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Optically Induced Deexcitation of Rare-Earth Ions in a Semiconductor Matrix

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We report on verification of the proposed energy transfer mechanism responsible for photoluminescence of rare earth (RE) ions in semiconductors. Using two-color spectroscopy in the visible and the midinfrared regions (with a free-electron laser) we demonstrate reversal of the most important step in the excitation process. In that way, formation of the intermediate state bridging atomic states of the RE ion core and extended orbitals of a semiconducting host is explicitly confirmed and its characteristic energy spectroscopically determined. The study is performed for InP:Yb. It is argued, however, that the conclusions are valid for all semiconductor:RE systems, including the notorious Si:Er.

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Rare-earth (RE)-doped insulating crystals have proven to be efficient laser materials. They are widely used in optical amplifiers and lasers. Also, RE doping of semiconductors has been extensively studied in view of the potential applications in optoelectronics and telecommunication.

Photoluminescence (PL) from the intra-$4f$-shell transitions of a RE ion is spectroscopically sharp and highly independent of the surroundings due to effective shielding by the outer $5s$ and $5p$ complete electron shells. This is potentially interesting for the fabrication of optical devices from semiconductor:RE systems where the excitation occurs via the host. A practical device requires stable and efficient room-temperature operation. To achieve this, the mechanism of energy transfer from the host lattice to the RE ion needs to be understood and optimized. It is generally believed that the energy of a recombining electron-hole pair, generated in the host material by band-to-band excitation or carrier injection [1], can be used to bring the RE ion into an excited state, from which the radiative emission follows. Yb-doped InP is commonly used as a model system to investigate these processes, because Yb^{3+} has only one excited state and forms only one optically active center in InP. Detailed investigations established that in this case Yb substitutes for In and forms an isoelectronic acceptorlike electron (AE) trap at 30 meV below the conduction band [2]. The mechanism of energy transfer from the InP host to the Yb^{3+} ion was originally proposed by Takahei *et al.* [3] and theoretically supported by Lannoo [4]. This mechanism is depicted in Fig. 1. It involves the isoelectronic AE trap capturing an electron (2), which makes it negatively charged. A hole is then bound by the resulting Coulomb potential (3), which lowers the energy by approximately 10 meV [5]. The recombination energy of the bound electron-hole pair is used to bring the Yb^{3+} ion from the $^2F_{7/2}$ ground state to the $^2F_{5/2}$ excited state in an Auger process involving electrons in the $4f$-electron shell (4). The excess energy is released by generation of (local) phonons [6]. Because of the similarity in electronic structure of all the RE ions, excitation of other semiconductor:RE systems is believed to occur in a similar way, by localization of an electron-hole pair at a RE related level, with minor differences in the properties of the trapping level depending on the host material. In

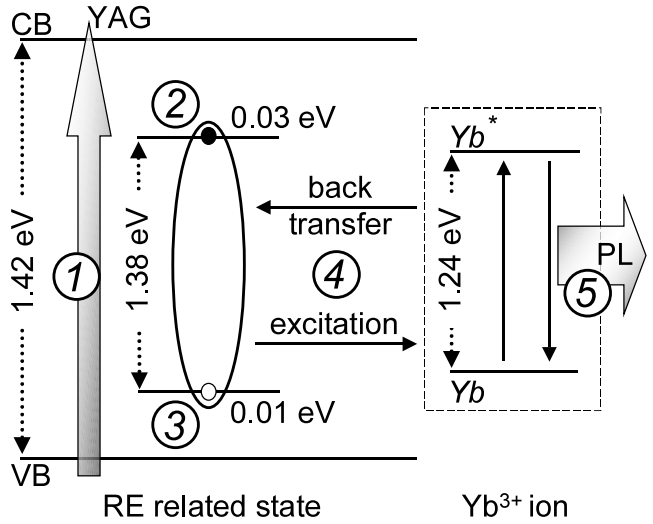

FIG. 1. Model of excitation of Yb^{3+} in InP. After band-to-band excitation (1) the generated free electrons can be captured at the Yb related trap (2). Binding of a hole (3) forms an electron-hole pair on the trap. Nonradiative recombination of the pair leads to excitation of the Yb^{3+} ion (4), producing the observed PL (5).

particular, a comparable excitation scheme is considered for the most prominent semiconductor:RE system Si:Er. Consequently, the energy transfer between the recombining electron-hole pair and the $4f$-electron shell of the RE ion is the crucial step in the excitation mechanism of all RE ions in semiconductor hosts. The reverse of this process, an energy "back transfer," is believed to be responsible for the decrease of PL intensity in these systems at elevated temperatures. This thermal quenching hampers the PL efficiency and is the major obstacle for the construction of semiconductor:RE based devices. Following the proposed excitation model, the energy back-transfer process in InP:Yb involves the deexcitation of excited Yb^{3+} by generation of an electron-hole pair. The energy deficit, in this particular case ~140 meV, is compensated by the annihilation of lattice phonons.

