EXCITATION AND DE-EXCITATION MECHANISMS OF RARE-EARTH IONS IN III-V COMPOUNDS: OPTICALLY DETECTED MICROWAVE-INDUCED IMPACT IONIZATION OF Yb DOPANT IN InP

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ABSTRACT

The excitation mechanisms of rare-earth dopants in III-V semiconductors are being reviewed. The discussion is focused on ytterbium-doped InP crystals for which a particularly large amount of experimental data has been gathered. Here, the results obtained recently by optically detected microwave-induced impact ionization are being examined in detail. On the basis of the experimental findings it is argued that the intrashell luminescence is excited by an intermediate state involving binding of an exciton. Direct evidence for the existence of such a state, of pseudoacceptor type, will be given. The nonradiative recombination channel responsible for the fast decay of Yb luminescence will also be discussed and, for the first time, evidence for an Auger process will be presented. It will also be shown that the nonradiative channel may be effectively blocked by impact ionization of a participating carrier.

INTRODUCTION

Over the past decades, many investigations have been devoted to the optical properties of rare-earth (RE) ions (lanthanides) in ionic solids such as wide-gap sulfides (ZnS, CaS) and garnet oxides (Y_2O_2S, $Y_3Al_5O_{12}$). In these hosts the $4f$ ions exhibit strong visible and near-infrared luminescence. They find applications in laser materials such as YAG : Nd^{3+}. Rare-earth-activated sulfides have the advantage of obtaining multicolor devices due to internal $4f$-shell transitions of RE^{3+} ions. In recent years, also RE-doped III-V semiconductors have been intensively studied because of their possible applications in opto-electronic devices. The characteristic feature of the electronic structure of RE elements in solids is the presence of incompletely filled $4f$-core orbitals, surrounded by closed $5s^2$ and $5p^6$ shells. The $4f$ electrons are thus effectively screened and are only weakly affected by their crystalline environment. As a consequence, rare-earth ions in solids may show sharp luminescence spectra arising from atomic-like, intra-$4f$-shell transitions. Semiconductor lasers based on these materials have a well defined lasing wavelength which, due to rare-earth-related internal transitions, is relatively insensitive to ambient temperature and almost independent of the III-V host material.

ELECTRICAL AND OPTICAL PROPERTIES OF Yb IN InP

The most extensively studied rare-earth-doped III-V semiconductor is ytterbium-doped InP (InP:Yb). The electron configuration of the free Yb atom is $[Xe]4f^{14}6s^2$. The

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core configuration of the 3+ charge state, being the stable one (in InP) and responsible for the luminescence, is unclear. Besides the two $6s^2$ electrons participating in bonding, a third electron from the $4f$ shell is involved. Two possible configurations arise: either one electron is missing directly from the $4f$ shell ($4f^{13}$ configuration), or the $4f$ orbitals hybridize with those of the host, the bound hole being partly localized on the $4f$ core and partly on the bonds (linear combination of Yb^{2+} and Yb^{3+} configurations) [1].

Also, despite the large number of studies, a controversy exists on the electrical and optical behavior of ytterbium in InP. Körber *et al.* [2] observed *p*-type conductivity in InP:Yb grown by liquid phase epitaxy (LPE), with Yb concentrations exceeding the residual donor concentration. From temperature dependent Hall-effect measurements they found an acceptor level located at about 45 meV above the valence band (VB), which they ascribed to the Yb^{3+}/Yb^{2+} transition. Indeed, cluster calculations by Hemstreet [1] predicted a single acceptor state as the Yb ground state with a hole binding energy of approximately 0.26 eV.

In contrast to this, Yb-doped InP grown by metalorganic chemical vapor deposition (MOCVD) showed *n*-type conductivity [3, 4], even for Yb concentrations much higher than those obtained in LPE-grown material. Synthesized InP:Yb epilayers were also found to be *n* type [5]. Whitney *et al.* [3], using Hall-effect and deep-level transient spectroscopy (DLTS) data, proposed that ytterbium introduces an acceptor-like level at about 30 meV below the conduction band (CB). These authors suggested that this level would be related to the Yb^{3+}/Yb^{2+} acceptor level. However, electron paramagnetic resonance (EPR) measurements [6] provide some evidence that it is not possible to locate the Yb^{3+}/Yb^{2+} level in the InP band gap since both neutral shallow donors (at $\approx E_{CB} - 7$ meV) and Yb in its 3+ charge state could be detected simultaneously, even in *n*-type samples. Although InP crystals studied in this case were not very homogeneous and therefore the EPR results have to be treated with some caution, the observed *p*-type conductivity of LPE Yb-doped InP is unlikely to be due to Yb ions acting as acceptor impurities in InP, as proposed by Körber *et al.* [2]. It is more likely to result from unintentional co-doping with shallow acceptors (Zn, Mg, Ca), present as residual contaminants in the Yb metallic source [7].

