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Resonance effects in energy transfer in CdF_2:Er,Yb crystals

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The mechanism of light up and down (infrared ⇄ visible) conversion in CdF_2:Yb,Er crystals is presented. It is shown that the temperature dependence of the efficiency of these processes is governed by the temperature dependence of the spectral overlap between Er and Yb ions.

Since the discovery in 1966 of an efficient infrared (ir) to visible (VIS) light up-conversion in heavily doped crystal hosts by Yb-Er, Ho, or Tm ions, this phenomenon has been studied very intensively (see Ref. 1 for recent review). One of the main stimuli was practical applicability of the up-conversion effect in construction of efficient green, blue, and red emitters pumped by the very efficient GaAs:Si ir light-emitting diodes (LED's).[2] In spite of the research efforts in this field several aspects of the mechanism of the energy transfer and energy migration in this system remained unclear. The main object of this work was to clarify the role of spectral overlaps between various optical transitions in Er^{3+} and Yb^{3+} ions in energy transfers leading to the light converter action, in the Yb-Er system.

The light conversion was studied in CdF_2 crystals doped with 10 mol% Er and 1 mol% Yb. Such a concentration was shown by Greenblatt and Banks[3] to give a very efficient ir to green light conversion in CdF_2 crystals.

Ir excitation in the region of Yb^{3+} absorption (0.9–1 μm) leads to an efficient characteristic Er^{3+} green emission (Fig. 1). Besides the dominant ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ green emission, intense red ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ and infrared ${}^4S_{3/2} \rightarrow {}^4I_{13/2}$ emission was observed. The intensity of these emission bands shows an almost perfect quadratic dependence on the ir pump light intensity. This proves that the ${}^4S_{3/2}$ and ${}^4F_{9/2}$ Er^{3+} levels are populated in a two-quantum excitation process by the energy transfer from Yb^{3+} to Er^{3+}. At higher ir pump intensity a blue emission is also observed. This is due to a triple energy transfer.

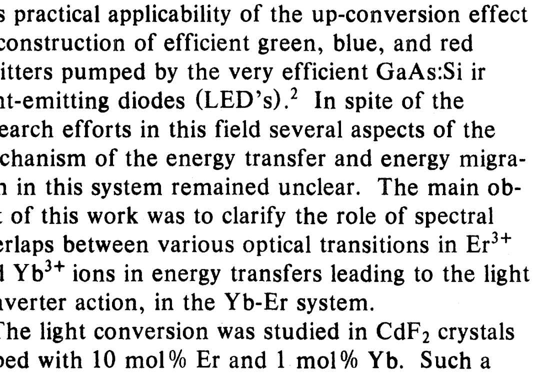

FIG. 1. Ir (0.9-λ_{exc}-1 μm) excited spectrum of CdF_2:Er, Yb crystal. Er^{3+} radiative transitions are shown in the diagram.

The probability of a nonradiative energy transfer between Yb^{3+} and Er^{3+} ions has been estimated from the temporal evolution of the Er^{3+} emission under pulsed ir excitation. An analysis based on the rate equation model proposed by Kingsley[4] showed that the energy transfer probability is greater than 2×10^4 s^{-1} at 295 K.

In CdF_2 crystals the rare-earth R impurities are known to substitute for divalent Cd ions.[5] The nonisoelectronicity of R^{3+} ions in the fluorite host requires charge compensation in order to maintain the 3+ charge impurity state. It can be achieved in several ways but the most common is the interstitial F^- compensation.[6] In fluorite-type crystals the R^{3+} ions are easily converted to a 2+ charge state[6] deleterious for the converter action. CdF_2 is very advantageous in this respect, since such charge conversion does not occur for R [except Eu (Ref. 7)] neither by chemical nor by photochemical reactions. Such a pecularity caused by the high electron affinity of CdF_2 compared to the other fluorites leads also to a unique property of CdF_2, namely, to the possibility of its conversion from an insulating to a highly conducting state (see Ref. 8 for review). Trivalent R ions act here as the shallow donors.[9] A high electron conductivity can also be harmful for the light conversion since it may lead to the luminescence quenching by the Auger effect.[10] Therefore, all the crystals studied were prepared in a nonconducting form. It is worth pointing out, however, that a very intense uv light degraded temporarily the up-converter action, which could be caused by local electron photogeneration leading to the above-mentioned Auger quenching.

Due to the nonisoelectronic character of both the R ions in CdF_2 as well as to their high concentration, various symmetries[11] and ion complexing[12] may be expected. A comparison of the emission spectra of the converter with those observed in CdF_2:Er^{3+} (Ref.