Although generally accepted, evidence to support the above outlined excitation model in general and, specifically, the proposed energy back-transfer mechanism for InP:Yb, is almost exclusively derived from measurements of thermal quenching of PL intensity and decay time. As such, it is of indirect character; by increasing the temperature many processes are activated simultaneously and their contributions cannot be reliably separated [7]. Consequently, the excitation mechanism comprising the formation of an intermediate state remains speculative and its exact properties are unclear. Yet understanding this step is essential for all models used to describe semiconductor:RE systems and constitutes a necessary condition for development of practical devices.

In two-color experiments, with band-to-band optical excitation as the primary beam and a powerful midinfrared (MIR) laser as the secondary beam, we can hope to reverse the excitation process optically, providing the energy deficit by illumination with photons of the appropriate quantum. In this way we can effectively probe the back-transfer process and therefore address the intermediate level in a direct manner. In the past, an intense MIR beam from a free-electron laser (FEL) was shown to quench emission from Si:Er, which was attributed to the ionization of the RE related intermediate state. From this, the multistage character of the excitation was inferred. However, the characteristics of the intermediate stage remained unclear [8].

In the current contribution, we show that the energy back-transfer process can be activated selectively with photons of the appropriate energy. In this way we explicitly prove the existence of the intermediate state linking the RE ion core states and the energy bands of the semiconducting host, thus confirming the excitation model for the semiconductor:RE system as postulated by Takahei *et al.* [3]. We also spectroscopically determine the activation energy governing this process. The experiments are performed at low temperature (4 K), where the PL intensity is high and its changes can be monitored accurately. The band-to-band excitation is achieved with the second harmonic (532 nm) of a Nd:YAG laser with a repetition rate of 5 Hz and a pulse length of ~100 ps. A FEL provides the MIR beam. The photon energy of the 4–6 μs long pulse of the FEL is tuned between 65 and 175 meV. The FEL pulse is activated with a selected time delay Δt_F with respect to the Nd:YAG laser pulse. Both beams illuminate the same sample area with a diameter of approximately 5 mm. The emerging PL is gathered with a system of lenses, dispersed using a single grating monochromator, and detected with a near-infrared photomultiplier tube with a flat response over the wavelength range from 300 to 1600 nm.

Figure 2 shows the effect of the FEL pulse (depicted relative to the Nd:YAG pulse in the top-left part of the image) on the Yb^{3+} PL signal (bottom-left) for a delay time of $\Delta t_F = -1$ and 4 μs. The decay characteristics are not influenced by the system response time, which was experimentally determined to be 0.3 μs. A clear quenching of Yb^{3+} PL is observed. This quenching occurs only during the FEL pulse; as can be seen in Fig. 2(*A*), MIR photons applied after the Nd:YAG laser pulse induce quenching on a time scale of microseconds: since thermal effects have a relaxation time of milliseconds, this observation excludes the influence of lattice heating on Yb^{3+} ions in the excited state as a possible explanation for

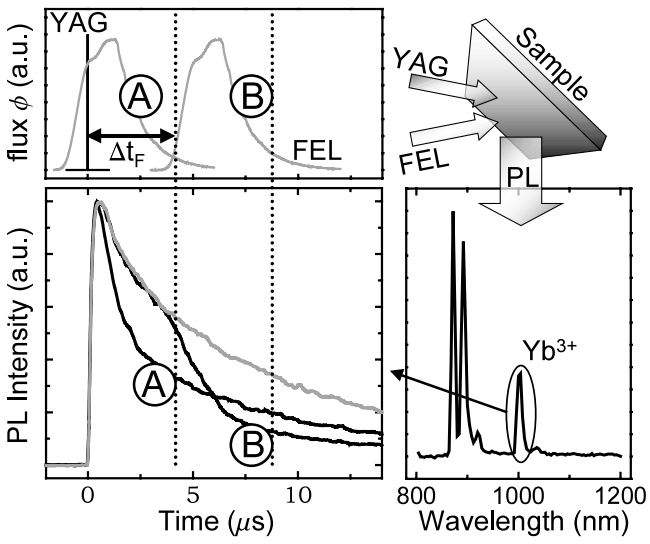

FIG. 2. Quench of Yb^{3+} PL by application of the FEL at a photon energy of 110 meV. The top left graph displays the time relation between the Nd:YAG laser pulse (~ 100 ps), used for band-to-band excitation, and the FEL pulse (~ 5 μs), with delay times Δt_F of -1 μs (*A*) and $+4$ μs (*B*). Both the Nd:YAG and FEL beams illuminate the sample (top right) and the characteristic PL spectrum of the InP:Yb system is observed (bottom right). A measurement of the decay dynamics of the Yb PL (1 μm) can be seen at the bottom left: the gray line depicts the luminescence transient with only the Nd:YAG applied, and the black curves (*A* and *B*) indicate the effect of the FEL at the two delay times.

