Optical and Photonic Glasses

Lecture 32:
Rare Earth Doped Glasses II

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As an **example**, let us consider the **ground state of the Er^{3+} ion**.

Er has the electronic configuration $[Xe]4f^{12}6s^2$, so Er^{3+} has 11 f electrons ($[Xe]4f^{11}$).

With such a large number of electrons in its f-shell, many different values of L, S and J are possible.

For example, values of L corresponding to S, F, H, I, …etc., are possible. When L = 6 (corresponding to state I) and S = 3/2 (the total spin quantum number for 11 f electrons can be 3/2, with 3 unpaired, or 1/2, with only one unpaired), one has the following combinations leading to the possible values of J:

$$J = L+S, L+S-1, …, |L-S| \qquad or \qquad J = 15/2, 13/2, 11/2, 9/2$$

Therefore, the four lowest energy states of the Er^{3+} ion (those with larger spin) are:

$$^4I_{15/2} \,, \, ^4I_{13/2} \,, \, ^4I_{11/2} \text{ and } ^4I_{9/2}$$

with the first (of > J) being the ground state, of lowest energy. Each $^{2S+1}L_J$ term is itself a *multiplet*, composed of (2J+1) degenerate energy levels (the Stark components), which may however be split by an electric field due to ion-lattice interactions, particularly in crystals.

Electronic energy terms: $^{2S+1}L_J$

where: $L = |\mathbf{L}| = |\Sigma\, \mathbf{l_i}|$ $S = |\mathbf{S}| = |\Sigma\, \mathbf{s_i}|$ $\mathbf{J = L + S}$

this corresponds to the so-called L-S (or Russell-Saunders) spin-orbit angular momentum coupling scheme, which is generally favored for lighter atoms (including most RE ions). For the heavier atoms, the so-called j-j coupling may be used, where the individual angular momenta are first coupled, for each electron and the resultant j values of the individual electrons couple for the whole atom, in the end.