It seems now to be rather generally accepted that Yb introduces an acceptor-like electron trap AE (pseudoacceptor) which can capture an electron at a level of about 30 meV below the conduction band and a hole trap DH at E_{VB} + 30-40 meV. The capture of an additional carrier does not lead to a change of the ytterbium charge state which remains Yb^{3+} (in ionic notation) [3, 5, 8, 9]. To explain this pseudoacceptor (or donor) behavior it was proposed that Yb in InP acts as an isoelectronic trap with a short-range attractive potential either due to a lattice distortion around the Yb site or to a difference in electron affinities of Yb and In [3, 9].

Yb-related photoluminescence (PL) is well known to occur near 1.0 μm, being due to intra-$4f$-shell transitions of trivalent $Yb^{3+}(4f^{13})$ ions substituting on In sites. These transitions are forbidden as electric dipole transitions. They become possible when the crystal field as experienced by the RE ion, lacks a center of symmetry. As a result, the wavefunction is of mixed parity and the PL intensity is determined by the small admixture of opposite parity.

Most likely due to a wide spread of materials used for PL studies, the dominant Yb photoluminescence excitation (PLE) mechanism was until very recently not understood. Several mechanisms were proposed to account for all features of Yb PL and PLE spectra, especially with respect to their temperature dependencies.

(a) Kasatkin and co-workers [10, 11] proposed that in their melt-grown crystals Yb^{3+} PL is induced via an energy transfer from donor–acceptor pair (DAP) recombination to Yb ions, leading to Yb^{3+} core states excitation. (The excess energy is transferred in

an Auger-type process to an additionally bound particle residing on a neighboring acceptor or donor.) In fact, some evidence for such an energy transfer was found for heavily doped samples [9].

(b) Körber and Hangleiter [12], assuming that Yb behaves as a shallow acceptor, concluded that Yb 4*f*-shell excitation proceeds by direct capture of free excitons or by impact excitation by hot carriers.

(c) Takahei *et al.* [9] proposed an Yb-related DAP → Yb energy transfer mechanism, in which the Yb itself, acting as an acceptor-like electron trap, donates an electron which then interacts with a hole in the valence band or at neutral acceptors. This mechanism is expected to be effective for samples in which the average distance between Yb traps and neutral acceptors is relatively small. Indeed, some evidence for this could be found in highly Yb-doped samples [9] and also in *p*-type LPE samples [12] with high acceptor concentration.

(d) Thonke *et al.* [8] could explain the majority of their data by assuming that Yb acts as an isoelectronic trap which binds an exciton. Yb intra-4*f*-shell emission is then induced via an impurity (defect) Auger recombination [13] by an energy transfer from this bound exciton (BE) excited state to Yb 4*f*-core orbitals resulting in nonradiative BE recombination and 4*f*-shell excitation. Such a PLE process has been previously proven to be very efficient for rare-earth intrashell emissions in ZnS [14, 15].

(e) Finally, Lhomer *et al.* [16] suggested that upon laser excitation an Yb BE is formed with both its constituents being captured at relatively deep trapping levels. On the basis of temperature dependent Hall-effect measurements the appropriate energies were determined as E_{CB} - 30 meV and E_{VB} + 40 meV for the electron and hole trap, respectively. The BE would then decay nonradiatively and excite the Yb ion generating intrashell PL.

Exciton binding is expected to occur for neutral RE ions (and their complexes) which have their 3+/2+ ionization level within the forbidden gap [13, 17], or which do not change their charge state from 3+ to 2+ but have one of their excited states in the energy gap [13]. The latter is the case for Yb in InP. The RE ion in its 3+ charge state is an isovalent (isoelectronic) dopant when substituting for the cation in the III-V compound. Such centers may introduce a short-range attractive potential for one type of free carriers. Once the first carrier is localized, the second one is trapped by the long-range attractive Coulomb potential of the first carrier, thus forming a RE-bound exciton.

