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HYDROGEN-LIKE EXCITATIONS OF 3*d* AND 4*f* ISOELECTRONIC IMPURITIES IN SEMICONDUCTORS

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In the paper the energy states of structured isoelectronic impurities of transition metals and rare earth elements, donor and acceptor excitons of 3*d* and 4*f* impurities, the role of donor and acceptor excitons of 3*d* and 4*f* impurities in energy transfer from the matrix to impurities are discussed. It is shown that structured impurities may be classified as "open" and "closed" isoelectronic impurities. The number of electrons in the 3*d* or 4*f* shells is changed at $\hbar\omega < E_g$ for open impurities and is not changed for closed impurities. The structure of energy levels generated by 3*d* and 4*f* impurities in a forbidden gap, the properties of donor and acceptor excitons of those impurities and energy transfer mechanisms from the matrix to an impurity (a capture of carriers into 3*d* or 4*f* shells for open impurities and the Auger process for closed impurities) are essentially distinguished for two kinds of structured isoelectronic impurities. For closed impurities a model is discussed in the frame of which the spectra of electroabsorption, photoluminescence, cathodoluminescence are described.

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Properties of semiconductors doped with transition 3*d* metals or rare earth 4*f* elements have attracted increasing research attention. These materials are of practical interest as optical emitters and photodetectors especially important for producing fast optoelectronic devices. The light emitters operating in injection regime (low field electroluminescence) or in impact excitation regime (high field electroluminescence) are also of special interest for practical use. In both cases the mechanisms of excitation of impurities in the concrete matrix are not clear in all details.

The 3*d* impurities in II–VI compounds and 4*f* impurities in III–V semiconductors are isovalent impurities. If a perturbation due to an isovalent impurity is small, then a smooth change of the energy gap takes place. If a perturbation is large, then energy states are split off from the edges of the valence band or the conduction band. These states are deep states because they are split off by δ-potential [1]. The 3*d* and 4*f* impurities not only split off the energy states from bands but also strongly mix the $3d$ shell wave functions with the valence and conduction band states of host semiconductors. Due to a different nature of impurity states introduced by it into the energy spectrum of crystals the isovalent impurities were classified as "simple" and "structured" impurities [2]. The simple impurities introduce one-electron energy states into the spectrum of a crystal whereas the structured impurities introduce many-electron energy states into the crystal energy spectrum. A degree of mixing of the impurities states with the band states both affect on the structure of energy states produced by impurities and play a significant role in a formation of a mechanism of energy transfer from the crystals to an impurity.

The impurities of $3d$ and $4f$ elements contain many electrons in d and f shells, which result in many-electron energy levels [1,3]. We shall consider a quasi-molecular model of an impurity which was firstly applied to simple isoelectronic impurities [4]. It allows us to understand the lowering of the bottom of the conduction band near an impurity in ZnTe:O, this is an origin of the acceptor level of oxygen, which serves as an electron trap. In the case of increasing the top of the valence band for ZnS:Te, there is the donor level of tellurium. A radius of localization and a depth of the energy states are related in the model of potential well

$$R_b = \hbar/(2m^* E_i)^{1/2}, \tag{1}$$

where m^* is an effective mass of a band edge from which a splitting of states to the forbidden gap takes place.

The impurities of $3d$ transition metals or $4f$ rare earth elements substitute cations in the lattices of II–VI and III–V semiconductors and give up to the valence band the number of electrons needed to saturate all the chemical bonds. The electrons of partially filled d and f shells interact with band states. A one-electron d state in the crystal field is split into e and t_2 states. The former does not interact with band states while the latter mixes with the valence band states. The wave function is presented in the following form:

$$\psi = \phi_d + \sum \phi_p. \tag{2}$$

This interaction may be approximately taken into consideration in a quasi-molecular model. In Fig. 1 two variants of localization of the t_2 level with respect to the top of the valence band are presented. In the case when the t_2 level lies above the valence band top, the crystal field resonance (CFR) state according to the terminology of Zunger [3] originates in the forbidden gap, which is mainly formed from the t_2 states. In contrast, the dangling bond hybrids (DBH) state originates in the forbidden gap and this state is constructed for the most part from the p state of the valence band.

