Excitation Mechanisms and Optical Properties of Rare-Earth Ions in Semiconductors

Stefan Schmitt-Rink, Chandra M. Varma, and Anthony F. J. Levi

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 20 February 1991)

The optical activity of rare-earth ions in semiconductors is discussed taking into account the large $4f$-level correlation energy. In addition to crystal-field effects, three many-body excitation mechanisms of $4f$-$4f$ transitions are identified; coherent or incoherent energy transfer via electron-hole pairs and non-equilibrium electron excitation. The first two give rise to novel nonlinear optical effects, while the last promises a simple means of achieving optical gain.

PACS numbers: 71.55.−i, 72.10.−d, 78.45.+h, 78.55.−m

The sharp $4f$-$4f$ transitions of rare-earth ions present an interesting possibility for linear and nonlinear optical processes when they are inserted into semiconductors and insulators.[1] The use of rare-earth lasers and amplifiers in optical fibers is well known.[2] Recently, optical luminescence and electroluminescence from $4f$-$4f$ transitions for rare-earth impurities in Si and compound semiconductors have been reported; however, the microscopic excitation mechanism has remained unclear.[3]

Because of the very large $4f$-level correlation energy, the energy transfer from the semiconductor states to the rare-earth impurities must be between isocharge states of the latter. The excitation processes are then of the (resonant) Auger variety. This introduces new physical considerations not usually found for other kinds of impurities. We derive below an effective Hamiltonian for such processes and analyze it to discover novel optical and electro-optical properties unique to rare-earth-doped semiconductors.

First we discuss the framework in which electronic levels of rare-earth ions in semiconductors ought to be discussed, since the one-electron manner of thinking is often unhelpful.[4] The charge configuration of a rare-earth ion with m $4f$ electrons and m' electrons in the outermost shells is assigned a valence on the basis of the number of $4f$ electrons, since the outer electrons are bound loosely enough that in the solid state they usually spread out. Consider the electronic configurations $4f^{m-1}$, $4f^m$, $4f^{m+1}$ of an ion, with respective ground and excited states $|4f^i, J_\alpha^{(i)}\rangle$, where J_α are the multiplet total angular momentum quantum numbers. Let μ be the chemical potential of a reservoir with which such ions are very weakly in contact. There will exist some boundary $E_{m-1,m}$ such that (at $T=0$) the ion will be in the $|4f^{m-1}, J_g^{(m-1)}\rangle$ ground state for $\mu < E_{m-1,m}$ and in the $|4f^m, J_g^{(m)}\rangle$ ground state for $\mu > E_{m-1,m}$. Similarly, a boundary $E_{m,m+1}$ can be defined. $E_{m-1,m}$ is the ionization level for the $4f^m$ configuration and $E_{m,m+1}$ is the affinity level. The difference between the two is the intra-atomic Coulomb repulsion

$$U \equiv E_{m,m+1} - E_{m-1,m}, \tag{1}$$

which in a rare-earth ion is typically ~ 10 eV. For mixed-valence ions like Ce or Yb, the boundaries are very asymmetric.[4] For instance, the total energies of the $4f^{13}$ and $4f^{14}$ configurations differ by ~ 1 eV, while that of $4f^{12}$ differs from these by ~ 10 eV. Since optical matrix elements are enhanced by mixing with outer states due to crystal-field effects, such ions are ideal for optical activity.

The affinity levels of a semiconductor are the conduction bands and the ionization levels are the valence bands, both labeled by crystal momentum k and band index n. The affinity and ionization levels are separated by a band gap E_g. When rare-earth ions are inserted into a semiconductor, the relative positions of $E_{m-1,m}$, $E_{m,m+1}$, and the band edges are determined by considerations of charge neutrality and local lattice deformations, leading to Franck-Condon shifts. If $E_g \ll U$ and interatomic Coulomb interactions and lattice deformations are small, the relative positions of $E_{m-1,m}$ and $E_{m,m+1}$ can be determined by ignoring the gap; i.e., by considering the semiconductor as a metal to a first approximation and using the Friedel sum rule. This may then be corrected by forming impurity gap states (rather than Friedel oscillations). However, the rare-earth impurities and semiconductors of interest are usually different enough in terms of ion size and pseudopotentials that Franck-Condon shifts will be large. We do not address these problems of detail here. The intramultiplet energy differences of the rare-earth impurities are affected only in the meV range by these effects, but the optical matrix elements for $4f$-$4f$ transitions can be strongly enhanced.