this intensity quenching. We found that for fixed photon energy E_{ph} and photon flux ϕ_F of the FEL the percentage of PL that is quenched is independent of the delay time Δt_F. According to this observation, the ratio of the PL intensity observed with and without the FEL pulse ($I_{\mathrm{on}}/I_{\mathrm{off}}$), hereafter called the "quenching ratio" Q, can thus be described as follows:

$$Q(t, \Delta t_F, E_{\mathrm{ph}}, \phi_F) = \frac{I_{\mathrm{on}}(t, \Delta t_F, E_{\mathrm{ph}}, \phi_F)}{I_{\mathrm{off}}(t)} = Q(E_{\mathrm{ph}}, \phi_F), \quad t > \Delta t_F + \tau, \tag{1}$$

with τ being the duration of the FEL pulse. The quenching ratio Q does not depend on the time t, because after the FEL pulse the same fraction of the original signal remains for different t and Δt_F. We can approximate the MIR pulse by a square pulse of duration τ and with an effective photon flux ϕ. Because the decay of PL shows a single exponential behavior both before and after the FEL pulse, we can write that

$$-\ln[Q(E_{\mathrm{ph}}, \phi)] = -\ln\left[\frac{I_0 e^{-tW_1} e^{-\tau W_q(E_{\mathrm{ph}}, \phi)}}{I_0 e^{-tW_1}}\right] = \tau W_q(E_{\mathrm{ph}}, \phi), \quad t > \Delta t_F + \tau. \tag{2}$$

Here W_1 is the effective decay rate of Yb^{3+} in InP without the FEL applied; the quenching term $W_q(E_{\mathrm{ph}}, \phi)$ represents the effective deexcitation ratio induced by the FEL beam. We have assumed that during the MIR pulse the total decay rate is given by $W_1 + W_q(E_{\mathrm{ph}}, \phi)$. We have measured the dependence of $W_q(E_{\mathrm{ph}}, \phi)$ as a function of the photon energy E_{ph} in the FEL beam. In that case, the photon flux ϕ of the FEL has to be recorded simultaneously, because it has a strong dependence on E_{ph}.

The top panel in Fig. 3 shows the quenching effect as a function of photon energy, normalized for a few values of constant MIR flux density. While quenching is observed for the whole photon energy range investigated, the magnitude of this effect increases stepwise for photon energies $E_{\mathrm{ph}} \gtrsim 145$ meV. The bottom-left part of the figure shows the flux dependence of the quenching effect measured for the FEL photon energy range from 70 to 140 meV. The square root dependence on the flux density is evident. For the higher photon energy range ($E_{\mathrm{ph}} \gtrsim 145$ meV) this dependence, as shown at the bottom right, proves to be linear.

As discussed before, in the proposed excitation scheme an energy mismatch of ~140 meV exists between the recombining electron-hole pair on the AE trap and the energy of the Yb^{3+} excited state. In the reversal of the excitation process, this energy has then to be added to the system. Therefore, upon exposure to a highly intense beam of photons with energy higher than this energy mismatch, deexcitation of the excited Yb^{3+} can be expected, with a subsequent generation of an electron-hole pair. This is indeed observed in the current study. The