An account of n electrons in the d shell gives rise to many-electron intracenter states. For each configuration d^n $(1 < n < 10)$ there is a definite number of intracenter states. Transitions between them occur without changing the number of electron in the d shell. In principle the d–d transitions are forbidden and they manifest themselves in optical spectra as weak lines the most intensive of which occur between the energy terms with the same spin multiplicity.

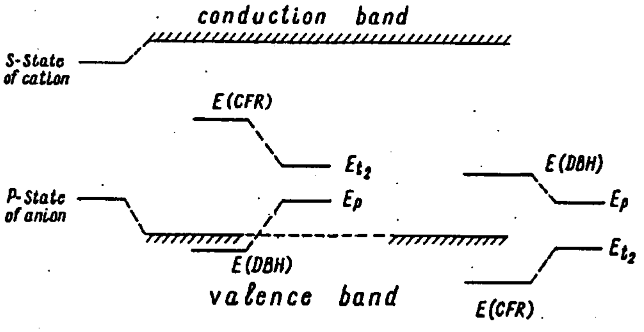

Fig. 1. Origin of the deep CFR and DBH levels of $3d$ impurities in a quasi-molecular model of a defect.

In addition to the narrow intracenter absorption peaks broad unstructured bands are observed due to photoionization of impurities, i.e. a transfer of one electron from the d shell into the conduction band (Fig. 2a)

$$d^n + \hbar\omega_{\mathrm{D}} \rightarrow d^{n+1} + e. \tag{3}$$

The energy $h\omega_{\mathrm{D}}$ of the transition (3) counted from the bottom of the conduction band gives the position of the donor level designated by the number of electrons in the d shell before and after the transition $E_{n,n-1}$ or by the charge states before and after the transition (0/+). Those transitions are named as "diagonal" Allen transitions (slanting arrows in Fig. 2a). The many-electron ground states of the d^n configuration are combined with the (0/+) level. For the $3d$ impurity with the CFR level the transitions of electrons from the valence band to impurities have been often observed (Fig. 2a)

$$d^n + \hbar\omega_{\mathrm{A}} \rightarrow d^{n+1} + h. \tag{4}$$

The appropriate level is designated as $E_{n,n+1}$ or (0/−). The transition A can be described as the transition of a hole into the valence band, when the number of holes in d shell decreases by unity. Many-electron levels of d^{10-n} configuration coincide with the levels of d^n configuration, but the former are counted down from the (0/−) level (the hole representation of many-electron levels).

In principle for impurities with the DBH level, the d-state lies deeply in the valence band and the photoionization of an impurity into the conduction band is not possible for $h\omega < E_{\mathrm{g}}$. Manganese in II–VI compounds is an example of such impurity. Numerous investigations of photoemission spectra while using the X-rays show that the d-state of Mn lies approximately 3 eV below the top of the valence band. The authors of the paper [5] investigated the excited state absorption spectra of Mn in ZnS and ZnSe and found the evidence that the (0/−) CFR levels of Mn lie 1.3 eV for ZnSe and 0.8 eV for ZnS above the bottom of the conduction band. However, in certain cases, features are observed in electroabsorption, electroexcitation and intracenter photoluminescence excitation spectra under illumination with $h\omega < E_{\mathrm{g}}$. They are considered as results of transitions from the donor level near the valence band to the conduction band (Fig. 2b)

$$(d^5 + v) + \hbar\omega_D \rightarrow (d^5 + h) + e. \tag{5}$$

The parentheses denote the DBII state.

The energy states of $4f$ impurities in II–VI and III–V semiconductors have been studied much less than $3d$ impurities both experimentally and theoretically. However, for Yb and Er in III–V semiconductors (InP, GaP, GaAs) some evidence was found that $4f$ impurities have the charge state Re^{3+} and the configuration f^n has not been changed under the action of light with energy smaller than E_g. The rare earth $4f$ impurities create an acceptor level near the bottom of the conduction band. This state is a trap for electrons. The transition of electrons from the valence band to this level is shown in Fig. 2b as the transition A. It may be considered as a hole transition from this level to the valence band.