Although in view of the available information the excitation mechanism intermediated by BE appears to be the most probable one, it has never actually been confirmed by experiment. Sofar the most convincing evidence for the participation of excitons in inducing Yb PL comes from Thonke *et al.* [8]. In this study it has been observed that the characteristic 1μm PL of ytterbium could be excited with subband energy corresponding to that of free excitons in InP while, at the same time, no photocurrent could be detected indicating no generation of free carriers. Here we present a study of the Yb excitation mechanism by means of microwave-induced impact ionization spectroscopy. We will show that although the excitation process can proceed in a variety of ways depending on the impurities present and the actual concentrations ratio between ytterbium ions and shallow dopants, the dominant PLE mechanism at low temperatures is the one in which the Yb BE state is the intermediating one. We will also show that the DAP → Yb energy transfer - mechanism (a) is inefficient and can be rejected.

PRELIMINARIES: MICROWAVE-INDUCED IMPACT IONIZATION

The microwave-induced impact ionization technique is in principle based on the phenomenon of cyclotron resonance. If a semiconductor is placed in an external magnetic field, free carriers travel along helical orbits about the axis of the magnetic field $\boldsymbol{B}$. The angular rotation frequency is:

$$\omega_c = \pm \frac{e\,B}{m^*}\,, \tag{1}$$

where m^* is the electron, light-hole, or heavy-hole effective mass. Resonant absorption from a rf electric field perpendicular to the static magnetic field occurs when the radiating frequency is equal to the cyclotron frequency $\nu_c = \omega_c/2\pi$. Electrons and holes spiralize in opposite sense, which is reflected by the $\pm$ sign in Eqn. (1). Since its first observation in semiconductors in 1953, the technique of cyclotron resonance (CR) has been successfully applied to probe conduction or valence band parameters for a given semiconductor near the band edges [18]. In order to observe cyclotron resonance, the following condition has to be fulfilled:

$$\omega_c\,\tau \geq 1\,. \tag{2}$$

Here, τ is the average time between collisions of carriers with lattice imperfections such as phonons and impurity atoms. Eqn. (2) states that CR will occur if the electron (or hole) can complete one or more revolutions between collisions. For the cyclotron frequency to be larger than the collision frequency, it is generally necessary to work with high-purity samples at liquid-helium temperature to reduce both impurity and phonon scattering as much as possible. Application of higher radiating frequencies relaxes these requirements. Under the conditions of pure samples and low temperatures the number of free carriers available in thermal equilibrium to participate in CR may be so small that, e.g., photoexcitation is necessary to create them. Indeed, it is possible to detect CR on both types of carriers under optical excitation using above-gap light.

If $\omega_c\tau < 1$, free carriers will be nonresonantly heated by the electric part of the microwave field. At low temperatures ($k_B T \ll E_x$, with E_x the exciton binding energy) and in the absence of an external electric field, few free carriers are energetic enough to dissociate (ionize) excitons by collisions (impact): in this situation of thermal equilibrium each exciton ionization process is balanced by a corresponding formation process. The microwave electric field accelerates (photoexcited) free carriers, thus increasing the number of carriers which have an energy sufficient to impact ionize excitons. The detailed balance between exciton ionization and formation is changed, the impact-ionization rate being significantly increased by the electric-field-induced carrier heating. A critical microwave field exists [19] at which the impact-ionization rate starts to predominate both exciton recombination and ionization by phonon absorption, which is the dominant ionization process in thermal equilibrium [20].

At microwave electric fields larger than the critical value, the exciton concentration sharply drops with a simultaneous avalanche increase in the free-carrier density. This can be observed optically by recording the change of exciton-related luminescence when the microwave power is increased. (The microwave power P_μ is related to the microwave electric field $\boldsymbol{E}$ via $P_\mu \propto E^2$.) By combining the application of microwave power with the PL technique, the different contributions from deep or shallow bound excitons (BE's) and free excitons (FE's) can be separated in the impact-ionization process. This makes optical detection of microwave-induced impact ionization (ODMII) a very powerful technique. It is quite similar to ODCR, in which also the influence of microwaves on PL is studied: ODCR monitors PL changes under cyclotron resonance, whereas ODMII records nonresonant changes, when the CR condition is not fulfilled. The characteristic feature of

ODMII is the existence of a critical value (threshold) of the microwave electric field and thus the microwave power, above which PL intensity changes are observed. This critical value in turn depends on the type of exciton and on the sample purity.

