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Role of electron traps in the excitation and de-excitation mechanism of Yb³⁺ in InP

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An experimental study concerning the excitation mechanism of the Yb impurity in *n*- and *p*-type InP crystals was performed by the method of optically detected microwave-induced impact ionization. Based on the results it is argued that the Yb³⁺ core excitation is intermediated by a nonradiative recombination of a bound exciton. A fingerprint of the existence of such an excitonic state is given. Also, the nonradiative decay channel is discussed and shown to involve an Auger process with the energy transfer to a locally bound electron. Experimental evidence is presented that by the impact ionization of the bound electron the nonradiative recombination channel may be removed, leading to an increase of the characteristic Yb³⁺ luminescence. An unprecedented microwave-induced 5% increase of the Yb³⁺ intrashell emission has been recorded. © 1995 American Institute of Physics.

I. INTRODUCTION

The characteristic feature of the electronic structure of rare-earth (RE) elements is the presence of incompletely filled *4f* shells, surrounded by closed *5s*² and *5p*⁶ shells. The *4f* electrons are well screened and consequently, when placed in solids, are only slightly affected by the crystalline field. As a result they show under excitation sharp atomic-like photoluminescence (PL) spectra arising from intra-*4f*-shell transitions. In view of the above, rare-earth-doped III-V semiconductors, and recently also RE-doped silicon, belong to the perspective optoelectronic materials. They attract much attention because of possible applications to new optical devices characterized by sharp and temperature-stable luminescence, such as light emitting diodes or lasers. Here, in addition to optical also successful excitation by minority carrier injection has been reported for Er-doped GaAs¹ and Yb-doped InP.² However, the luminescence intensity rapidly decreases at high temperatures, thus seriously hampering possible practical applications. In order to overtake this thermal quenching and to increase PL efficiency at high temperatures it is necessary to clarify, and then optimize, the luminescence mechanism of the RE ions. For a number of reasons the InP:Yb system seems especially suited for such studies and has been intensively investigated. The ytterbium photoluminescence spectra indicate that the Yb atoms form only one kind of luminescence center of a universal character, independent of the preparation method. Such a center has only one excited state within the band gap of InP. Furthermore, it gives strong luminescence at low temperature, which considerably simplifies the experimental study. It is

generally believed that the understanding of the excitation and de-excitation mechanisms of RE's in III-V semiconductors will shed light also on the behavior of RE dopants embedded in silicon. Therefore the basic importance of silicon in modern device manufacturing provides major motivation for such studies.

II. PRELIMINARIES

At low temperatures and under optical excitation with energy exceeding the band gap of the host crystal, only a small fraction of the free carriers are energetic enough to dissociate (ionize) excitons by collisions (impact). In thermal equilibrium each exciton ionization process is counterbalanced by a corresponding formation process. Under application of a microwave field, (photoexcited) free carriers are accelerated by the electric field and some of them gain sufficient energy to impact ionize excitons as well as some other loosely bound particles. A critical microwave field exists³ at which the impact-ionization rate starts to predominate both exciton recombination and ionization by phonon absorption, which is normally the dominant process in thermal equilibrium.⁴ For microwave fields larger than the critical value the electron gas is heated and diminishes the number of low-energy carriers that are being effectively captured by shallow impurities.⁵ Heating of the electron gas results in reduction of the effective capture rate of such centers. In that way the impact ionization of the shallow excitons, which have a fast recombination rate, blocks an efficient recombination channel and thus can enhance emissions related to deep impurities. As a result of the microwave fields application the concentration of excitons bound to shallow centers sharply drops with a simultaneous avalanche increase of the free-carrier density and their lifetime. In that way an in-

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creased number of carriers is available to participate in re-combinations via deep centers and free-to-bound transitions.

The exciton binding mechanism by isoelectronic centers has been well described.⁶ It is generally accepted that such centers can introduce a short-range potential capable of localizing either an electron or a hole (the so-called primary particle). Once it becomes bound, it provides a Coulomb field in which a particle of the opposite charge can be captured (secondary particle). In this way the bound exciton system is formed. Since the secondary particle is loosely bound it can be easily impact-ionized, although such a process is not very effective in view of the long-range character of the binding potential; the impact-ionized particle can be easily recaptured. The impact ionization of the primary particle can take place only for much higher energies and would lead to a steady dissociation of the bound-exciton (BE) system.

The application of a microwave field does not have any influence on the lattice temperature of the crystal being studied. At low temperatures (2 K) the interactions of phonons with free carriers are negligible, and the application of a microwave field results in heating of free carriers. The actual energy gain depends on the effective mass of the carrier and the microwave power. In InP the conduction-band electrons have effective mass smaller than that of (light and heavy) holes. Therefore, a more efficient microwave heating of electrons than holes is expected. At high temperatures the electron-phonon interaction becomes dominant resulting in a less effective acceleration of the carriers; thus the optically detected microwave-induced impact ionization (ODMII) effect cannot take place significantly.

The impact ionization effect can be measured directly by monitoring the influence of the microwaves on the PL spectrum. In this case, the standard PL spectrum is compared with the one recorded under the application of constant microwave power; to permit the lock-in detection technique in both cases the laser excitation is modulated. On the other hand, the spectral dependence of the impact ionization effect can be investigated. To perform this one monitors the changes of the PL spectrum in phase with the on-off modulated microwave field set at different power levels, under constant laser excitation power.

In view of the preceding remarks one should expect that the impact ionization thresholds depend on the quality of the crystal. It is well known that the presence of randomly distributed charged donors and acceptors in compensated semiconductors causes some fluctuations of the electrical potential in the material.⁷ In this way semiconductors with large concentrations of dopants have strong electrostatic potential fluctuations which result in considerable broadening of the energy level position of impurities. Taking into account that the purest crystals of InP have *n*-type conductivity,⁸ *p*-type material is expected to have higher absolute dopant concentrations and consequently show some "smearing" of the (shallow dopant) ionization levels. As a result of this effect and, at the same time the considerably higher impurity scattering, one expects that the impact ionization effect will be more difficult to observe in *p*-type InP.