It is important to note for our purposes that two distinct situations can arise: (i) Stable valence of the rare-earth impurity, i.e., $E_{m-1,m}$ and $E_{m,m+1}$ not in the band gap of the semiconductor. (ii) Mixed or fluctuating valence[4] of the rare-earth impurity, i.e., $E_{m-1,m}$ or $E_{m,m+1}$ in the band gap of the semiconductor. Then the $4f$ number of the impurity can also change by excitation to band states. These situations are illustrated in Fig. 1. In the latter case, the chemical potential is pinned at $E_{m-1,m}$ or $E_{m,m+1}$ (for pure semiconductor host) and the rare-earth ions fluctuate quantum mechanically between the $4f^m$ and the $4f^{m-1}$ or $4f^{m+1}$ configurations. (A strong possibility exists in this case for "inhomogene-
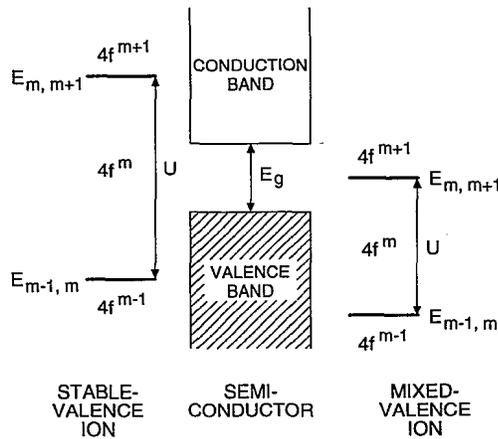
FIG. 1. The relative positions of ionization levels $E_{m-1,m}$ and affinity levels $E_{m,m+1}$ of rare-earth ions with respect to the semiconductor levels for both the stable-valence and the mixed-valence cases.
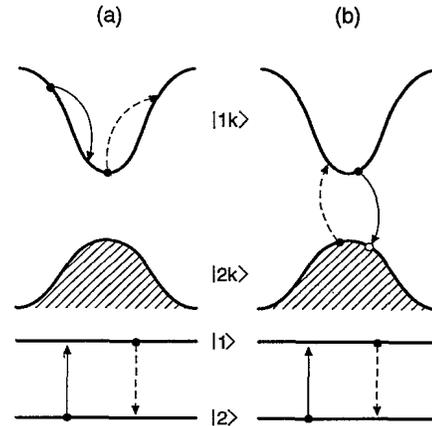

FIG. 2. (a) Intraband and (b) interband excitation (solid curve) and deexcitation (dashed curve) of $4f$-$4f$ transitions. The semiconductor need not be direct, since momentum is not conserved. Also, the absolute energetic position of the $4f$ multiplets with respect to the semiconductor band gap is arbitrary; only their splitting is important.

ous mixed valence," i.e., two different stable valences in sites of different coordination.) We will defer discussion of case (ii), which is expected to be less frequent, to another time. We note, however, that in general intramultiplet optical transitions of both configurations are expected if the decay rate of each is much faster than the energy difference between the two. In the opposite ("motionally narrowed") case, only one set of optical transitions occurs at intermediate frequencies.

We will now derive the coupling of the intramultiplet transitions to the excitations of a semiconductor for case (i) of a stable $4f^m$ configuration with multiplets labeled by α. The energy levels $E_{m-1,m}$ are abbreviated as ε_α, and the energy levels $E_{m,m+1}$ as $\varepsilon_\alpha + U$. The repulsion between electrons in any two multiplets is taken to be the same, equal to U, and the (small) crystal-field splittings in a given multiplet are ignored. A good representation of the problem is in terms of the Anderson model[5]

$$H = H_0 + V, \tag{2a}$$

where

$$H_0 = \sum_\alpha \varepsilon_\alpha c_\alpha^\dagger c_\alpha + \frac{U}{2} \sum_{\alpha \neq \beta} n_\alpha n_\beta + \sum_{nk} \varepsilon_{nk} c_{nk}^\dagger c_{nk} \tag{2b}$$

and

$$V = \frac{1}{\sqrt{N}} \sum_{ank} (V_{nk\alpha} c_{nk}^\dagger c_\alpha + V_{nk\alpha}^* c_\alpha^\dagger c_{nk}). \tag{2c}$$

The hybridization V couples the multiplets α to a linear combination of semiconductor states with the same point symmetry about the impurity sites. N is the number of lattice sites. For $V \to 0$, we may use the Schrieffer-Wolff transformation[6] to eliminate V to second order. For $U \to \infty$, we obtain

$$H = H_0 + H_1 + H_2 + H_3. \tag{3a}$$

Here, H_1 represents the impurity-band interactions,

$$H_1 = -\frac{1}{2N} \sum_{\substack{nkn'k' \\ \alpha \neq \beta}} (J_{n'k'\alpha,nk\beta} c_\alpha^\dagger c_\beta c_{nk}^\dagger c_{n'k'}$$

$$- J_{n'k'\beta,nk\beta} c_\alpha^\dagger c_\alpha c_{nk}^\dagger c_{n'k'}). \tag{3b}$$