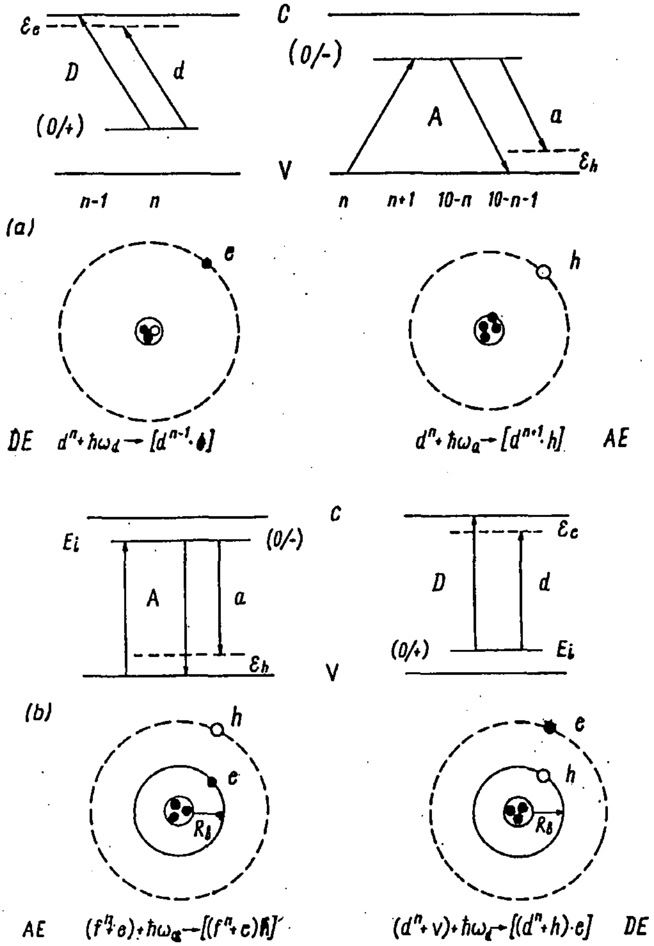

Fig. 2. Deep donor (0/+) and acceptor (0/–) levels for open (a) and closed (b) impurities. Transitions to hydrogen-like states are also shown. In lower parts of the figures the corresponding hydrogen-like formations are presented.

Therefore, the structured isoelectronic impurities, that is $3d$ and $4f$ impurities, may be classified in two groups. For the first group the number of electrons in d or f shells may be changed for the energy of light smaller than the energy E_g. We shall call them "open" impurities. The examples of systems with open impurities are ZnSe : Ni, ZnO : Cu, GaP : Fe and others. For the second group of impurities the number of electrons in d or f shells is not changed at $\hbar\omega < E_g$ (II–VI semiconductors doped with Mn, InP, GaP and other doped with Yb, Er). We shall call those impurities as "closed" impurities. The closed impurities split off the energy states from the edges of the allowed bands, which is analogous in many respects to the energy states of the simple isoelectronic centers.

The impurities of $3d$ elements have intracenter excitations and hydrogen-like states. For the latter an electron from the d shell is put in the hydrogen-like orbit by light (transition "d" in Fig. 1a). This state of impurity is represented as a charged core with $n-1$ electrons in $3d$ shell and the electron located at hydrogen-like orbit. These states are called donor excitons (DE) of $3d$ impurities.

$$d^n + \hbar\omega_D \rightarrow [d^{n-1}e]. \tag{6}$$

The square brackets denote a Coulombic interaction. For impurities with deep acceptor levels (0/–) the hydrogen-like excitations are named the acceptor excitons (AE). For closed impurities hydrogen-like excitations are also possible and the corresponding transitions are described as follows (Fig. 1b):

$$(d^5 + v) + \hbar\omega_D \rightarrow [(d^5 + h)e], \tag{7}$$

$$(f^{13} + c) + \hbar\omega_A \rightarrow [(f^{13} + e)h]. \tag{8}$$

The first carrier is located at the distance R_b from an impurity (1), the second carrier is left in a hydrogen-like orbit.