From the luminescence studies in semiconductors it is known that the PL intensity of the free-to-bound (FB) transitions increases with temperature; this is due to gradual ionization of the shallower impurity levels. On the other hand, the probability of the FB emission can be significantly reduced if the free-carrier lifetime becomes much smaller than the radiative lifetime of the free-to-bound process, such a situation being typically a result of carrier capture at (shallow) impurities.⁹ The microwave heating results in a decrease of shallow impurity capture rates and thus increases the free-to-bound emissions due to both: the increase of carrier lifetime and the simultaneous decrease of the available number of neutral donor exciton traps. In that way a number of neutral acceptors which participated in donor-acceptor pair (DAP) recombination become available for the free-to-bound transitions.

III. EXPERIMENT

The crystals were grown at the University of Stuttgart, Germany, and the CNET laboratory in Lannion, France; the details of the preparation procedure have been described elsewhere.^{8,10-12}

- (i) The crystal KS 175 was grown by metalorganic chemical vapor deposition (MOCVD). The epitaxial InP:Yb layer was grown on a semi-insulating Fe-doped InP substrate; the layer thickness was 3 μm . The crystal exhibited *n*-type conductivity with a carrier concentration of $n = 10^{15} \text{ cm}^{-3}$ at 300 K. The total Yb concentration was in the range of $10^{18} \text{ atoms/cm}^3$, as determined by secondary-ion mass spectroscopy (SIMS).
- (ii) The crystal WK 82 was grown by liquid phase epitaxy (LPE). The InP:Yb layer was grown in a graphite sliding-boat system by a supercooling process at high growth temperatures up to 800 °C. The Yb concentration in the In growth melt was 0.2% mole fraction. The crystal exhibited *p*-type conductivity with carrier concentration of $p = 7 \times 10^{16} \text{ cm}^{-3}$ at 300 K, with Zn being the residual acceptor.
- (iii) The 133 B single crystal was grown by the high-pressure gradient freeze synthesis method. By this method, unintentionally doped samples are *n* type with a residual electron density of about $5 \times 10^{15} \text{ cm}^{-3}$ and when Yb is diluted in the semiconductor with a concentration of about $[\text{Yb}] = 10^{17} \text{ atoms/cm}^3$ they are still *n* type and the carrier density ranges between 10^{16} and $5 \times 10^{16} \text{ cm}^{-3}$ at 300 K.

In the experiment the samples were mounted in a TE_{011} cavity with slits for optical access. The carriers were excited with the 514.5 nm line of the Ar^+ laser operating with an output power of typically 50 mW. The luminescence was collected from the laser-irradiated side and was dispersed with a high-resolution 1.5 m *F*/12 monochromator (Jobin-Yvon THR-1500) with a 600 grooves/mm grating blazed at 1.5 μm . The signals were detected with a liquid-nitrogen-cooled germanium detector (North Coast EO-817) and amplified using the conventional lock-in technique with a modulation frequency at typically 730 Hz. Optically detected

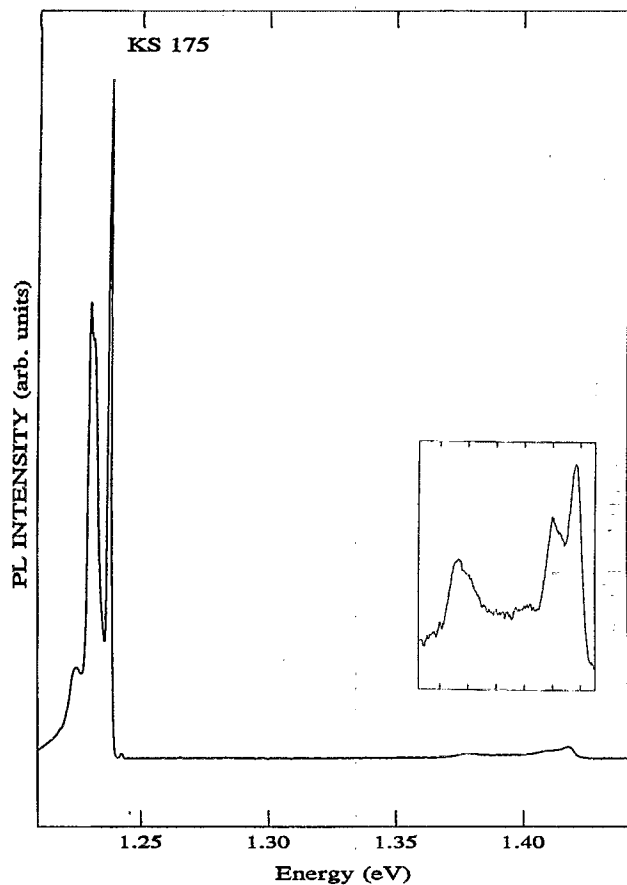


FIG. 1. Photoluminescence (PL) spectrum of *n*-type InP:Yb crystal (KS 175) measured at 2.1 K under Ar⁺ ($\lambda=514.5$ nm) excitation.

