A review of the Yb impurity related centres in mixed InP-based crystals has been presented. It is shown that Yb$^{3+}$ ions can be utilized to probe alloy disorder, both in cationic (GaInP) and anionic (InPAs) alloys. The existence of alloy disorder manifested itself in the photoluminescence spectra reflecting local atomic structure of the Yb centres. The dominant emissions have been ascribed to the Yb—P$_4$Ga$_{12}$ and Yb—P$_4$Ga$_{11}$In complexes in GaInP and to Yb—P$_4$ and Yb—P$_3$As centres in InPAs. The excitation and relaxation mechanisms of the 4f-shell of Yb$^{3+}$ ions were also investigated. It was found that the temperature quenching of the Yb$^{3+}$ luminescence was accompanied with the appearance of two thermally activated photoluminescence bands. It is suggested that photoluminescence at an energy of 25 meV below the energy gap is due to recombination of excitons bound at Yb-related centres. Relaxation of the excited 4f-shell of Yb$^{3+}$ ions proceeds via back transfer of the excitation energy from the 4f-shell to excitons bound at Yb-centres.

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1. Introduction

Rare-earth (RE) doped III–V semiconducting compounds are considered as promising materials for potential application in novel light emitting devices, characterized by sharp and temperature stable luminescence originating from the intra-4f-shell emission of RE$^{3+}$ ions, excited with charge carriers of the semiconductor host. Light emitting diodes operating on the intra-4f-shell electronic transition have been already demonstrated (i.e. [1, 2]).

The practical use of RE-doped semiconductors requires a high doping level to be achieved. This is due to the long, of the order of milliseconds, radiative lifetime of REs [3]. Doping of covalent semiconductors with REs during crystal growth has met difficulties owing to their high chemical activity. Another problem is associated with the ionic character of bonding of lanthanides to elements of the group V of the atomic periodic table. It results in a structural misfit between the zinc blende type structure of semiconductor hosts and the local structure preferred by RE ions, (usually a cubic, rock salt structure). The structural misfit introduces distortions to
the lattice and limits seriously the equilibrium solid solubility. Of course, the solid solubility limit can be easily overcome by application of nonequilibrium doping methods, as i.e. ion implantation or doping during MBE and MOCVD growth processes, however, it often results in precipitation of RE-rich metallic phases (i.e. [4,5]).

One of the basic problems to be solved is excitation and quenching of the $4f-4f$ photoluminescence (PL) of REs in semiconductors. It is believed that excitation of the $4f$-electron shell of RE ions in semiconductors is accomplished by the transfer of energy from the recombining charge carriers trapped at RE impurities to the $4f$-electrons [6,7]. Therefore, the energy levels in the forbidden gaps associated with lanthanide ions and their electrical character have to be identified. Information indispensable for such identification is the atomic structure of the RE-related centres and, in particular, the location of RE ions in crystalline lattices. In one case only, namely for Yb in InP, the structure and electrical properties of the RE-related centre seem to be well established. Whitney and co-workers [8] identified an acceptor-like electron trap (AE) due to Yb impurity, located at 30 meV below the conduction band of InP. Aszodi et al. [9] determined the symmetry of the emitting $\text{Yb}^{3+}$ ion as $T_d$, suggesting the substitutional position of the Yb atoms. Kozanecki and Groetzschel [10] confirmed this suggestion using Rutherford backscattering (RBS) and channeling spectroscopy. They also showed that substitutional location of Yb atoms in InP is an exception for III-V : RE systems. Ytterbium [10,11] and neodymium [12] atoms implanted into gallium compounds (GaP, GaAs, AlGaAs, GaAsP) were found to locate non-substitutionally. Unfortunately, their exact positions could not be determined, because of incomplete annealing of post-implantation damage. It was also found that Er atoms locate close to the tetrahedral interstitial positions in GaAs [13,14], and at the hexagonal interstitial positions in Si [5].

The spatial extension of the $4f$-electron wave function in a crystalline host is still of free ion size. This ensures that only the nearest environment of an RE impurity is sampled by its $4f$-electrons. Because of the screening of the $4f$-electron states by the outer closed $5s^2$ and $5p^6$ shells, the $4f$-states are only weakly affected by the crystal field. Nevertheless, the ground and excited states of RE$^{3+}$ ions are split in a crystal field. As a result, the number of lines and their energy separation reflect the symmetry and intensity of a local electric field. It offers a unique possibility to study perturbations of the highly symmetrical surroundings of the RE$^{3+}$ ions due to isovalent doping of binary crystals with a third component. The condition necessary to observe the effect of isovalent doping is, apart of the confinement of the electron wave function, the substitutional location of impurity atoms. Therefore, Yb impurity in InP-based compounds has been selected to study the structure of the RE-related centres in mixed III-V compounds.