In Fig. 3 the experimental spectra showing the existence of AE of Ni for ZnS : Ni are presented [6]. For Ni impurities in other II–VI compounds AE and DE are well documented [6–8]. A possibility of experimental observation of DE or AE of $3d$ impurities is mainly limited by a coexistence of hydrogen-like and intracenter excitations of impurities. Figure 4a shows tunneling transitions from DE $[d^7e]$ of Ni to intracenter states of the d^8 configuration. It has been suggested that such transitions may be used for understanding very strong temperature dependence of DE line in CdS : Ni [9]. The tunneling efficiency may depend on the number and the symmetry of the final states. Many-electron intracenter states of $3d$ impurities and energy levels (0/+) and (0/–) for all $3d$ impurities in ZnS are shown in Fig. 5. It is very difficult to observe DE or AE for impurities with a large amount of intracenter states near the energy levels (0/+) or (0/–), for example for ZnS : Fe or ZnS : Cr. Really there is no information about observations of DE or AE of Fe or Cr in ZnS. There were experimental studies of InP : Fe, GaAs : Fe and GaP : Fe, in which experimental data were interpreted in terms of hydrogen-like excitations of Fe impurities [10–12]. A more detailed discussion of these results is presented in Ref. [7]. In principle, other $3d$ elements could have hydrogen-like excitations if they create (0/–) and (0/+) levels in the band gap. Figure 6 summarizes data on the energy levels of $3d$ impurities in II–VI and III–V semiconductors. The energy levels are counted from the vacuum level, and they follow a definite trend. This representation of the experimental data is of much practical significance, since it is predictive. For example, we would expect that DE would be observed for V, Ti, Sc in ZnS and ZnTe; for V, Ti in GaP; etc. [7,13,14].

For closed impurities there are experimental data which may be interpreted as results of DE or AE of a corresponding impurity. In Fig. 7 the electroabsorption spectra of CdTe: Mn are presented which are due to the influence of electric field on the DE $[(d^5+h)e]$ of an Mn ion [15]. Similar results have been obtained for ZnSe: Mn [16]. It is evident from [8,17] and Fig. 7 and 8 that the temperature dependence for AE of Ni $[d^9h]$ and DE of Mn $[(d^5+h)e]$ is very different. Many experimental results show a strong temperature dependence for DE and AE of Ni in different II–VI semiconductors [6–10], whereas for DE of Mn in CdTe and ZnSe the observable temperature dependence is relatively weak [15–17] over the temperature range of 4.2–77 K. For Yb and Er in III–V compounds there are experimental results which give us an indirect evidence of AE existence of these impurities.

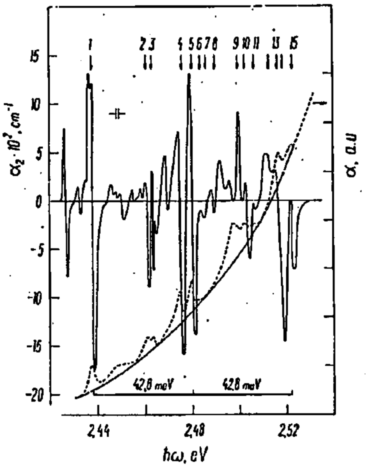

Fig. 3. Electroabsorption spectrum for ZnS: Ni (solid line), absorption spectrum (dashed line) [6].

It is well known that introducing $3d$ impurities into the II–VI compounds gives an essential change of the edge luminescence. The free exciton lines and the localized exciton lines disappear in the edge spectrum due to an energy transfer from the matrix to $3d$ impurities. The information about channels of energy transfer may be obtained by investigating photo-, cathodo- or electroluminescence spectra, electroabsorption and photoluminescence spectra, from the influence of temperature on different spectra. Experimental results give evidence that the mechanisms of excitation for open and closed impurities are essentially distinguished.

The photoluminescence excitation spectrum of ZnS: Ni [8,17] consists of a zero phonon line and its vibrational replicas. The zero phonon line is due to transitions to the Ni AE $[d^9h]$. Similar spectra have been observed for ZnSe: Ni [18].