By varying the applied electric field, the relative concentration of free carriers and excitons will be changed, as well as the free-carrier lifetime and the recombination probabilities of the different emissions. Impact ionization of FE's and BE's (which have fast Auger recombination rates) blocks an efficient nonradiative recombination channel and drastically increases the carrier lifetime. This may promote recombination via deeper centers such as isoelectronic bound excitons (IBE's), donor–acceptor pairs (DAP's), and also free-to-bound recombination. It is even possible to enhance deeper emissions which are not seen in the absence of an electric field. In the past the ODMII technique has been successfully applied to defect studies in silicon and GaAs. Weman *et al.* [21] reported the enhancement of a new broad emission band of unknown origin around 1 eV in *n*-type Si, which had never been observed before. For sufficiently high microwave powers the spectral dependence of their broad ODMR background signal showed an increase of both this new 1 eV band and IBE recombination lines together with a decrease of BE recombination at neutral phosphorus donors. Also, Wang *et al.* [22] reported that in high-purity epitaxial GaAs layers the shallow BE and DAP luminescence was quenched in the high-microwave-power case, while the FB emission was enhanced. These results are a clear fingerprint of the impact ionization mechanism: above a critical value of the microwave power shallower emissions are quenched, simultaneously enhancing deeper and/or less probable recombination channels. Moreover, they allow for direct verification which is the mechanism responsible for the common nonresonant background in ODMR studies. Impact ionization by "hot" (accelerated) free carriers affects shallow recombination channels and leads to large changes of relevant PL intensities. In the range of $\omega_c\tau < 1$, this results in damped cyclotron resonance of free carriers which is observed as the nonresonant background in an optically detected magnetic resonance spectrum.

EXPERIMENTALS

The samples used in this study were kindly provided by dr. F. Scholz of the Universität Stuttgart, Germany. They were grown by metalorganic chemical vapor deposition (MOCVD). In the MOCVD-growth process zone-refined trimethylindium – triethylphosphine (Me_3InPEt_3), phosphine, and tri(methyl-cyclopentadienyl)ytterbium ($Yb(MeCp)_3$) were used as the In, P, and Yb sources, respectively. More details on the growth process can be found elsewhere [4, 23]. The epitaxial InP:Yb layer was grown on a semi-insulating Fe-doped InP substrate; the layer thickness was 3 μm. The samples exhibited *n*-type conductivity with a carrier concentration of $n = 10^{15} - 10^{16}\,\mathrm{cm}^{-3}$ at 300 K. The total Yb concentration, as determined by secondary-ion mass spectroscopy (SIMS), was in the $10^{17} - 10^{19}\,\mathrm{cm}^{-3}$ range.

Experiments were performed at 2.1 K using a cw Ar^+-ion laser operating at 514.5 nm to excite the sample. The luminescence was dispersed by a high-resolution 1.5 m F/12 monochromator (Jobin-Yvon THR-1500) with a 600 grooves/mm grating blazed at 1.5 μm, and detected by a liquid-nitrogen-cooled Ge detector (North-Coast EO-817). Impact ionization measurements were performed at 35 GHz using a split-coil superconducting magnet (Oxford Instruments Spectromag 4). Samples were mounted in a cylindrical TE_{001} cavity with slits for optical access. Microwaves, supplied by a Gunn-oscillator, were on-off modulated with a *p-i-n* diode, typically at 730 Hz. Changes of total PL intensity were monitored setting the monochromator to zeroth order.

PHOTOLUMINESCENCE AND IMPACT IONIZATION RESULTS

Fig.1 presents PL spectra of two of the samples used in the present study. As can be seen both spectra are rather similar with approximately the same intensity of Yb PL. Both spectra differ considerably only in the band-edge luminescence. For sample #KS 185 - Fig.1(a) - this band consists of three components at at 1417.5 meV, 1387.5 meV, and 1344.6 meV, attributed to free exciton (FE)/donor-bound exciton (DBE) recombination, donor–acceptor pair (DAP) recombination and its LO phonon replica, respectively [24, 25, 26]. The total intensity of this sub-edge band exceeds the Yb PL. For the second sample #KS 175 - Fig.1(b) - the intensity of band-edge PL is very small and amounts only to ≈1% of the Yb PL. As can be seen in the insert of the figure the band consists of three peaks at 1419.3 meV, 1410.9 meV, and ≈1380 mev, which can be identified as FE, DBE, and DAP recombinations, respectively.