H_2 and H_3 represent renormalizations of the impurity and band electron states by $O(J)$ and may be ignored for our purposes. The coupling constant J is given by

$$J_{n'k'\alpha,nk\beta} = V_{n'k'\alpha}^* V_{nk\beta} \left[\frac{1}{\varepsilon_\alpha - \varepsilon_{n'k'}} + \frac{1}{\varepsilon_\beta - \varepsilon_{nk}} \right]. \tag{3c}$$

For clarity, we consider only a single valence band $|2k\rangle$ and a single conduction band $|1k\rangle$, as well as the ground multiplet $|2\rangle$ and a single excited multiplet $|1\rangle$ of the impurity, ignoring the degeneracies of the latter (see Fig. 2). On the basis of the Hamiltonian Eq. (3), four possible excitation (or deexcitation) mechanisms result then for state $|1\rangle$; two of these are "coherent" and two are "incoherent."

(i) Most obviously, the impurity may be excited directly and coherently by light via forced electric dipole transitions. This crystal-field effect is well documented in the literature[1] and is not the subject of this article.

(ii) In direct-gap semiconductors, the impurity may be excited indirectly but coherently by light via intermediate electron-hole pair states. The latter can be either real or virtual. This process can be readily understood by considering only the resonant terms in Eq. (3b) and averaging over the semiconductor degrees of freedom:

$$H_1 \to \sum_\alpha (\bar{\varepsilon}_\alpha - \varepsilon_\alpha) c_\alpha^\dagger c_\alpha - (\Delta c_1^\dagger c_2 + \Delta^* c_2^\dagger c_1), \tag{4a}$$

where

$$\bar{\varepsilon}_a - \varepsilon_a = \frac{1}{2N} \sum_{\substack{nk \\ \beta \neq a}} J_{nk\beta,nk\beta} \langle c^\dagger_{nk} c_{nk} \rangle \tag{4b}$$

and

$$\Delta = \frac{1}{2N} \sum_k J_{1k1,2k2} \langle c^\dagger_{2k} c_{1k} \rangle . \tag{4c}$$

Equation (4b) describes a shift of the multiplets $|1\rangle$ and $|2\rangle$ induced by a population in the conduction band $|1k\rangle$ or valence band $|2k\rangle$, while Eq. (4c) describes a coherence of the multiplets induced by a coherence of the semiconductor. The problem defined by Eqs. (2b) and (4) is thus the same as that of a two-level system with transition energy $\bar{\varepsilon}_1 - \bar{\varepsilon}_2$ excited by an applied field Δ (and hence can be solved exactly).

For a monochromatic laser field $Ee^{-i\omega t}$ exciting the semiconductor via an interband dipole matrix element μ_{12k}, we have, to lowest order in E,

$$\Delta = \frac{1}{2N} \sum_k \frac{J_{1k1,2k2}\mu_{12k}Ee^{-i\omega t}}{\varepsilon_{1k} - \varepsilon_{2k} - \omega - i0} = O(E|E|^2) . \tag{5a}$$

The induced population $n_1 = \langle c^\dagger_1 c_1 \rangle$ in the excited multiplet $|1\rangle$ is then given by

$$n_1 = \frac{2\gamma_\perp}{\gamma_\parallel} \frac{|\Delta|^2}{(\varepsilon_1 - \varepsilon_2 - \omega)^2 + \gamma_\perp^2} + O(|E|^4) . \tag{5b}$$

Here, $\gamma_\perp$ and $\gamma_\parallel$ are the transverse and longitudinal relaxation rates of the 4f-4f transition, resulting, e.g., from radiative decay and coupling to phonons.

Expression (5b) shows resonances at the 4f-4f transition energy $\omega = \varepsilon_1 - \varepsilon_2$ and, through Δ, at the continuum of interband transition energies $\omega = \varepsilon_{1k} - \varepsilon_{2k}$. In fact, if the momentum dependence of J and μ is neglected, Δ is proportional to the complex linear optical susceptibility

of the semiconductor. The physical process described by Eqs. (5) is one whereby an electron hops from the impurity ground state $|2\rangle$ to a valence-band state $|2k\rangle$, absorbs a photon and is promoted to a virtual or real conduction state $|1k\rangle$, and finally hops back to the excited impurity state $|1\rangle$. In direct-gap semiconductors, 4f-4f transitions can thus be excited efficiently at all energies close to or above the band gap.