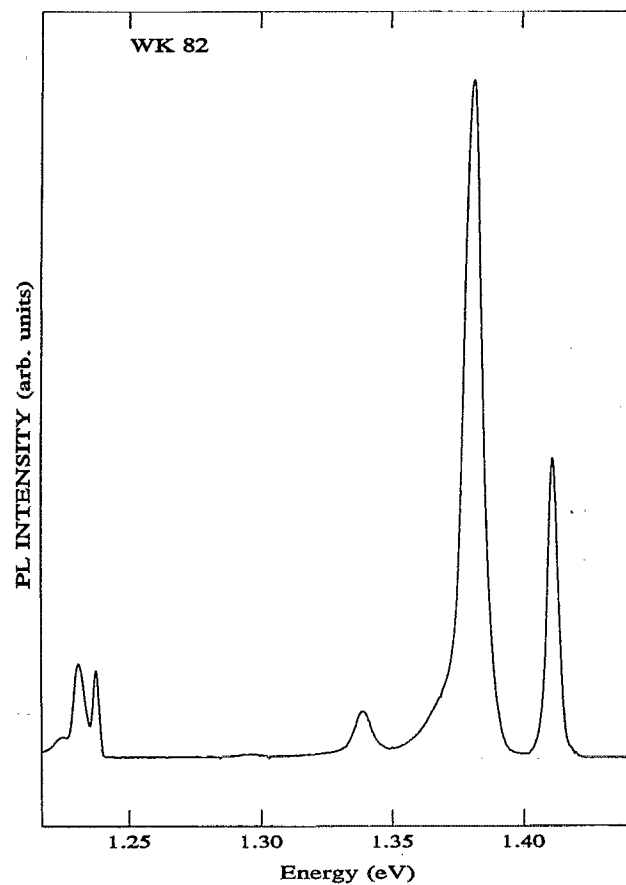


FIG. 2. Photoluminescence (PL) spectrum of *p*-type InP:Yb crystal (WK 82) measured at 2.1 K under Ar⁺ ($\lambda=514.5$ nm) excitation.

impact ionization measurements were performed in the *Q* microwave band around of 35 GHz at liquid-helium temperature. During the measurements the helium bath was pumped to prevent noise due to liquid evaporation, keeping the temperature of the crystal at about 2 K.

IV. EXPERIMENTAL RESULTS: PHOTOLUMINESCENCE AND IMPACT IONIZATION

The PL spectrum of the *n*-type InP:Yb crystal KS 175 is presented in Fig. 1; it is characterized by a clear Yb band and a relatively much weaker $\approx 4\%$ band edge luminescence. As shown on the high-sensitivity insert this latter emission consists of three peaks at 1419.3, 1410.9, and 1380 meV which can be identified as free exciton (FE), donor-bound exciton (DBE), and donor-acceptor-pair (DAP) recombinations, respectively. Figure 2 presents the PL spectrum of the *p*-type InP:Yb crystal WK 82, with characteristic stronger intensity of the band edge components. The band edge luminescence consists of acceptor-bound exciton (ABE), FB, and DAP recombinations at 1412, 1388, and 1381 meV, respectively.^{13,14} In addition an extended shoulder line between 1343 and 1373 meV, and a phonon replica of the DAP at 1338 meV can be distinguished. The PL spectra of both samples have an identical second group of lines at 1248.6, 1242, 1238.1, and 1230.7 meV which has been ascribed to internal *4f*-shell transitions of the Yb³⁺ ion.¹⁵ Figure 3 shows the PL spec-

trum as recorded for the *n*-type bulk crystal 133 B, with characteristic strong Yb³⁺ luminescence and without showing any band edge luminescence.

The application of a microwave field influences the observed PL spectra. In the *n*-type crystal (KS 175), microwave power of 200 mW decreases the band edge and increases the Yb³⁺ luminescence by approximately 10% and 1%, respectively. In the *p*-type LPE-grown crystal, the results are qualitatively similar while being approximately one order of magnitude smaller. The change of PL was directly recorded with constant laser excitation and on-off modulated microwave power at a frequency of 730 Hz. Spectral dependencies obtained in this way are depicted in Figs. 4–6, for *n*-, *p*- and *n*-type crystals, respectively. For the KS 175 and WK 82 samples the microwave-field influence on both groups of PL lines can be seen: it is negative for the band edge luminescence and positive for Yb³⁺. For the bulk material only enhancement of the Yb band can be seen.

Figures 7–9 show the power dependence of the ODMII signal for the three materials used in the current study. The relative changes of the PL intensities were measured from the maximum power of 200 mW (0 dB attenuation) down in the order of dB. As expected,^{16,17} there is a threshold of microwave power which starts the impact ionization of excitonic states. The actual threshold values for the impact ionization of the shallow states are apparently larger in the *p*-

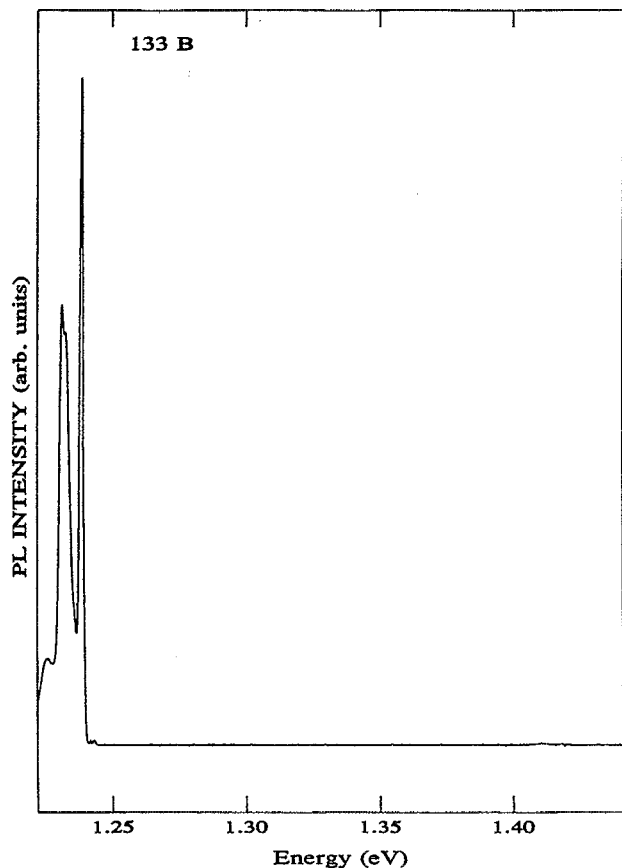


FIG. 3. Photoluminescence (PL) spectrum of high-pressure gradient freeze synthesis-grown InP:Yb crystal (133 B) measured at 2.1 K under Ar^+ ($\lambda = 514.5$ nm) excitation.

than in the n -type sample (as shown in Figs. 7 and 8). Additionally, for the n -type crystal (Fig. 7) there is a local maximum of Yb^{3+} PL enhancement at about 80 mW microwave power followed by a sharp increase for still higher powers. For the bulk sample (Fig. 9), the total increase of luminescence at the maximum value of the microwave field is by far the most pronounced and amounts to about 5%.

