the energy E_1. The scattering coupling the states $\vec{k}=\vec{k}_i$ and $\vec{k}=0$ then leads to a population of FE: a group of high-energy lines appears in the luminescence spectrum corresponding to free-exciton recombinations. At sufficiently high temperature, this second group of lines dominates the luminescence spectrum of GaSe.[4]

To derive the equation of recombination corresponding to this model, we assume that the electrons in ICB have the temperature of the crystal (low excitation) and that they are distributed according to Fermi-Dirac statistics. Moreover, since the excited crystal contains electrons in ICB even at $T=0$ °K, we assume the quasi Fermi level ξ of the electrons to lie at the bottom of ICB, i.e., we set ξ equal to IG. If then n_1 denotes the number of electrons in ICB and n_2 that of the electrons forming excitons, we have in the stationary state

$$\frac{dn_1}{dt}=N-n_1P_1-n_1FP_3+n_2P_3=0\ , \tag{1}$$

and

$$\frac{dn_2}{dt}=n_1FP_3-n_2(P_2+P_3)=0\ , \tag{2}$$

where N is the number of electrons which are excited per second into ICB, P_1 is the probability of transitions from ICB to states in the forbidden gap including D_1, P_2 is the probability of direct exciton recombination, and P_3 is the transition probability $\vec{k}=0\leftarrow\vec{k}=\vec{k}_i$. F is the Fermi function which with ξ equal to IG is

$$F=(1+e^{E_1/kT})^{-1}\ . \tag{3}$$

From Eqs. (1)–(3) one readily obtains

$$n_2P_2=A/(1+Be^{E_1/kT})\ , \tag{4}$$

where

$$A=NP_2P_3/(P_1P_2+P_1P_3+P_2P_3)$$

and

$$B=P_1P_2+P_1P_3/(P_1P_2+P_1P_3+P_2P_3)\ .$$

Equation (4) describes the temperature dependence of the intensity of the free-exciton recombination lines and its successful application to the interpretation of the experiments in GaSe first-lent support to the present model.

IV. EXPERIMENTAL RESULTS

A. Temperature dependence of the free-exciton recombination in GaS_xSe_{1-x}

In Fig. 2 we have plotted the temperature dependence of the intensity of the line corresponding to the exciton ground state, measured for a series of mixed crystals $0\leq x\leq 0.2$. For each composition, the measurements were limited to temperatures low enough that the intensity integrated over the whole spectrum remained approximately constant. This limitation assured a rough balancing of the recombination via free excitons and of that

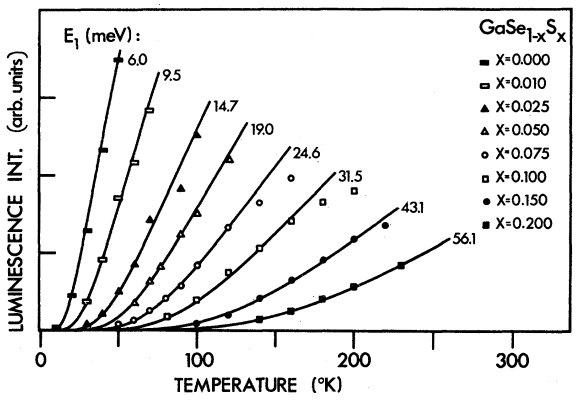

FIG. 2. Intensity vs temperature plots of the radiative recombination of the exciton ground state of GaS_xSe_{1-x} for eight different compositions x. The E_1 values obtained by fitting Eq. (4) to the experimental results are indicated.

via the bottom of ICB. Also plotted in Fig. 2 are theoretical curves obtained from fitting Eq. (4) to experiment by suitable adjustments of E_1 for each composition x. The curves were calculated under the assumption that A and B do not depend on x and that $B \approx 1$, i.e., $P_1 > P_2, P_3$. This last assumption implies that most of the electrons in ICB thermalize in the donor states D_1 or in other states in the forbidden gap from which they recombine without contributing to the luminescence in the region of the spectrum of interest here.

A linear relationship $E_1 = E_1(x)$ is obtained from the fitting of the intensity vs temperature curves. This relationship (Fig. 3) affords an independent verification of the proposed recombination model. Indeed, the difference E_1 between direct free exciton and indirect gap is an approximative measure for the difference E_2 between direct and indirect gap. While E_2 cannot be determined by direct optical observation, the difference between exciton ground state and donor state can. This difference also is a measure for E_2, and its experimentally determined dependence on x is shown in Fig. 3. Yet another experimentally accessible measure for E_2 is the difference between direct and indirect exciton ground states. The variation with composition of this difference has recently been determined by Depeursinge[8] and is given in Fig. 3 as dashed line. The approximative parallelism of the three lines in Fig. 3 corroborates the proposed model, and this corroboration is not lessened by the fact that the parallelism is not perfect. Indeed, the plotted curves differ from one another by the ionization energies of donors and indirect exciton or by the difference between the two. Since these ionization energies tend to increase slightly with x, the slight divergence of the curves in Fig. 3 is understood.