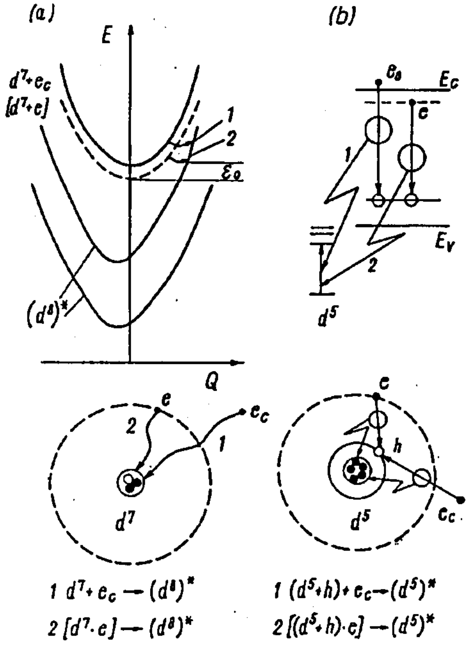

Fig. 4. Diagrams of energy states illustrating the possible variants of the tunneling captures for the open impurities (a) and Auger defect recombinations for the closed impurities (b) (example for Mn).

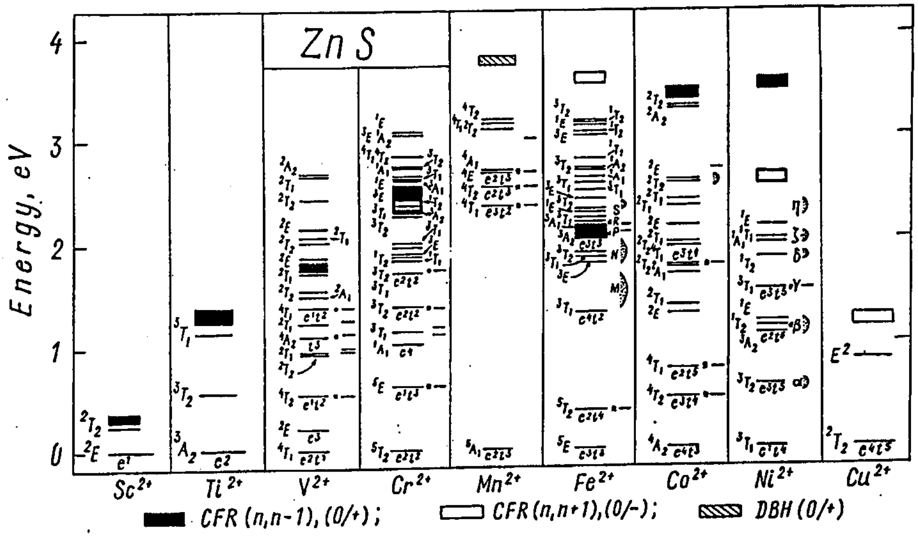

Fig. 5. Many-electron intracenter energy states of 3d impurities in ZnS : 3d and positions of donor (0/+) and acceptor (0/−) levels of these impurities in ZnS.

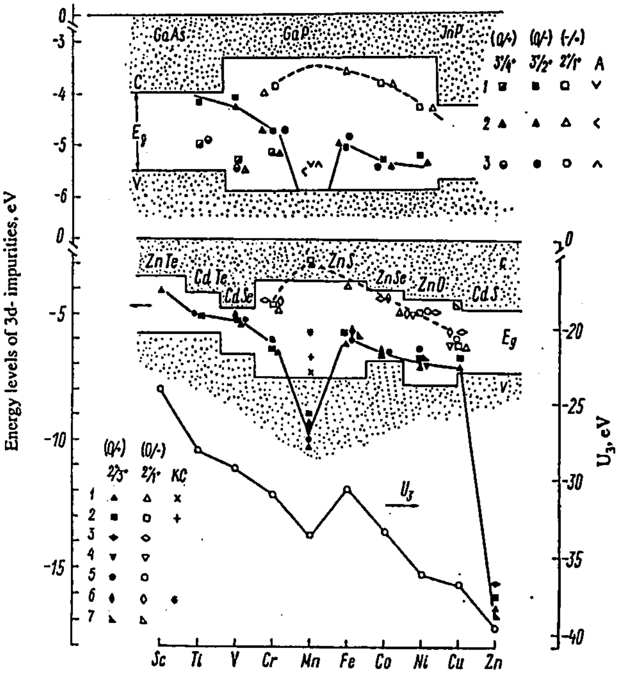

Fig. 6. Energy positions of the (0/+), (0/–) and (–/=) levels of $3d$ impurities in II–VI and III–V compounds. II–VI: 1 — ZnS, 2 — ZnSe, 3 — ZnTe, 4 — CdS, 5 — CdSe, 6 — CdTe, 7 — ZnO. III–V: 1 — GaAs, 2 — GaP, 3 — InP. Here KS are antibonding DBH states of Mn in the Koster–Slater model, and U_3 is the third ionization potential of the $3d$ atoms [7].