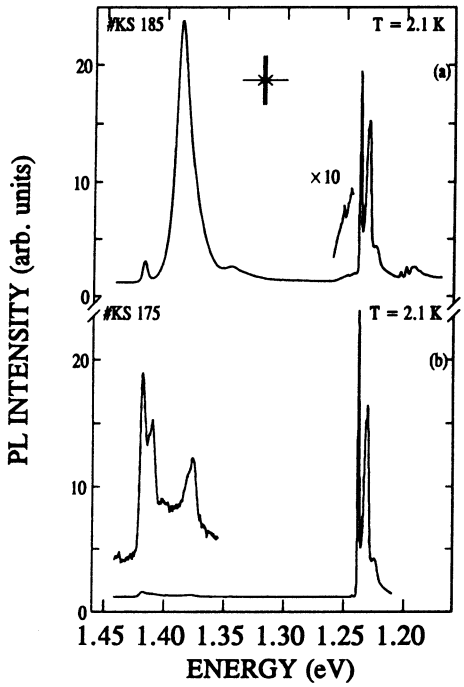

Figure 1: *Photoluminescence (PL) spectra of InP:Yb samples used in this study:* **(a)** *#KS 185 and* **(b)** *#KS 175. The spectra are recorded at 2.1 K under Ar^+(λ=514.5 nm)-excitation.*

For both samples a second group of lines is observed at 1248.6 meV, 1242.5 meV, 1238.1 meV, and 1230.7 meV. This characteristic luminescence was first reported by Zakharenkov *et al.* [27] and is ascribed to 4*f*-to-4*f*-shell transitions between the spin–orbit levels $^2F_{5/2}$ and $^2F_{7/2}$ of $Yb^{3+}(4f^{13})$ split by the crystalline electric field experienced by the Yb_{In}. Since, as discussed before, the 4*f* electrons are screened by the outer-lying closed $5s^25p^6$ shells, the crystal-field splitting of the $^2F_{5/2}$ and $^2F_{7/2}$ levels is rather small as compared to the spin–orbit splitting. Thus the identical spectrum is observed in all InP:Yb samples irrespective of the growth method: LPE, MOCVD, and ion implantation.

The introduction of a magnetic field B, by setting it to 0.5 T, causes no change of photoluminescence. The PL intensity can be influenced by a simultaneous introduction of microwave power. For sample #KS 185 this is illustrated in Fig.2; in this case a 5–6 %

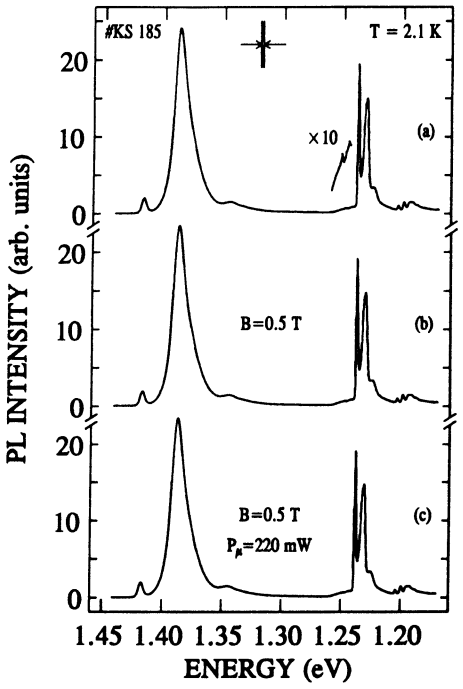

Figure 2: *Photoluminescence (PL) spectrum of InP:Yb sample #KS 185 measured at 2.1 K under Ar^+ (λ=514.5 nm)-excitation* (a) *without magnetic field B and microwave power P_μ,* (b) *with B=0.5 T and P_μ=0 mW, and* (c) *with B=0.5 T and P_μ=220 mW. The identification of particular PL lines is discussed in the text.*