An attractive idea is to study excitation and quenching of the intra-$4f$-shell PL as a function of alloy composition. InPAs alloys are particularly interesting in this respect, as the band gap can be changed between 1.42 eV (InP) and 1.24 eV, for the As content of 20%, which is equal to the energy of the $4f-4f$ radiative transitions of the Yb$^{3+}$ ions.
2. Ytterbium as a probe of the local alloy disorder in GaInP and InPAs crystals

It is well known that isovalent impurities added to binary III–V compounds introduce strain that is accommodated differently by the two sublattices [15]. The mixed sublattice tends to form a virtual crystal, while the common sublattice tends to preserve the covalent bond length associated with the nearest-neighbour atoms. As a result, the common sublattice suffers significant bond angle distortions. Because of the different behaviour of the two sublattices as a result of alloying, the reaction of an atomic probe to isovalent doping should depend on its location in one of the sublattices. It is clear at this point that the substitutional position of an impurity atom in both cationic and anionic alloys is a key factor for the possibility to observe the differences in the atomic structure of the centres in both types of alloys.

2.1. GaInP: Yb alloys

The effect of Ga-doping on the intra-4f-shell PL of Yb$^{3+}$ is presented in Fig. 1 (Ref. [16]). It is seen that the spectra are strongly influenced by the presence of gallium atoms already for Ga concentrations as low as 0.5%. A comparison of the Yb$^{3+}$ PL in InP (the lowest curve in Fig. 1) and in Ga$_x$In$_{1-x}$P ($x < 10\%$), shows that four new lines, denoted with $A$–$D$, appeared. The intensity of the 4f–4f PL characteristic of InP decreases considerably as the Ga content increases. The wavelengths and relative intensities of the $A$–$D$ lines do not seem to depend on composition. Therefore, it is supposed that they are all related to radiative transitions between the sublevels of a single centre.

An ytterbium atom occupying a cation site in GaInP crystals is tetrahedrally coordinated by four P atoms at the nearest-neighbour (NN) positions and by 12 In and Ga atoms altogether at the next-nearest-neighbour (NNN) cation sites. Assuming a random statistics of Ga and In atoms in the mixed sublattice, the probability $P(x_n)$ that Yb is surrounded by $n$-Ga atoms and $(12-n)$ In atoms is given by the binomial distribution

$$P(x_n) = \binom{12}{n} x^n (1-x)^{12-n},$$

where $x$ is the composition (gallium content). For $x < 10\%$ the probability of finding an environment with $n \geq 2$ is very low in comparison with that of finding configurations with $n = 0$ and $n = 1$. A simple analysis of the zinc blende lattice shows that for two Ga atoms in the NNN positions five inequivalent combinations of In and Ga atoms exist: one for the case when two Ga atoms are bound to the same P atom, and four configurations when Ga atoms are bound to different P atoms. Therefore, it should not be expected that any luminescence transitions related to the presence of two or more Ga atoms could be resolved in the PL spectrum of Yb$^{3+}$. As a result, the existence of the configurations with $n \geq 2$ contributes mostly to the broadening of the PL lines [16].

Taking into account these statistical arguments only two independent PL spectra, from Yb–P$_4$Ga$_{12}$ and Yb–P$_4$–Ga$_{11}$In centres, can be expected for an
atomic probe substituting one of the host atoms in a mixed sublattice. This is in accordance with the experimental data presented in Fig. 1 and reported in Ref. [16].

As the bond length in alloys is nearly preserved in the full range of compositions, it can be expected that also the Yb–P bond length is nearly constant in GaInP. Therefore, it seems that a replacement of an In atom with a Ga atom at a site NNN to YbIn causes only a local distortion of the Yb–P₄ tetrahedron, as one of the P atoms NN to a Yb⁺⁺ ion has to accommodate three different bond strengths: P–Yb, P–In, and P–Ga. As a result of this distortion the symmetry of the local electric field is lowered to nearly axial causing splitting of the $\Gamma_8$ sublevels in the ground and excited states of Yb⁺⁺. Therefore, it is suggested that the A–D PL lines observed for low Ga admixture (Fig. 1) are due to the $4f$–$4f$ PL of Yb⁺⁺ in axial Yb–P₄–Ga₁₁In complexes [16].