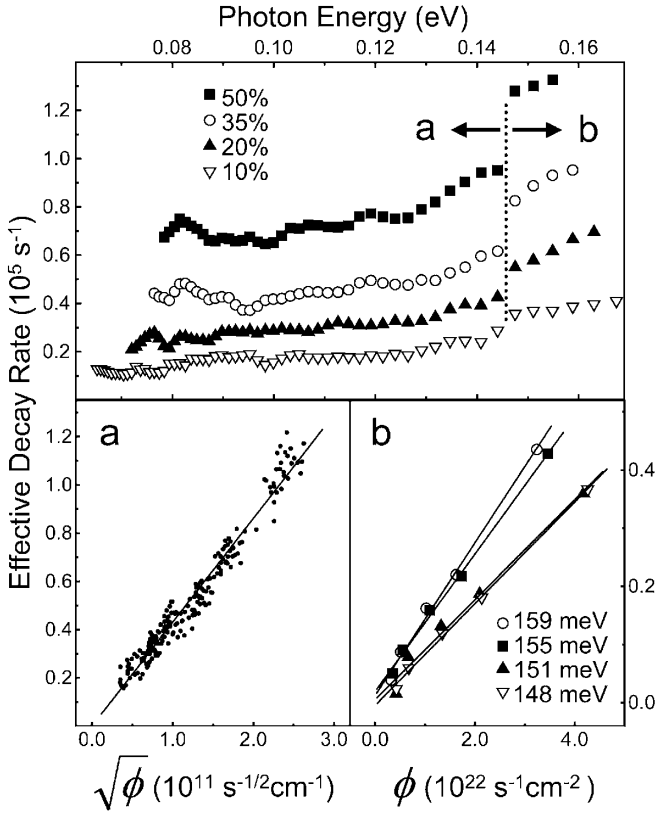

FIG. 3. The top graph shows the effective decay rate during the FEL pulse as a function of FEL photon energy, for four different flux densities. Two regimes can be distinguished with a step at 145 meV separating them. The top curve is moved 0.1×10^5 s^{-1} upwards for clarity. The percentages indicate the FEL photon flux compared to the maximum flux of 6.8×10^{22} photons $\cdot$ s^{-1} cm^{-2} measured at a photon energy of 95 meV. In the bottom graphs the flux dependence of the PL quenching is depicted for the photon energy range smaller (a) and larger (b) than 145 meV. It was found to be proportional to the square root of the flux and to the flux, respectively.

experimental result depicted in Fig. 3 shows direct spectroscopic evidence of an energy "back transfer" with an effective optical activation energy of approximately 145 meV, thus proving its existence and confirming the validity of the excitation mechanism discussed earlier. Moreover, because the quenching effect is measured directly on the PL of the excited Yb^{3+} ion, this activation energy is related to the optically active center, an aspect that remained open in previous studies based on thermal activation. The dependence of parameter W_q on flux is linear for photon energies larger than 145 meV, as can be expected for a one-photon absorption process (Fig. 3). This is in agreement with the identification of the quenching process as an energy back transfer.

The quenching effect observed at small FEL photon energies ($E_{\mathrm{ph}} < 145$ meV) is clearly less efficient, and has a sublinear dependence on the FEL flux, proving that it has a different origin. To account for this effect two

mechanisms can be considered: Auger quenching and carrier tunneling. In the following, these will be discussed briefly.

First, the energy of an excited Yb^{3+} ion can be transferred to free or bound carriers in an Auger process. Indeed, such a mechanism has been proposed for p- and n-type InP:Yb [9] and Si:Er [10]. Free carriers can be generated due to trap ionization by intense MIR radiation [11]. The efficiency of the quenching process is proportional to the concentration of ionized carriers, and in the current case (p-type material) it saturates when all N_A acceptor levels are ionized. The change of the free hole concentration can be described as a competition between ionization and capture processes:

$$\frac{dp}{dt} = C_I(N_A - p)\phi - C_C p^2 = 0 \longrightarrow p = \frac{-C_I(E_{\mathrm{ph}})}{2C_C}\phi + \sqrt{\left(\frac{C_I(E_{\mathrm{ph}})}{2C_C}\right)^2\phi^2 + 2\left(\frac{C_I(E_{\mathrm{ph}})}{2C_C}\right)N_A\phi}, \quad (3)$$

with $C_I(E_{\mathrm{ph}})$ being the ionization cross section at a given FEL photon energy, and C_C the recombination constant between free holes and electrons bound at acceptors. For low flux values, the second term under the square root dominates, and the free hole concentration will be proportional to the square root of the photon flux. This is indeed measured—Fig. 3, bottom left. Since the quenching effect is practically independent of the FEL photon energy, the traps involved in the process are likely to be very shallow.

Alternatively, the PL intensity can be quenched due to deexcitation of the Yb^{3+} ion by a tunneling process between the intermediate state and states in the band [12]. In the limit of small photon energy, this tunneling effect depends on the electric field intensity of the radiation in the laser beam ($\sim$ square root of power), and not on the photon energy, in agreement with the experiment.

In conclusion, we have confirmed the excitation model proposed for RE ions in a semiconductor host in a direct time-resolved spectroscopic experiment. At low temperature, quenching of intra-4f-shell PL from the $^2F_{7/2} \Rightarrow {}^2F_{5/2}$ transition of Yb^{3+} was found upon application of a highly intense, tunable MIR beam from a FEL. A large decrease of PL was observed for photon energies above 145 meV with the effect scaling linearly with the MIR photon flux. This is identified as an optically induced back-transfer mechanism of excitation reversal. The experiment links the isoelectronic level measured at 30 meV below the conduction band to the optically active Yb^{3+} center in InP and validates the previously proposed model, with a RE related level intermediating the excitation process.

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