decrease of the overall PL intensity can be noted. Careful analysis of the spectra reveals that the change of PL intensity is different for three different recombination transitions. Whereas the intensity of the FE, DBE and DAP PL is reduced, the Yb^{3+}-related PL intensity is slightly enhanced (by $\approx$1 % for both samples). This could be monitored more directly by recording the change of PL intensity while scanning through the luminescence. In this way we could also establish the influence of both P_μ and B on PL intensity. A characteristic example of the spectral dependence of impact ionization, as measured for sample #KS 175 with constant laser excitation and on-off modulated microwave power of 200 mW, is depicted in Fig.3. A relatively high microwave chopping frequency was used (730 Hz) in order to minimize the influence of the so-called bolometric effect on PL intensity; it has been observed before that lattice heating by hot carriers dominates the PL changes for low P_μ chopping frequencies [21]. At high chopping frequencies the dominant mechanism for the PL changes measured in phase with chopped microwaves may be due to impact ionization of excitons and shallow centers by free carriers heated nonresonantly by microwave power.

Relative changes of the PL intensities for B = 0.5 T and for different values of P_μ are shown in Figs.4(a) and 4(b) for samples #KS 185 and #KS 175, respectively. ODMII spectra were measured from the maximum power of 220 mW (0 dB attenuation) for #KS 185 and 200 mW for #KS 175 - down, in steps of 2 dB. Data shown in this figure are in fact consistent with the impact ionization mechanism of microwave-induced PL intensity changes. As expected for this mechanism, a threshold dependence on P_μ is observed [21, 28].

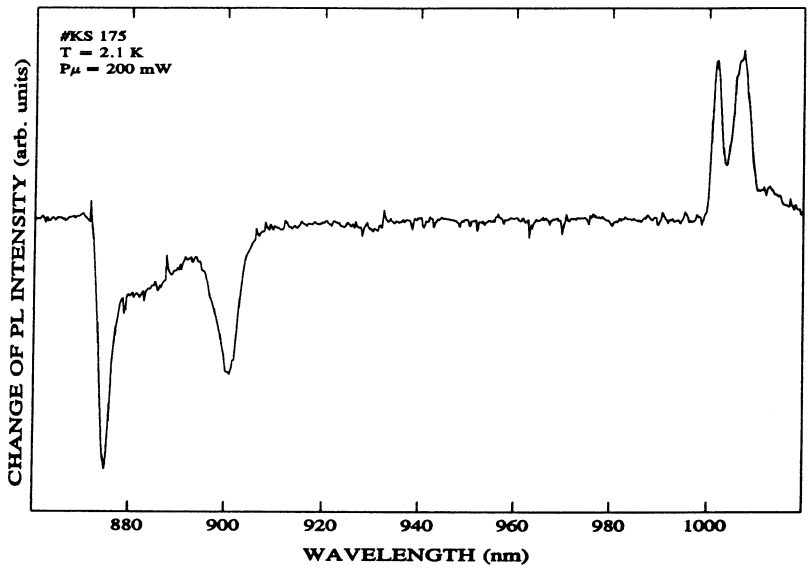

Figure 3: *Spectral dependence of impact ionization as measured for sample #KS 175 at 2.1 K and with B=0.5 T using 50 mW of constant laser excitation power. The PL signal was detected in phase with the applied microwave power of 200 mW, on-off modulated at 730 Hz.*

In view of absolute intensities, the actual threshold values for DBE and DAP transitions could only be determined for the #KS 185 sample; in this case they were found to be 2.2 mW and 5.5 mW, respectively. However, the general behavior of these two bands is similar for both samples. The only difference is that, while in #KS 185 both signals could be quenched by a few percent only, in #KS 175 the band-edge emission could be reduced by more than 50%. In contrast to this, the observed increase of the Yb^{3+} PL differs considerably between the two samples. For #KS 185 it starts to show some saturation for the maximum value of the microwave power; for #KS 175 ytterbium luminescence shows a clear local maximum at ≈80 mW followed by a sharp increase for still higher powers.