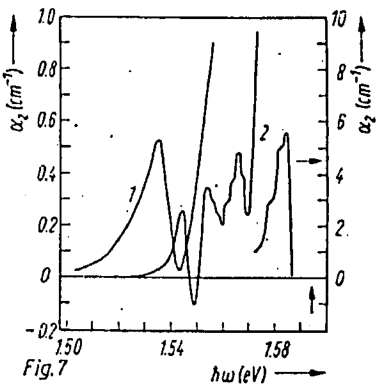

Fig.7

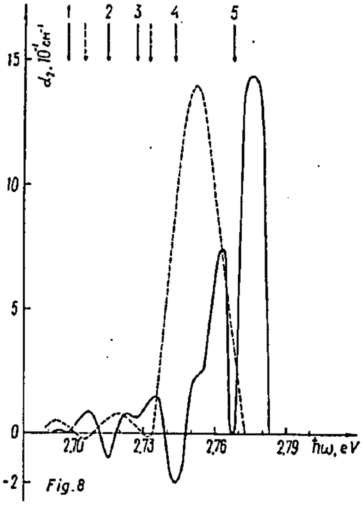

Fig.8

Fig. 7. Electroabsorption spectrum for CdTe:Mn, $T = 77$ K (1), 4.2 K (2) [15].
Fig. 8. Electroabsorption spectrum for ZnSe:Mn, $T = 4.2$ K (1), 77 K (2) [16].

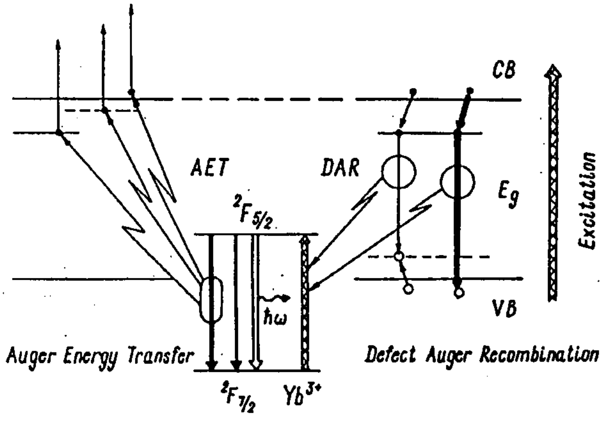

Fig. 9. Model for excitation and deexcitation of intracenter luminescence of closed impurities taking InP : Yb as an example.

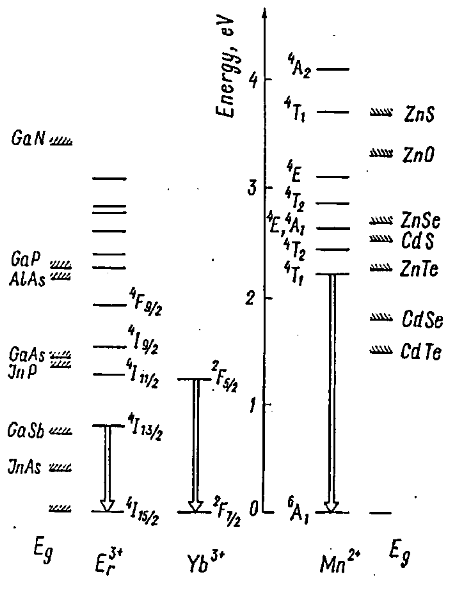

Fig. 10. Energy levels of some closed impurities in comparison with energy gaps of II–VI and III–V semiconductors.

For ZnO : Cu and ZnS : Cu the photoluminescence excitation spectra have been also observed [19,20]. All these results provide a key for understanding the energy transfer mechanism for open impurities. The lines of Ni AE and Ni DE are strongly temperature dependent. In the paper [9] the temperature dependence has been investigated and interpreted as a result of tunneling transitions from Ni DE state to intracenter states of Ni^{2+} ion. The temperature dependence was explained in the model of configuration diagram (Fig. 4a). A tunneling capture of Ni DE in one of the excited states of the d^8 configuration has been suggested. If the system is in the state $d^7 + e$ then the tunneling capture is also possible. In Fig. 4a the tunneling transitions are presented as wave arrows. The tunneling efficiency may depend on the barrier width, on the symmetry and multiplicity of final states. It may be suggested that for high temperature the tunneling capture of electron from the conduction band into d^8 excited states is the most efficient mechanism for open impurities especially with many intracenter states.