V. DISCUSSION

The Yb PL is excited upon laser illumination of the crystal. Figures 1–3 depict PL spectra as obtained for the different materials used in the current study. Regardless of the actual sample preparation method, the Yb^{3+} luminescence appears remarkably identical being thus indicative that the same centers are created in each case.¹⁸ Zeeman analysis of the Yb-related characteristic 1240 meV band, had shown that it is arising from intra- $4f$ -shell transitions of an Yb^{3+} ($4f^{13}$) center of cubic symmetry, presumably an Yb ion occupying a substitutional cation site in the InP lattice.¹⁹ The intensity of PL for the p -type crystal apparently is much lower in comparison with the n -type MOCVD-grown sample. This is most probably due to lower effective bulk lifetime of free carriers and to a large surface band bending as proposed by Rosenwaks *et al.*²⁰

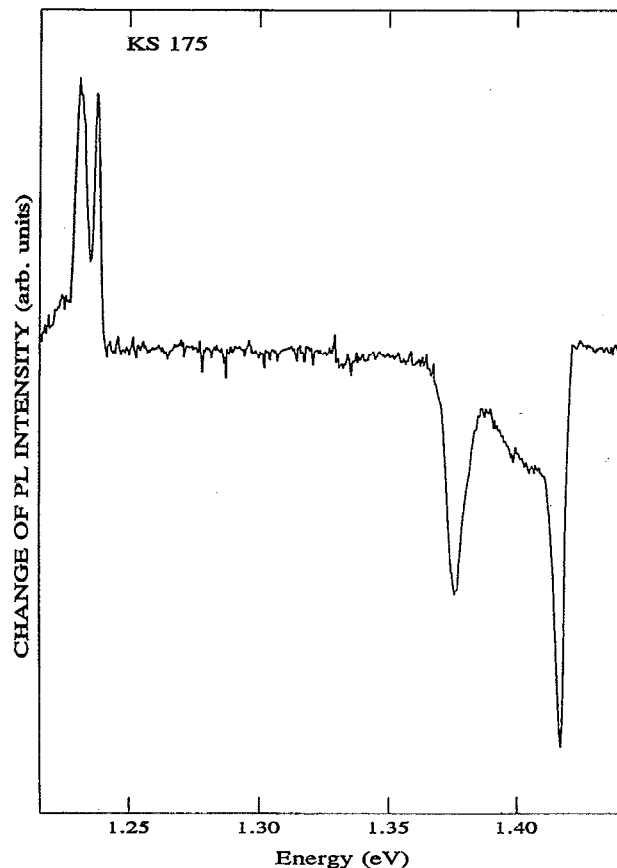


FIG. 4. Spectral dependence of the impact ionization of n -type InP:Yb crystal (KS 175) at 2.1 K using 50 mW of constant laser excitation power. The PL signal was detected in phase with the applied microwave power of 200 mW, on-off modulated at 730 Hz.

The application of a microwave field increases the temperature of the free carriers, enabling them to impact-ionize shallow localized states. In the crystals studied here, upon exposure to the microwave power, free carriers reach sufficient energies to impact ionize levels related to band edge emissions. Consequently, the intensity of these PL bands decreases for higher microwave power. The decrease of these bands is accompanied by a parallel enhancement of the Yb^{3+} luminescence. As mentioned previously, this effect can easily be understood as the carriers participating in the band edge transitions become available for the recombination processes involving deeper centers. Examining this part of the microwave power dependence one can immediately reject the possibility of a DAP \rightarrow Yb energy transfer being the dominant channel for Yb^{3+} PL excitation, for both n - and p -type crystals. Such a proposition had been put forward by Kasatkin and Savel'ev.²¹ The experimental data show that microwave-induced blocking of the DAP recombination channel is accompanied by an enhancement of the Yb^{3+} luminescence; a simultaneous decrease should have occurred if one process would follow from the other.

Closer examination of the ODMII spectral dependence depicted in Fig. 5 reveals that under the influence of the microwave field a new spectral component is observed at