DISCUSSION

As discussed in the preliminary section the application of a microwave field increases the temperature of laser-excited free carriers. Upon the increase of microwave power, free carriers first reach energies sufficient for DBE impact ionization. As a result the DBE recombination is reduced. For still higher power – $P_\mu > 5.5$ mW for sample #KS 185 – the energy of carriers is large enough to impact ionize shallow donors in InP reducing also the efficiency of DAP recombination. Analyzing this part of the $I_{PL}(P_\mu)$ dependence we can immediately reject the possibility of a DAP → Yb energy transfer being the dominant channel for Yb^{3+} PLE in our samples, as proposed by Kasatkin and Savel'ev [10]. They used melt-grown crystals presumably containing a relatively high concentration of residual

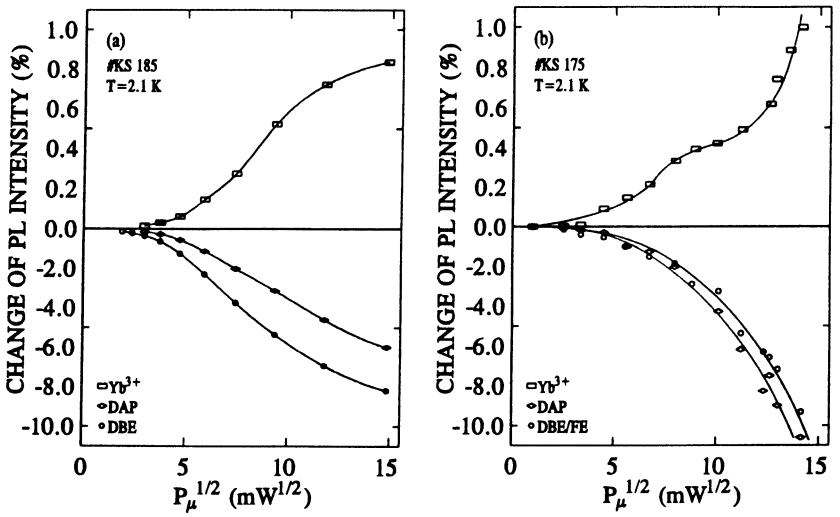

Figure 4: *Relative changes of PL intensity (%) versus the square root of applied microwave power chopped at 730 Hz for FE/DBE and DAP recombinations and Yb^{3+} intra-4f-shell emission for sample* (a) *#KS 185 and* (b) *#KS 175 (note an enlarged vertical scale for clarity). The experiment was performed at 2.1 K with B=0.5 T and constant Ar^+ laser excitation power of 50 mW. The experimental error margin has been indicated. The lines are drawn to guide the eye only.*

impurities. Once the DAP transition becomes less effective, Yb^{3+} PL is enhanced – see Fig.4 – being clearly inconsistent with a DAP → Yb PLE mechanism.

Retrapping of electrons impact ionized from shallow donors should enhance the recombination via a competing electron trap. Indeed, the Yb^{3+} PL starts to be enhanced at the same threshold value of P_μ which leads to DAP quenching, suggesting that electrons ionized from shallow donors are somehow retrapped by Yb^{3+} centres. At the same time electron trapping cannot proceed via the Yb^{2+} level, as suggested previously [29], since this level is not localized in the forbidden gap of InP [6]. Capture thus occurs without a simultaneous change of the ytterbium charge state, via an acceptor-like Yb trap state as discussed in Refs. [3], [6], [8], and [9]. Since it is very unlikely that, in our experiment, trapped electrons recombine with holes on acceptors giving rise to DAP-like transitions, we therefore conclude that upon electron capture, Yb^{3+} transforms to some intermediate state of relatively shallow character.

For higher P_μ the increase of the Yb^{3+} PL does not follow the decrease of the DBE and the DAP transitions. This is especially evident for sample #KS 175, Fig.4(b), where saturation of Yb PL intensity change, in some cases observed even as a local maximum, is found for $P_\mu \approx 80$ mW. Since impact ionization of Yb^{3+} core states is not expected in InP, such an effect must be due to impact ionization (dissociation) of the relatively shallow state intermediating Yb^{3+} excitation. Such an effect is fully consistent with a mechanism of exciton binding by isoelectronic Yb^{3+} centers. Yb^{3+} PL is then excited due to nonradiative recombination of such a BE state (impurity Auger recombination).

Although isoelectronic centres have charge neutrality with respect to the lattice, they can give rise to a short-range potential which creates a bound state for either an electron or hole [30]. The second particle is subsequently bound by the resulting long-range Coulomb potential. The carrier which is primarily bound by Yb can be either an electron [3, 8, 9] or a hole [8]. By combining DLTS and SIMS measurements, Whitney *et al.* [3] determined that the electrically identified acceptor-like electron trap at $\approx E_{CB} - 30$ meV is related to the Yb impurity. Also, Takahei *et al.* [9] could explain their Yb PLE and time-resolved PL data by assuming that Yb ions form electron trap states. From their data Thonke *et al.* [8] could hardly distinguish between the two complementary isoelectronic trap models, although some weak arguments in favor of the pseudodonor model, in which a hole is captured first in a local potential, were given. In either case, carrier capture does not necessarily lead to a change of the charge state of Yb itself; it means that the charge state of the complete cluster of an Yb atom with its phosphorus neighbors can be altered.