The closed impurities give a more intensive radiative recombination in comparison with open impurities. This is due to the existence of the effective excitation mechanism for d^5 Mn configuration in II–VI semiconductors and for f^{13} Yb and for f^{11} Er in III–V compounds. Numerous experimental investigations of Yb and Er luminescence in III–V semiconductors have been discussed by Masterov and Zacharenkov [21,22].

In Refs. [23–37] some experimental data are presented which will be discussed in the frame of the defect Auger recombination (DAR) and Auger energy transfer (AET) model (Fig. 9). The luminescence spectrum of InP : Yb includes peaks due to intracenter transitions [23–25,27]. Under the action of light, electron–hole pairs are created. Yb impurities capture electrons on the deep trap level near the conduction band. A second carrier is trapped by a Coulombic field of the center and thus the AE of Yb $[(f^{13} + e)h]$ is created. Then the energy of AE due to DAR process is transferred to the intracenter exciting state of f^{13} configuration. This process is shown by zig-zag arrows in Fig. 4b. The intracenter luminescence is provided by transitions ${}^2F_{5/2} \leftrightarrow {}^2F_{7/2}$ for Yb. The intensity of this luminescence is quenched with a characteristic energy. For the characteristic energy E different values were obtained: for InP : Yb $E = 115$ meV [23,25] and $E = 190$ meV [27]; for InP : Er $E = 9$ meV [30] and $E = 100$ meV [26]. The energies of deep levels split off from the conduction band bottom by $4f^{3+}$ ions were determined as 30 meV for Yb^{3+} [23,24] and 60 meV for Er^{3+} [23]. The reasons of temperature quenching of luminescence are accounted for by thermal ionization of deeply bound carrier (Fig. 9). With increasing temperature the number of trapped electrons is decreased and the intensity of DAR processes also weakens. The efficiency of the thermal quenching depends on the depth of $4f$ ion acceptor energy level. The authors have observed the weakening of the temperature quenching with the growth of E_g in solid solutions InGaP : Er [26]. It is due to increasing deep level energy with a change of solid solution composition.

Another evidence of this point of view is an observation of weak thermal quenching in GaP : Er [26,33] and actually independence of luminescence of GaN : Er and AlN : Er on temperature [26,34]. The analogous thermal quenching was observed in the cathodoluminescence spectra for ZnSe : Mn ($E = 78$ meV) [28] and ZnO : Mn ($E = 76$ meV) [29]. This quenching is due to ionization of the Mn deep donor level split off from the top of the valence band. The observations of peaks in the electroabsorption spectra of CdTe : Mn and ZnSe : Mn [15–17] and in the photoluminescence excitation spectra of ZnS : Mn [31] are considered as the experimental proof for existence of deep acceptor levels of Mn split off from the top of the valence band. For the DAR process it is very important to create resonance conditions. In Fig. 10 energy levels of closed impurities are presented in comparison with energy gap of II–VI and III–V semiconductors. It is clear that the resonance conditions may be obtained in solid solutions of proper materials. It is also interesting to investigate the role of higher intracenter energy states in the energy transfer mechanism for wide-gap materials.

The authors of Ref. [35] consider the quenching of intracenter luminescence of InP:Yb^{3+} as a result of back AET process (Fig. 9). The part of intracenter excitation energy is released in a form of radiative and nonradiative transitions and another part of excitation energy is released via AET process to free or bound carriers. This process is responsible for a quenching of intracenter luminescence for closed impurities in conducting materials [36,37]. It also makes possible to observe the intracenter photoconductivity InP : Er [32]. The theory of the AET process was given in [37].

Resume

1. The structured isoelectronic impurities may be classified as "open" and "closed" impurities.
2. Deep and hydrogen-like states are very different for two kinds of impurities.
3. Mechanisms of excitation of intracenter luminescence are the direct capture for open impurities and defect Auger recombination for closed impurities.

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