Selection rules

Selection rules are rules about the possible values of the quantum numbers of the initial and final states of a given transition, indicating whether it is *allowed* or *forbidden*. Most electronic transitions, such as those between electronic energy configurations of the RE ions, are *electric-dipole* in nature and, for those, the selection rules are:
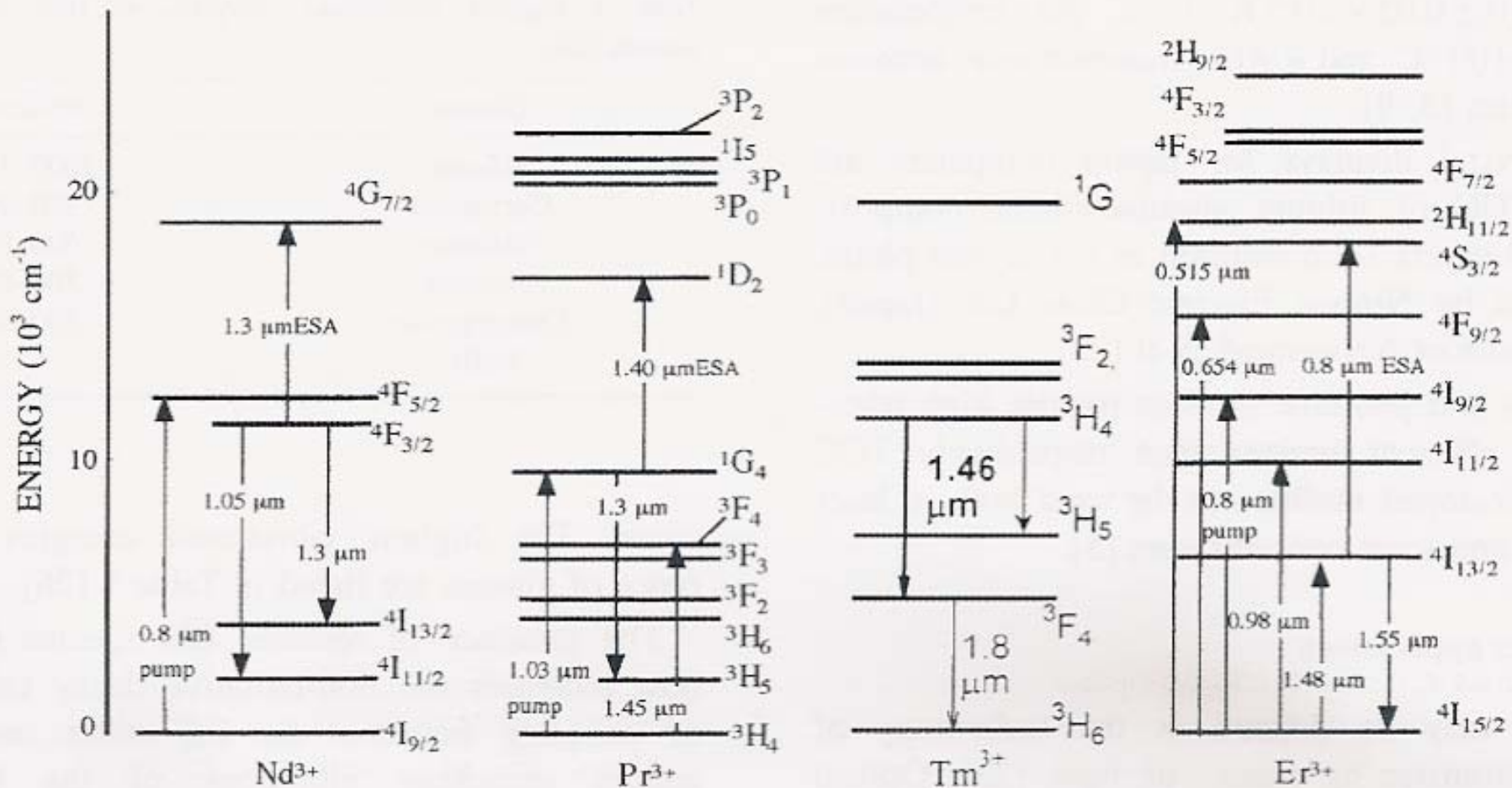
-The *parity* of the initial and final states must be different (g ⟵⟶ u , only), sometimes called the Laporte rule
- $\Delta L = \pm\, 1$
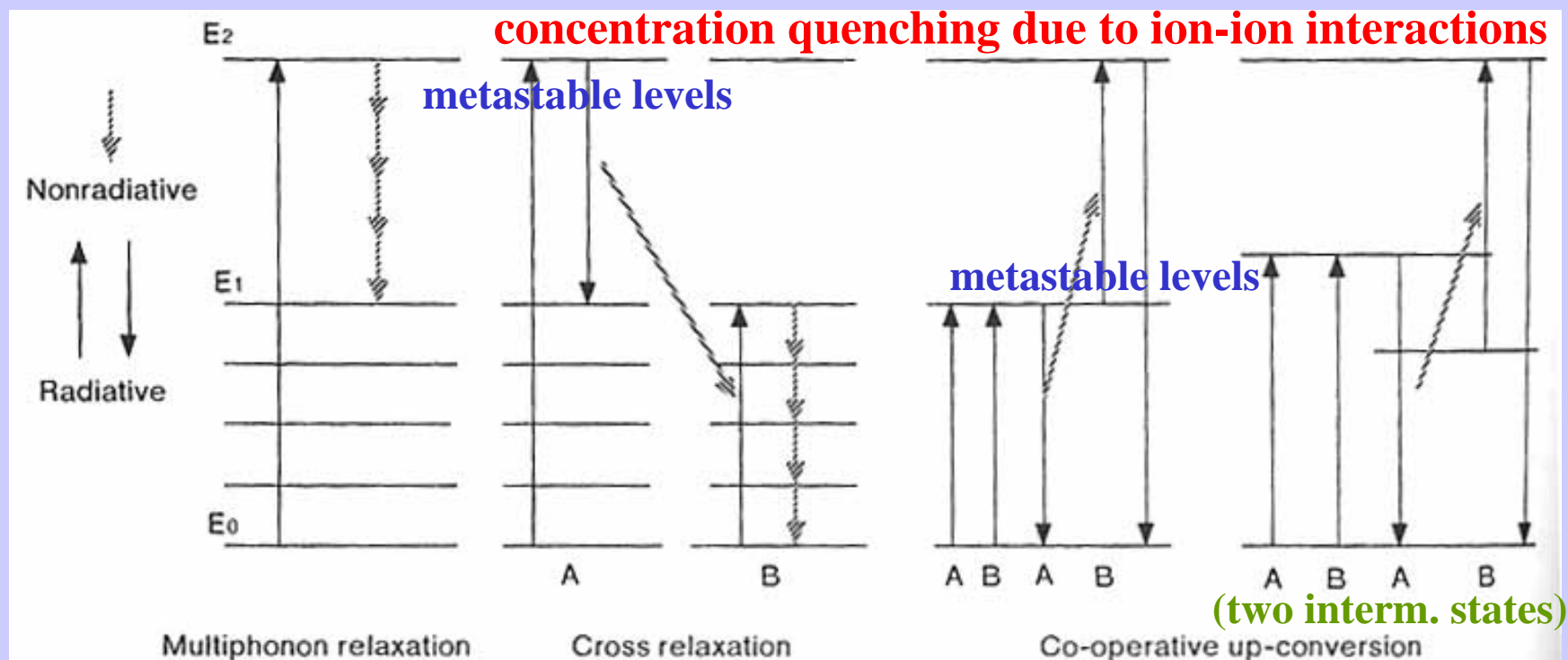- $\Delta S = 0$ (spin conservation)