In our experiment the ordering of the onset values for impact ionization of FE/DBE and DAP recombinations agrees well with the ordering of DBE and shallow donors levels in InP, i.e. >4 meV and ≈7 meV, respectively. For a pseudodonor model of the Yb BE system the electron is captured in a long-range Coulomb field and its ionization energy is then expected to be close to the EMT value, which for InP is 7.31 meV [31]. Since our experimental data show that the saturation of Yb PL occurs for (much) higher powers than the threshold value for impact ionization of shallow donors we take this as an experimental support in favor of a pseudoacceptor model with an electron being captured first, most probably at a deep acceptor-like trap at ≈30 meV below the conduction band. (For InP the effective mass of a hole is considerably bigger than that of an electron and thus higher power is needed for its impact ionization.) It should be added here that the impact ionization process is expected to be more effective for sample #KS 175 than for #KS 185 due to lower intensity of band-edge PL. One should note that, as soon as impurities become ionized, the threshold values for impact ionization are no longer linear in microwave power. Ionized impurities (donors) cause a drastic increase in the scattering cross section of nonresonantly heated carriers, thus greatly increasing the microwave power necessary to achieve conditions for impact ionization of centers.

Finally, we will address the increase of Yb PL which, for higher values of microwave power, follows its temporary saturation; this can be observed for sample #KS 175 in Fig.4(b). For this we notice that reported decay time constants of Yb^{3+} PL are of the order of ≈10 μs, [8, 12, 29, 9], which is two orders of magnitude faster than the decay of parity-forbidden intra-4*f*-shell transitions, which are expected to decay in milliseconds, as indeed observed for rare-earth ions in insulating hosts [32]. This large discrepancy is indicative of an efficient nonradiative recombination channel competing with the radiative decay. Takahei *et al.* [9] proposed that the Yb^{3+} decay time may be controlled by a nonradiative two-center Auger-type process involving Yb^{3+} in its excited state and an occupied shallow donor. Yb^{3+} decays due to an energy transfer from Yb to the nearby occupied donor resulting in ionization of this donor. An alternative mechanism assumes that, similarly to Yb^{3+} in the ground state, also the ytterbium ion in its excited state forms an acceptor-like electron trap. An electron localized on excited Yb could then take part in nonradiative recombination. In our opinion, the results depicted in Fig.4(b) present the first experimental fingerprint of such a process: upon increasing the microwave power a particle intermediating the process is impact ionized, which effectively blocks the nonradiative recombination channel. This effect strongly enhances radiative recombination of an excited Yb^{3+} ion clearly overcoming the earlier mentioned opposite effect of dissociation of Yb BE. (It should be noted here that the impact ionization of Yb BE is not expected to be very effective; the fact that it is the deepest of three radiative

recombination mechanisms taking place in the studied material, and that the binding field is of Coulombic, i.e., extended character, will lead to an efficient recapture of the impact-ionized holes by electrons bound to AE trap of ytterbium. On the other hand, the electron participating in the nonradiative Auger recombination of the BE is trapped in a local potential and, as such, can be effectively ionized.) At the same time, our data argue against the two-center Auger process involving shallow donors, the impact ionization of which observed for a relatively small microwave power does not result in any enhancement of YB PL.

CONCLUSIONS

Concluding, it has been shown that the dominant PLE mechanism of the $Yb^{3+}(4f^{13})$-related emission is due to the impurity Auger recombination. Ytterbium in InP binds an exciton which intermediates Yb core states excitation. Impact ionization data of this BE system indicate that the system is of a pseudoacceptor type with the electron being localized first, at a considerably deeper level. Our data also indicate that an Auger-type process, most probably involving an additional carrier localized by the ytterbium ion in an excited state, may be responsible for the fast nonexponential decay of the Yb^{3+} emission, as suggested previously by Takahei *et al.* [9]. It is shown that the nonradiative recombination channel can be effectively blocked by impact ionization. The latter observation is of particular importance in view of potential applications of rare-earth-doped III-V compounds for light-emitting devices.

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