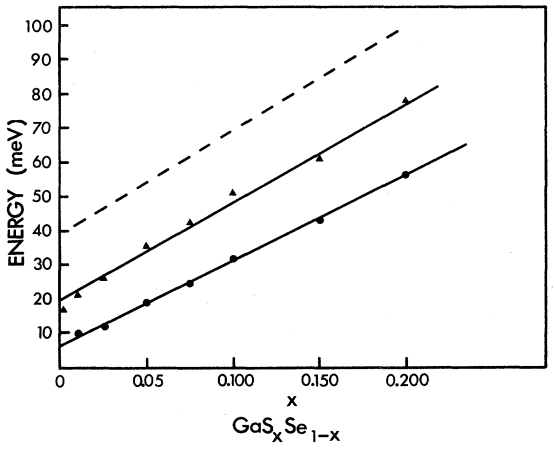

FIG. 3. ●, the difference E_1 between direct free exciton and indirect gap, determined from fitting Eq. (4) to the experimental intensity vs temperature plots of Fig. 2. ▲, the difference between exciton ground state and donor state obtained from optical absorption and from luminescence measurements. The dashed line is the difference between direct and indirect exciton ground states measured by Depeursinge (Ref. 8).

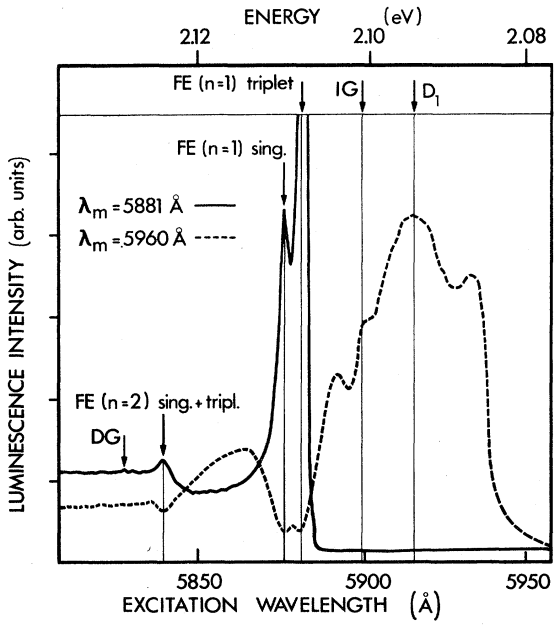

FIG. 4. Excitation spectra at 4.2 °K of the $n=1$ triplet state of the direct exciton in GaAe (continuous line) and of a line associated with the donor state D_1 (dashed line).

B. Excitation spectra of GaSe

Figure 4 shows the intensities at 4.2 °K of two luminescence lines of GaSe at $\lambda_{m_1} = 5881$ Å and at $\lambda_{m_2} = 5960$ Å as functions of the continuously varying excitation wavelength. The line $\lambda_{m_1} = 5881$ Å results from the triplet ground-state recombination of the direct exciton, and the corresponding excitation spectrum (solid line) shows that this state can best be populated by pumping the higher lying singlet ground state and the first excited state $n=2$ of the direct exciton. The line $\lambda_{m_2} = 5960$ Å is associated with the recombination through the donor states D_1. Its excitation spectrum (dashed line) shows negative contributions from the exciton states and strong positive contributions from the indirect gap IG and from D_1. All other lines lying on the low-energy side of the luminescence spectrum have essentially the same excitation spectra. These lines therefore correspond to recombination processes which are in competition with exciton recombination and, in fact, are conditioned by the population of IG and D_1. In view of these results, the hypothesis that the low-energy lines