A direct multiplet population inversion based on the above mechanism is of course not possible, because, for large values of Δ, n_1 will saturate at the value $\frac{1}{2}$. However, standard multilevel schemes may be employed to achieve an inversion of, say, a third multiplet $|3\rangle$ fed by $|1\rangle$ via fast nonradiative processes.[2] We also note that the above formalism may be extended to include the effects of Coulomb interactions among the semiconductor states (such as excitons) and nonlinear optical effects.[7] We expect a whole new class of such effects mediated by the "local field" Δ, such as novel four-wave-mixing and electronic Raman processes. Equations (4) and (5) also suggest the possibility of directly modulating the optical response at one frequency by the light of a different frequency. These phenomena will be addressed in a longer publication.

(iii) The impurity may also be excited incoherently by impact ionization, following optical or electrical carrier injection into the semiconductor. There are two possible mechanisms described by the first term in Eq. (3b), with $n = n'$ and $n \neq n'$, respectively. [The second term in Eq. (3b) conserves the multiplet population.] The intraband ($n = n'$) term describes a physical process wherein an electron in the conduction or valence band scatters from k to k'; simultaneously, the impurity electron undergoes a transition from $|2\rangle$ to $|1\rangle$ or $|1\rangle$ to $|2\rangle$ [see Fig. 2(a)]. The former case corresponds to impact excitation, and the latter to Auger recombination. In second-order perturbation theory, we obtain for the resulting temporal evolution of n_1

$$\left. \frac{\partial}{\partial t} n_1 \right|_{\text{intraband}} = - \left(\frac{1}{2N} \right)^2 \sum_{nkk'} |J_{nk'1,nk2}|^2 2\pi\delta(\varepsilon_1 - \varepsilon_2 + \varepsilon_{nk} - \varepsilon_{nk'})$$

$$\times [n_1(1 - n_2)f_{nk}(1 - f_{nk'}) - (1 - n_1)n_2(1 - f_{nk})f_{nk'}] , \tag{6a}$$

where $f_{nk} = \langle c^\dagger_{nk} c_{nk} \rangle$ is the band electron distribution. If a quasiequilibrium distribution is assumed for the latter, i.e., $f_{nk} = 1/\{\exp[(\varepsilon_{nk} - \mu_{nk})/k_BT] + 1\}$, the intraband collision term tries to establish a thermal multiplet population of the form $n_1 = 1/\{\exp[(\varepsilon_1 - \varepsilon_2)/k_BT] + 1\} < \frac{1}{2}$; i.e., a direct multiplet population inversion is again not possible. The situation is different if the band electrons are out of equilibrium. Then the second (impact) term in Eq. (6a) may dominate over the first (Auger) one, as is also obvious from Fig. 2(a). This may be achieved, for example, by high-field transport in an impact p-n diode.

(iv) The interband ($n \neq n'$) term describes a similar physical process, except that now the semiconductor electrons change bands as well [see Fig. 2(b)], leading to a collision term

$$\left. \frac{\partial}{\partial t} n_1 \right|_{\text{interband}} = - \left(\frac{1}{2N} \right)^2 \sum_{kk'} |J_{1k'1,2k2}|^2 2\pi\delta(\varepsilon_1 - \varepsilon_2 + \varepsilon_{2k} - \varepsilon_{1k'})$$

$$\times [n_1(1 - n_2)f_{2k}(1 - f_{1k'}) - (1 - n_1)n_2(1 - f_{2k})f_{1k'}] . \tag{6b}$$

In quasiequilibrium this yields

$$n_1 = 1/\{\exp[(\varepsilon_1 - \varepsilon_2 - \mu_1 + \mu_2)/k_B T] + 1\} < 1 ;$$

i.e., a direct multiplet population inversion becomes possible if $\varepsilon_1 - \varepsilon_2$ falls into the spectral range of stimulated emission from the semiconductor, $\varepsilon_1 - \varepsilon_2 < \mu_1 - \mu_2$. Note that this process is purely electronic and does not involve exchange of photons between the semiconductor and the impurity. (It also does not require the multiplet states to be energetically degenerate with the active semiconductor states, as often assumed.)

All of the above processes may be exploited directly or indirectly (in multilevel schemes) to obtain luminescence or even lasing action from rare-earth ions in semiconductors. In fact, (room temperature) excitation of $4f$-$4f$ transitions via semiconductor electron-hole pairs[8] or nonequilibrium electrons[9] appears to have been achieved recently in III-V compounds. Experimental results are also beginning to appear for rare-earth-doped Si.[10]

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