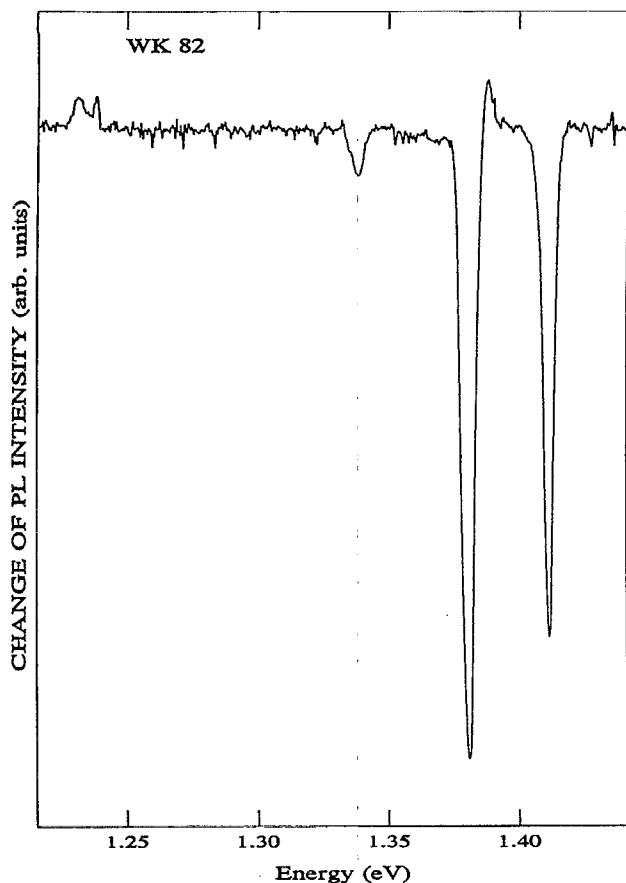


FIG. 5. Spectral dependence of the impact ionization of *p*-type InP:Yb crystal (WK 82) at 2.1 K using 50 mW of constant laser excitation power. The PL signal was detected in phase with the applied microwave power of 200 mW, on-off modulated at 730 Hz.

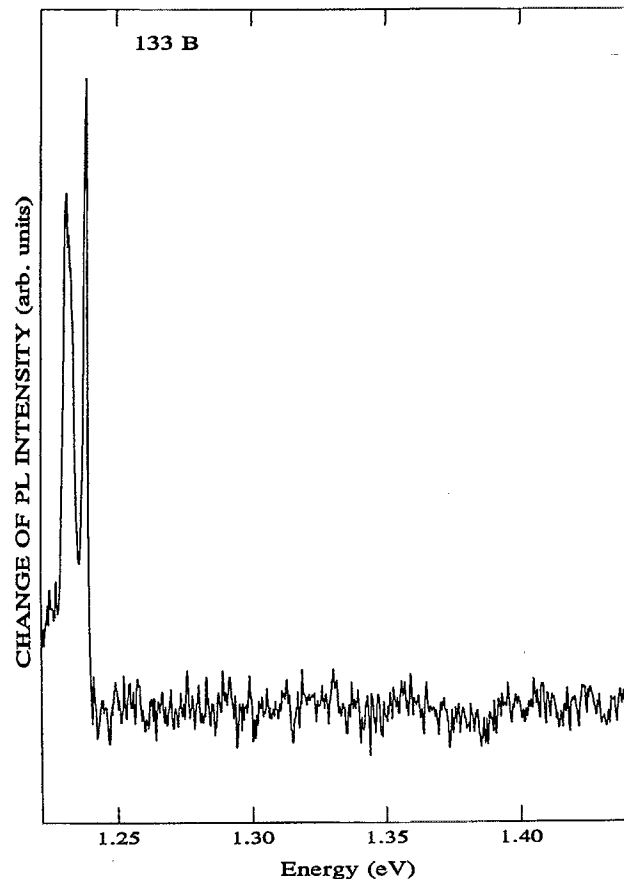


FIG. 6. Spectral dependence of the impact ionization of high-pressure gradient freeze synthesis-grown InP:Yb crystal (133 B) at 2.1 K using 50 mW of constant laser excitation power. The PL signal was detected in phase with the applied microwave power of 200 mW, on-off modulated at 730 Hz.

1388 meV. It can be identified as the free-to-bound transition, overlapping with the DAP line and therefore not resolved in the original PL spectrum. The energy difference of 7 meV, as mentioned in experimental results, between the FB and DAP peaks corresponds very well with the value of the donor level in InP of 7.3 meV.²² This example illustrates how the impact ionization technique can reveal details of a spectrum in a different way, and sometimes it enhances the experimental resolution of PL spectroscopy.

It can also be noticed that the threshold microwave power values for impact ionization are evidently larger for the *p*-type LPE sample than for the *n*-type MOCVD-grown crystal (Figs. 7 and 8). This can most probably be attributed to the aforementioned effects of shorter carrier life time and larger surface band bending in *p*-type material. As a result, the ODMII results for the *p*-type crystal resemble those obtained for *n*-type crystal in the low microwave power region.

The excitation mechanism of the Yb 4*f*-shell luminescence is a matter of considerable debate. The possibility of a direct trapping of an electron by an Yb³⁺ ion has been excluded on the basis of electron paramagnetic measurements (EPR) which have shown that the Yb²⁺ charge state related to such a process is not localized within the band gap of InP.²³ The EPR spectrum as measured for the bulk sample in

the *K* microwave band at 23 GHz is given in Fig. 10. The spectrum shows characteristic hyperfine structure of nine components due to the natural abundance of three different isotopes of ytterbium with nuclear spins of $I=0$, $I=\frac{1}{2}$, and $I=\frac{5}{2}$.²⁴ The observed EPR signal of Yb³⁺ does not exhibit any photosensitivity to white light illumination, thus confirming that the Yb atom has only one charge state in the band gap of the InP crystal. On the other hand, in a combination of DLTS (deep level transient spectroscopy) and SIMS (secondary ion mass spectroscopy) measurements, Whitney *et al.*²⁵ identified a Yb impurity-related acceptor-like trap at $E_{CB}-30$ meV. Also, Takahei *et al.*²⁶ could explain the PLE (photoluminescence excitation) and time-resolved data assuming that the Yb forms an electron trap. When considered together, all this information points toward a process in which the impact-ionized electrons could be retrapped by Yb³⁺ centers and transform them to some intermediate state of relatively shallow character, without a significant influence on the 3+ charge state of the core.^{23,25-27}

The trapping of an electron by a local potential opens the possibility for the formation of an Yb³⁺-bound exciton system, in analogy to the situation for isoelectronic impurities as outlined in the introductory part of the article. The secondary particle, in this case a hole, could become subsequently