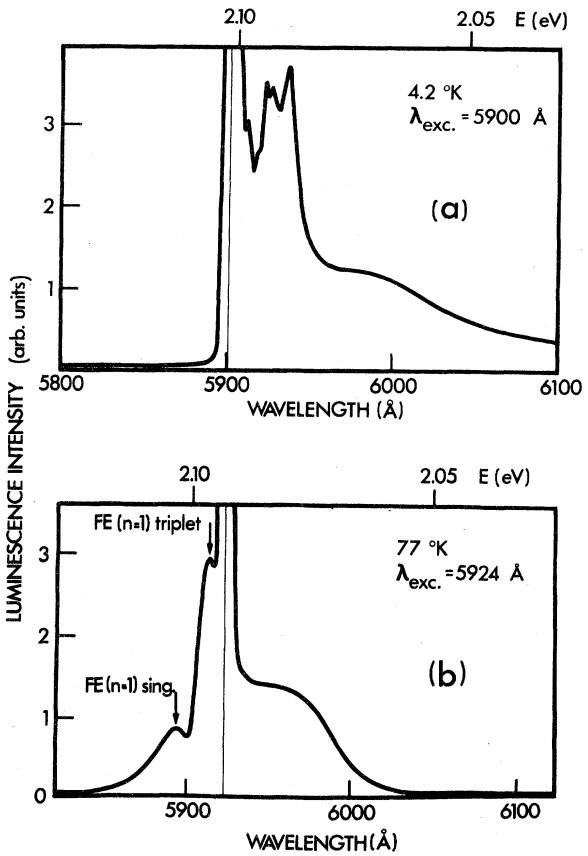

FIG. 5. Luminescence spectra of GaSe at (a) 4.2 °K and at (b) 77 °K obtained with an excitation energy corresponding to the indirect gap [λ_{exc}(4.2 °K) = 5900 Å, λ_{exc}(77 °K) = 5924 Å].

might arise from bound excitons can be discarded, and the proposed model is once again confirmed.

C. Resonant excitation in GaSe

To obtain direct evidence for the population at sufficiently high temperature of the direct exciton states via a population of the indirect conduction-band minimum, we have measured two luminescence spectra of GaSe at 4.2 and 77 °K with excitation energies corresponding to the indirect gap energies λ_{exc} (4.2 °K) = 5900 Å and λ_{exc} (77 °K) = 5924 Å. The two spectra are shown in Fig. 5 with the indirect gap energies aligned on the same abscissa. As seen from this figure, only the low-energy lines are visible at 4.2 °K, but at 77 °K the direct-exciton lines appear. Except for the peaks corresponding to the excitation wavelengths, the two spectra are in fact identical to the spectra obtained at the same temperatures with excitation energies higher than the direct gap. The hypothesis that the excited electrons in GaSe thermalize in ICB and from there populate the direct exciton states at sufficiently high temperature is thus born out by experiment.

D. Shape of the free-exciton absorption line in GaSe

Last but not least, the resonant nature of the direct exciton in GaSe is confirmed by the shape of the corresponding absorption lines. Figure 6 shows the exciton absorption spectrum (solid line) measured recently by Depeursinge[8] on a thin flake of transport reacted GaSe. Since the flake contained only the γ modification, the spectrum does not exhibit the usual ground-state splitting associated with polytypism,[9] and a comparison between observed and calculated line shapes is readily possible. According to Fano,[5] the intensity $I(\epsilon)$ of a resonant line as a function of the (reduced) distance ϵ from the center of the line is

$$I(\epsilon) \sim (q+\epsilon)^2/(1+\epsilon^2) , \qquad (5)$$

where q is a measure of the ratio between the oscillator strength of the discrete state and that of the continuum with which it interacts. With $q = -2.5$, excellent agreement is obtained between experiment and theory (circles) for the singlet and triplet ground states, and the measured shape of the line $n = 2$ clearly is also produced by resonance. The residual absorption (dashed line) probably is due to the indirect transitions.

V. CONCLUSIONS

On the basis of an extension of the model of recombination kinetics proposed earlier for GaSe, we were able to interpret the temperature dependence of the luminescence spectra of GaS_xSe_{1-x} for $0 \leq x \leq 0.2$. The ease with which the model

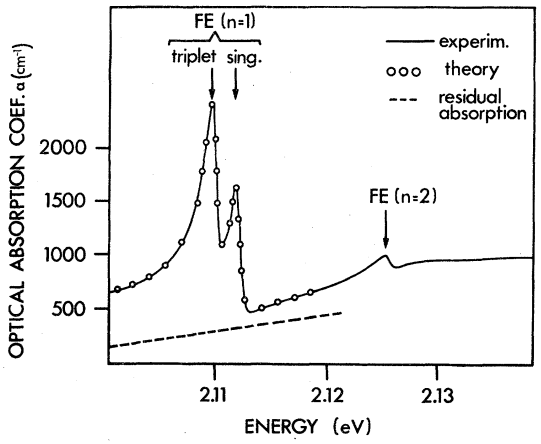

FIG. 6. Free-exciton absorption in GaSe at 4.2 °K according to Depeursinge (Ref. 8) (continuous line) and the fitted values (circles) derived from Fano's (Ref. 5) theory.

renders possible this interpretation lends credence to the hypothesis of the resonant exciton in GaSe. Additional confirmation of this hypothesis comes from the experimental verification of a series of predictable consequences concerning excitation spectra, resonant excitation, and line shape of the exciton absorption.

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