The fact that the volume of the Yb–P₄ tetrahedron does not change remarkably with the crystal composition is confirmed in Fig. 2 in which the $4f$–$4f$ PL spectra of Yb⁺⁺ ions in InP, Ga₀.₅In₀.₅P and GaP have been presented. It is seen that even for 50% Ga content there is no shift of the PL towards higher energies in spite of the decrease in the lattice constant from 5.8687 Å for InP to 5.6596 Å for Ga₀.₅In₀.₅P. The Yb emission in GaP is shifted approximately 20 meV towards higher energies. However, it cannot be decided whether this emission originates from substitutional Yb atoms, as the dominant sites occupied by Yb in GaP are interstitial, according to channeling measurements [11].
2.2. InPAs: Yb alloys

In the case of InPAs alloy a P–As replacement takes place in a position NN to Yb atoms. Due to the different bond lengths an As atom replacing one of the P atoms NN to an Yb$^{3+}$ ion induces distortion of the Yb-containing tetrahedron that lowers the symmetry of the cubic Yb–P$_4$ centre to an axial one. The volume of the distorted Yb–P$_3$As tetrahedron should increase slightly with increasing As content to satisfy the expansion of the mixed sublattice according to the Vegard’s law. As a result of this expansion a shift of the 4f–4f emission of Yb$^{3+}$ towards lower energies can be expected. This suggestion has been confirmed by spectroscopic measurements performed by the author [17–19]. The PL spectra of Yb$^{3+}$ ions appeared to be extremely sensitive to isovalent doping with arsenic. The addition of arsenic to InP results in new luminescence transitions (Fig. 3). For the lowest As content (2%) a weak doublet appeared on the low energy side of the most intense luminescence line at 9987 cm$^{-1}$, that is ascribed to the $T_8$–$T_8$ transition of a Yb$^{3+}$ ion sitting in an undistorted Yb–P$_4$ tetrahedron. The intensity of this doublet becomes dominant already for a 4% As admixture. Interestingly, the energy distance between the lines in the doublet is 9 cm$^{-1}$, and does not seem to depend on crystal composition. In contrast with the behaviour of the new PL in GaInP [16], in InPAs all the new PL lines shift to lower energies with the increase in As contents (Fig. 3). According to the arguments given above this emission is interpreted as originating from axial Yb–P$_3$As complexes [17–19].

An analysis of the temperature dependence of the Yb$^{3+}$ PL has given additional proof that the PL spectrum of Yb$^{3+}$ in InPAs consists of two emissions [17–19], ascribed to two centres: a cubic Yb–P$_4$ and an axial one — Yb–P$_3$As. It was also found that at higher temperatures the intensity of the PL originating from axial centres decreases in favour of the emission due to the cubic Yb–P$_4$ complexes.
3. Excitation and relaxation of the intra-4f-shell PL of Yb$^{3+}$ in InP and InPAs alloys

Yb-doped InP has been most widely used to study the excitation and quenching mechanisms (i.e. [6, 7]) as only one kind of optically active centre due to Yb impurity has been found and ascribed to Yb atoms at indium sites [9]. Binding of electrons at Yb AE-traps has been well documented using optically detected cyclotron resonance [20–22]. Electron paramagnetic resonance experiments revealed a strong Yb$^{3+}$ signal in both n- and p-type InP [23], indicating that the 30 meV AE-trap cannot be due to the Yb$^{3+}$/Yb$^{2+}$ acceptor level. It provides evidence that the bound electron is located outside the atom core and can be considered as effective-mass-like. Such negatively charged Yb-centres can attract holes with Coulomb forces, forming excitons.