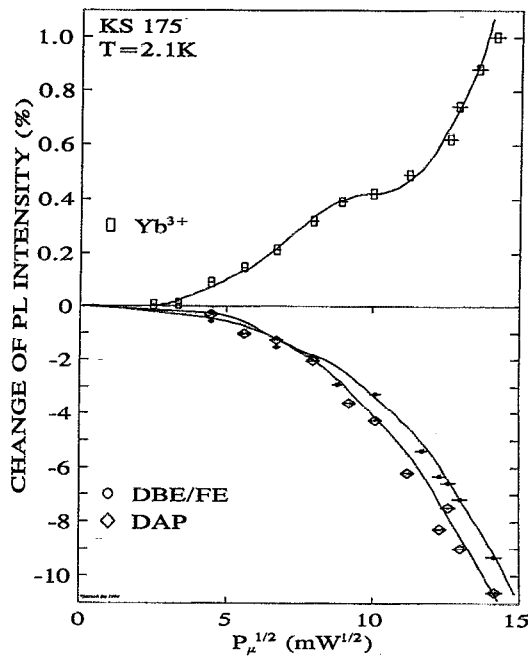


FIG. 7. Relative changes of PL intensity (%) vs the square root of applied microwave power chopped at 730 Hz for FE/DBE and DAP recombinations, and Yb^{3+} intra-4*f*-shell emission for the *n*-type InP:Yb crystal (KS 175).

bound by the long-range Coulomb potential of an electron captured at the local-field electron trap. The PL of Yb^{3+} would then be excited due to nonradiative recombination of such a BE state (impurity Auger recombination). The exist-

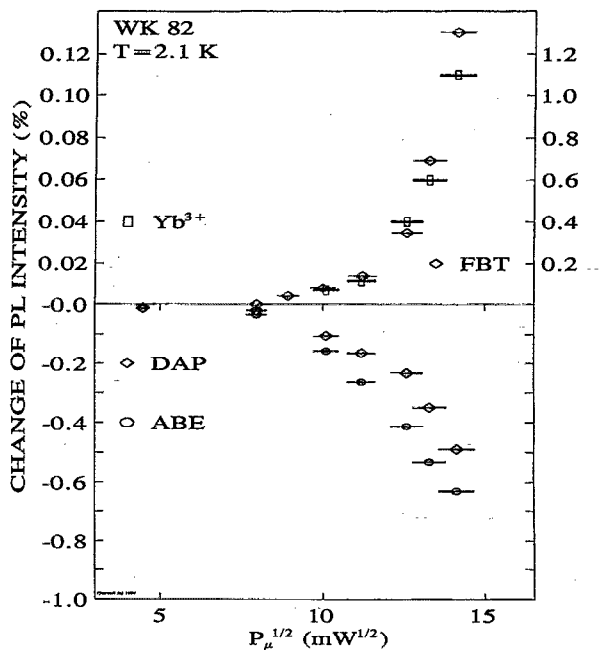


FIG. 8. Relative changes of PL intensity (%) vs the square root of applied microwave power chopped at 730 Hz for FB transition, ABE and DAP recombinations, and Yb^{3+} intra-4*f*-shell emission for the *p*-type InP:Yb crystal (WK 82).

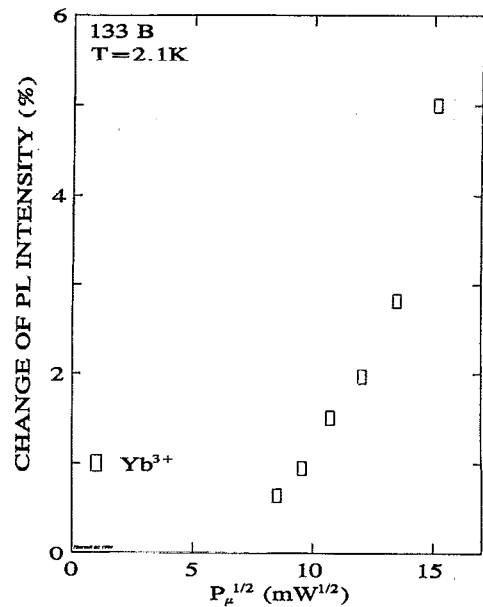


FIG. 9. Relative changes of PL intensity (%) vs the square root of applied microwave power chopped at 730 Hz for Yb^{3+} intra-4*f*-shell emission of the high-pressure gradient freeze synthesis-grown InP:Yb crystal (133 B).

ence of an Yb^{3+} BE system intermediating the core excitation has been postulated before.²⁷ Since the binding of one component of such an exciton is shallow, one should expect to observe its ionization in the impact ionization experiment as a decrease of Yb-related PL for higher values of microwave power. This has not been seen in the previously reported measurements,²⁸ which were done on the MOCVD sample, where only some saturation-like behavior of the Yb band could be concluded.

For the MOCVD-grown *n*-type sample studied here the situation is different. For higher microwave power the impact ionization of DAP and DBE follows the same behavior pattern as observed before,²⁸ but the change of Yb^{3+} luminescence exhibits saturation, in some experimental results

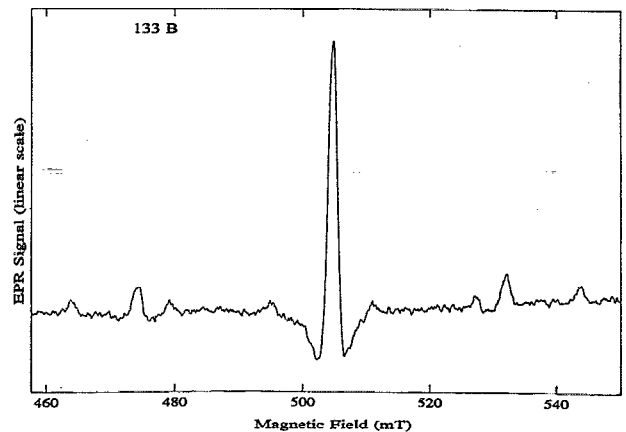


FIG. 10. Electron spin resonance spectrum of InP:Yb at 23.271224 GHz, and at temperature 4.2 K.