Possible RE ion dopants for glassy hosts

Simplified electronic energy level diagrams of three different RE ions and relevant transitions for pumping and emission.

For RE ions, f → f transitions are *electric dipole* **forbidden**, since all states are odd (**u**) and the **Laporte** *selection rule* (i.e., the initial and final states must have different parity) is not obeyed. In **solids**, however, quantum admixing of higher lying states of opposite parity into the $4f^n$ configuration introduce a *degree of electric dipole strength* into the f → f transitions, as long as the ion site lacks inversion symmetry, as it usually does in glasses. However, for Er^{3+} at 1.5 μm, the electric and magnetic dipole strengths are comparable, particularly for a silica glass host.

Non-radiative transitions may be the result of interaction of the RE ions with **vibrations** of the host, either *intrinsic* or due to *impurities*. The ion makes a non-radiative transition to a lower electronic state through the emission of multiple phonons to conserve energy. When the non-radiative relaxation rate is comparable to the radiative one, the PL efficiency is degraded. Higher order multiphonon (MP) processes can be significant, because the electron-phonon interaction is strong and the phonon density of states is high for any solid. Yet, such transition rates fall off rapidly with increasing order of the process, i.e., with the number of phonons required to bridge the energy gap between two J multiplets. Therefore, the dominant contribution always comes from the highest energy phonons of the host.

Different types of possible non-radiative relaxation processes

concentration quenching due to ion-ion interactions

metastable levels

Nonradiative

Radiative

E_2

E_1

E_0

A   B

A B A B

metastable levels

A B A B

(two interm. states)

Multiphonon relaxation   Cross relaxation   Co-operative up-conversion

Nonradiative relaxation processes, (a) Multiphonon relaxation, (b) Cross relaxation, (c) Co-operative up-conversion. **(b) and (c) → concentration quenching.**

(Adapted from: *Glasses for photonics*, M. Yamane and Y. Asahara, Cambridge Univ. Press, 2000)