On the basis of these observations a model was proposed, in which the 4f-electron shell is excited via non-radiative Auger-type transfer of energy from the exciton bound at a Yb$^{3+}$ion [6, 7]. Time resolved measurements of Taguchi et al. [24] suggest that the dominant quenching mechanism of the 4f–4f PL of Yb$^{3+}$ is the back transfer of energy from the excited $^2F_{5/2}$ state of the 4f-shell to band states of InP. Other authors proposed a model in which the energy of the excited $^2F_{5/2}$ state of Yb$^{3+}$ is back transferred to excitons bound at Yb$^{3+}$ions [7]. However, the trouble with this model is that a PL originating from radiative recombination of such excitons has not been observed yet. The reason for this is quite simple. In the process of back transfer of energy to excitons bound

![PL spectra of Yb$^{3+}$ in selected InPAs crystals.](image)
at the AE-trap the energy mismatch $\Delta E \approx 150$ meV has to be accommodated by absorption of phonons. This mismatch is many times larger than the binding energy of excitons ($\approx 10$ meV) and electrons at AE-trap ($\approx 30$ meV). Therefore, radiative recombination of the Yb-bound excitons is hardly possible due to their immediate thermal dissociation at temperatures at which the back transfer of energy becomes efficient ($T > 100$ K in InP [24]). On the other hand, the conditions favouring thermal stability of the Yb-bound excitons can be met in materials with smaller band gaps and, consequently, with a smaller energy mismatch between the 4f–4f and excitonic emissions. InPAs:Yb crystals are particularly well suited to search for the Yb bound exciton, as the energy mismatch $\Delta E$ changes continuously from ca. 150 meV (InP) to 0 meV for InP$_{0.8}$As$_{0.2}$.

Temperature dependencies of the PL spectra were measured to study the quenching of the Yb$^{3+}$ PL in InPAs [25, 26]. Figure 4 shows a semilog-plot of the integrated Yb$^{3+}$ PL intensity versus inverse temperature for InP and InPAs alloys. Assuming a two-step quenching process of the PL intensity the experimental data were fitted to a relationship

$$I(T_0)/I(4.2 \text{ K}) = [1 + A_1 \exp(-E_1/kT) + A_2 \exp(-E_2/kT)]^{-1},$$

where the prefactors were taken as constant. It has been found that the $E_1$ values depend strongly on composition (Table) and are close to the energy mismatch $\Delta E$ between the 4f–4f transition and the recombination energy of excitons bound at Yb$^{3+}$ ions. On the other hand, the $E_2$ values do not reveal any regular dependence on composition and they are within the range of 10–35 meV, which is comparable to the energy position of the AE-trap in the forbidden gap.

In the papers [18, 25, 26] it was shown that the quenching of the 4f–4f PL of Yb$^{3+}$ in InPAs with $x < 8\%$ is accompanied with the appearance of two thermally stimulated emissions, which were assigned to band-to-band recombination and to recombination of the e–h pairs bound to Yb$^{3+}$ ions (the emission $E_{Yb}$ at 25 meV below the band gap [25, 26]), respectively. This is confirmed by the temperature dependence of PL in InP$_{0.88}$As$_{0.12}$ (Fig. 5). For this composition the Yb$^{3+}$ PL
disappears already at 55 K, but two emissions in the near band-edge region are observed [27]. To prove directly that the emission at an energy of 25 meV below the band gap is related to Yb, the PL of an InP_{0.32}A_s_{0.08} undoped crystal was measured and the results are presented in Fig. 6. In contrast to the Yb-doped crystal with a similar composition, at $T > 50$ K only one thermally stimulated emission was observed in the near band edge region. It is apparently the band-to-band recombination. No PL at an energy of 25 meV less than $E_g$ was detected. Also, no trace of the Yb$^{3+}$ PL was observed in the region of 9900-10000 cm$^{-1}$.

4. Conclusions

On the basis of the presented results several conclusions can be drawn:

1. In GaInP alloys the 4f-4f PL spectra reflect the existence of two emitting Yb-centres: a cubic one — Yb-P$_4$Ga$_{12}$ and an axial one — Yb-P$_4$Ga$_{11}$In.

2. In InPAs alloys for each composition the spectrum is interpreted as consisting of two independent emissions due to the Yb-P$_4$ and Yb-P$_3$As centres.

3. The line splitting (9 cm$^{-1}$) related to an axial local strain induced by isovalent doping seems to be independent of composition, suggesting that the local strain is alloy composition independent.
4. It seems that excitation and relaxation of the 4f-shell is mediated by an exciton bound to the Yb$^{3+}$ ion.

5. Near band gap luminescence due to the exciton bound at Yb$^{3+}$ (or electron trapped at Yb$^{3+}$ with a free hole) has been identified.

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