observed even as a local maximum, at about 80 mW. Taking into account that impact ionization (dissociation) of Yb^{3+} core states is not expected in InP, such an effect must be due to impact ionization of the relatively shallow state intermediating Yb^{3+} excitation, i.e., related to the mechanism of exciton binding by isoelectronic Yb^{3+} centers. The fact that the excitation mechanism is subject to impact ionization shows that at least one of the carriers forming a BE system is shallow. At the same time, since the effect takes place only for microwave power values exceeding those necessary for impact ionization of shallow donor states, the exciton bound to Yb^{3+} is concluded to consist of a deeply bound electron (≈ 30 meV) and a shallow bound hole ≤ 9 meV; in view of a larger value of its effective mass the impact ionization of the hole is expected to occur only for a somewhat higher value of the microwave field. This character of the Yb^{3+} BE system, as derived here from the impact ionization experimental data, sometimes is referred to as a pseudoacceptor and it is fully consistent with the DLTS measurements indicating an electron trap level being formed by the Yb impurity.

Therefore, the microwave power dependence for the n -type MOCVD sample, as depicted in Fig. 7, can now be explained. At relatively low power the shallow donor levels are ionized and the related recombination channels are becoming less effective; as a result the luminescence due to band edge excitons and DAP recombinations is reduced. At the same time the impact-ionized carriers become available for deeper recombinations; this leads to some increase of the Yb PL band. For higher values of microwave power the photoexcited carriers become energetic enough to impact ionize the shallow bound hole of the Yb^{3+} BE state intermediating the $4f$ core excitation; as a result further increase of Yb^{3+} PL is blocked. Though impact ionization of the effective-mass extended state cannot be very efficient, as it must compete with the simultaneous recapture process, it could lead to a decrease of Yb^{3+} PL at still higher microwave power levels. As can be concluded from Fig. 7, this is not the case; following a brief saturation/maximum at ≈ 80 mW the intensity of the Yb^{3+} band increases rapidly with the microwave power for higher values. Moreover, the total intensity of all the PL bands emitted by the sample exposed to the maximum value of the microwave field is stronger (by approximately 1%) than that measured in the absence of microwaves. One is then bound to conclude that a different and a much more important mechanism of increasing the PL mechanism is now competing with the dissociation of the Yb^{3+} BE. As a result a net increase of the PL intensity is observed.

To explain the high power part of experimental data one has to recall that the intra- $4f$ -shell transition, responsible for the studied Yb PL band, is parity forbidden. As a result the decay lifetime of the excited state is expected to be of an order of milliseconds, as indeed has been observed for the rare-earth ions embedded in insulating hosts.²⁹ In contrast to that the reported decay lifetime of Yb^{3+} PL in InP (semiconducting host) is two orders of magnitude smaller,³⁰ being thus indicative of an efficient nonradiative recombination channel competing with the radiative decay.^{27,30,31} The total increase of the luminescence intensity, as observed in the current study, is then a direct evidence that, on one hand,

such a nonradiative recombination channel indeed exists, and, on the other, that it can be effectively blocked by the microwave field.

Takahei *et al.*²⁶ proposed that, in n -type materials, the nonradiative decay is accomplished by a two-center Auger-type process involving Yb^{3+} in its excited state and an occupied shallow donor leading to ionization of this donor with its electron being excited high into the conduction band. Taguchi and Takahei¹⁸ proposed a similar mechanism for p -type crystals involving an occupied acceptor instead of a donor. An alternative mechanism involving energy transfer to a conduction-band electron has also been put forward. Finally, it has been suggested that, similarly to the ground state, also Yb^{3+} in the excited state forms an electron trap,²⁶ an electron localized at such a trap could then participate in an Auger process leading to a very effective nonradiative de-excitation of $(\text{Yb}^{3+})^*$.

Data obtained in this study and presented Fig. 7 give the indication of the mechanism where, upon an increase of the microwave power, impact ionization of a carrier participating in the nonradiative Auger process occurs. This effectively blocks the nonradiative recombination channel. Consequently, radiative recombination of Yb^{3+} ions is strongly enhanced overcoming the earlier mentioned opposite effect of dissociation of Yb^{3+} BE.²⁸ The current impact ionization spectroscopy data provide further insight into that process. First, the energy transfer to the conduction electrons in the Auger process can be excluded; application of microwave power increases the concentration of free electrons which should then lead to quenching rather than enhancement of the luminescence intensity. Also, the participation of the bound donor electrons in the nonradiative recombination can be ruled out since the ionization of shallow donor levels does not coincide with the increase of Yb^{3+} PL. We are, therefore, left with the last possibility, namely that similarly to the electron trap observed for Yb impurity in the ground state also Yb in its excited state can trap an electron. Such an electron, being localized at the Yb atom itself, can then intermediate a very effective Auger-type mechanism of nonradiative recombination. In view of the local character of the binding potential, the impact ionization of such a particle can be effective due to the small recapture probability. The actual ionization energy of the excited Yb electron trap Yb^* AE should then scale approximately with the position of the relevant Yb state and can be estimated as 10–20 meV below the bottom of the conduction band.

Even more convincing evidence of the nonradiative Auger recombination channel which can be blocked by impact ionization of the participating carrier can be found in Fig. 9, where the microwave power dependence of the impact ionization signal for the n -type bulk sample is shown. As can be seen, the Yb^{3+} PL can be enhanced by up to 5% while practically no other bands can be found in the PL spectrum of this material.

VI. CONCLUSIONS

The electron trap level introduced in InP by ytterbium doping has been shown to play a crucial role in both excitation as well as in de-excitation mechanisms of the Yb^{3+} ion.

The possibility of a DAP recombination energy transfer to Yb^{3+} core is excluded on the basis of direct experimental evidence. The excitation of the characteristic Yb PL is shown to be intermediated by the formation of the Yb^{3+} BE system. Trapping of an electron is also found to be responsible for the nonradiative recombination channel of the excited Yb^{3+} ion. It is argued that the nonradiative recombination proceeds via an Auger process which involves energy transfer to an electron localized at the excited Yb center itself. It is further shown that the Yb^{3+} PL intensity can be effectively enhanced by the microwave-induced impact ionization of the trapped electron which blocks the nonradiative recombination channel. The current findings constitute then a considerable advance on the way to optimize the excitation and the de-excitation mechanisms of RE ions in semiconductor matrices.

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- ¹P. S. Whitney, K. Uwai, H. Nakagome, and K. Takahei, *Electron. Lett.* **24**, 740 (1988).
- ²A. G. Dmitriev, L. F. Zakharenkov, V. A. Kasatkin, V. F. Masterov, and B. E. Samorukov, *Fiz. Tekh. Poluprovodn.* **17**, 1879 (1983) [*Sov. Phys. Semicond.* **17**, 1201 (1983)].
- ³D. L. Smith, D. S. Pan, and T. C. McGill, *Phys. Rev. B* **12**, 4360 (1975).
- ⁴A. A. Lipnik, *Fiz. Tverd. Tela* **3**, 2322 (1961) [*Sov. Phys.-Solid State* **3**, 1683 (1962)].
- ⁵V. N. Abakumov, V. I. Perel, and I. N. Yassievich, *Modern Problems in Condensed Matter Sciences* (North-Holland, Amsterdam, 1991), Vol. 33.
- ⁶J. J. Hopfield, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Lett.* **17**, 312 (1966).
- ⁷B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer, Berlin, 1984), Vol. XII, p. 388.
- ⁸W. Körber, J. Weber, A. Hangleiter, K. W. Benz, H. Ennen, and H. D. Müller, *J. Cryst. Growth* **79**, 741 (1986).
- ⁹P. J. Dean, J. R. Haynes, and W. F. Flood, *Phys. Rev.* **161**, 711 (1967).
- ¹⁰J. Weber, A. Molassioti, M. Moser, A. Stäpor, F. Scholz, G. Hörcher, A. Forchel, A. Hammel, G. Laube, and J. Weidlein, *Appl. Phys. Lett.* **53**, 2525 (1988).
- ¹¹G. Laube, U. Kohler, J. Weidlein, F. Scholz, K. Streubel, R. J. Dieter, N. Karl, and M. Gerdon, *J. Cryst. Growth* **93**, 45 (1988).
- ¹²R. Coquille, Y. Toudic, M. Gauneau, G. Grandpierre, and J. C. Paris, *J. Cryst. Growth* **64**, 23 (1983).
- ¹³J. U. Fischbach, G. Benz, N. Stath, M. H. Pilkuhn, and K. W. Benz, *Solid State Commun.* **11**, 721 (1972).
- ¹⁴J. U. Fischbach, G. Benz, N. Stath, and M. H. Pilkuhn, *Solid State Commun.* **11**, 725 (1972).
- ¹⁵L. F. Zakharenkov, V. A. Kasatkin, F. P. Kesamanly, B. E. Samorukov, and M. A. Sokolova, *Sov. Phys. Semicond.* **15**, 946 (1981).
- ¹⁶H. Weman, M. Godlewski, and B. Monemar, *Phys. Rev. B* **38**, 12525 (1988).
- ¹⁷M. Godlewski, H. Weman, F. P. Wang, B. Monemar, W. M. Chen, and Q. X. Zhao, *Mater. Res. Soc.* **104**, 117 (1988).
- ¹⁸A. Taguchi and K. Takahei, *Mater. Sci. Forum* **117-118**, 303 (1993).
- ¹⁹G. Aszodi, J. Weber, Ch. Uihlein, L. Pulin, H. Ennen, U. Kaufmann, J. Schneider, and J. Windscheif, *Phys. Rev. B* **31**, 7767 (1985).
- ²⁰Y. Rosenwaks, Y. Shapira, and D. Huppert, *Phys. Rev. B* **44**, 13097 (1991).
- ²¹V. A. Kasatkin and V. P. Savel'ev, *Fiz. Tekh. Poluprovodn.* **18**, 1634 (1984) [*Sov. Phys. Semicond.* **18**, 1022 (1984)].
- ²²P. E. Simmonds, J. M. Chamberlain, R. A. Hoult, R. A. Stradling, and C. C. Bradley, *J. Phys. C* **7**, 4164 (1974).
- ²³B. Lambert, Y. Toudic, G. Grandpierre, A. Rupert, and A. Le Corre, *Electron. Lett.* **24**, 1446 (1988).
- ²⁴V. F. Masterov, V. V. Romanov, and K. F. Shtel'makh, *Fiz. Tverd. Tela* **25**, 1435 (1983) [*Sov. Phys. Solid State* **25**, 824 (1983)].
- ²⁵P. S. Whitney, K. Uwai, H. Nakagome, and K. Takahei, *Appl. Phys. Lett.* **53**, 2074 (1988).
- ²⁶K. Takahei, A. Taguchi, H. Nakagome, K. Uwai, and P. S. Whitney, *J. Appl. Phys.* **66**, 4941 (1989).
- ²⁷K. Thonke, K. Pressel, G. Bohnert, A. Stäpor, J. Weber, M. Moser, A. Molassioti, A. Hangleiter, and F. Scholz, *Semicond. Sci. Technol.* **5**, 1124 (1990).
- ²⁸B. J. Heijmink Liesert, M. Godlewski, A. Stäpor, T. Gregorkiewicz, C. A. J. Ammerlaan, J. Weber, M. Moser, and F. Scholz, *Appl. Phys. Lett.* **58**, 2237 (1991).
- ²⁹B. Di Bartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), p. 521.
- ³⁰P. B. Klein, *Solid State Commun.* **65**, 1097 (1988).
- ³¹W. Körber and A. Hangleiter, *Appl. Phys. Lett.* **52**, 114 (1988).