13) shows similarities with the spectra of the very low-symmetry *U* centers. In contrast, a direct selective dye laser excitation of Er^{3+} shows also other types of centers, nonactive in the light conversion process. Since various R^{3+} centers contribute roughly in proportion to their concentration to the absorption spectra (this is strictly true for the MD transitions, but not for the symmetry allowed ED transitions), a comparison of the excitation spectra of the up (Yb to Er transfer) and down (Er to Yb transfer) light conversion with the Er^{3+} and Yb^{3+} absorption spectra in the CdF_2:Er,Yb crystals gives information on the initial path for the converter action (the energy migration between various centers should also be taken into account in the analysis). The similarity of the absorption and excitation spectra presented in Fig. 2 proves that the light conversion takes place among most Yb and Er ions present in the crystals and not in a special type of centers or complexes. Due to a very high impurity concentration, any discussion of the symmetry of the Er or Yb sites seems meaningless. This observation greatly simplifies a quantitative analysis of the process, allowing for treating Yb and Er ions as forming two interacting impurity subsets, characterized by average interaction parameters.

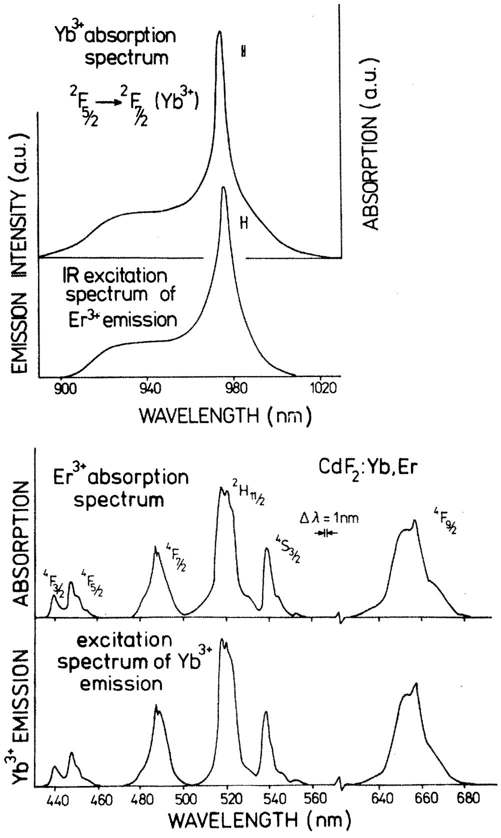

FIG. 2. Spectra of (a) up-conversion excitation spectrum and Yb^{3+} absorption, (b) down-conversion excitation spectrum and Er^{3+} absorption in CdF_2:Er 1 mol%, Yb 1 mol% crystals at 295 K.

The energy transfer between Yb and Er ions is due to the multipolar Coulomb interaction.[1,14] Its probability depends on the spectral overlap between the emission spectrum of the ion transferring energy (sensitizer) and the absorption spectrum of the ion accepting it (activator).[15] One may suspect that strong temperature changes of the up-conversion efficiency observed for Yb-Er couples in many crystal hosts[16] are due to the temperature changes of this overlap. In order to check this supposition the temperature dependence of the up- (Yb to Er) and down- (Er to Yb) conversion was measured in our samples. From Fig. 3 it is clear that major changes occur below 100 K indicating that neither changes of effective distance between impurities nor temperature dependence of the nonradiative phonon deexcitation at either Er or Yb ions can explain the observed dependence. Among the energy transfer paths on all but one the energy quantum transferred between the Er and Yb ions is larger than the energy necessary for activator excitation. The exception is the first transfer from Yb to Er: $({}^2F_{5/2},{}^4I_{11/2}) \rightarrow ({}^2F_{7/2},{}^4I_{15/2})$ proceeding under almost perfect resonance conditions. The reverse transfer belongs to the first class, although the energy surplus is minimal. Therefore, the temperature dependence of this first Yb-to-Er transfer may be responsible for the observed dramatic decrease of the up conversion efficiency shown in Fig. 3 and observed for Yb-Er couples in other crystal hosts.[16] A comparison of the high- and low-temperature Yb^{3+} emission and Er^{3+} absorption spectra in the vicinity of 10 000 cm^{-1} presented in Fig. 4 clearly indicates that the temperature decrease of the spectral overlap between these two spectra causes a switching off of the up-converter action.

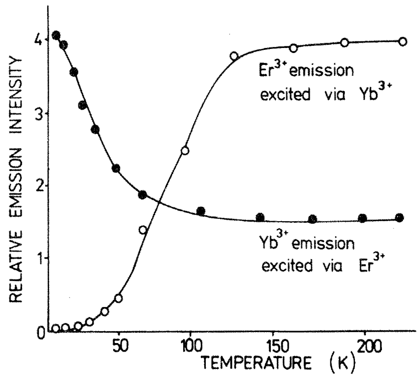

FIG. 3. Temperature dependence of up-conversion (emission at 11 700 cm^{-1} originating from ${}^4S_{3/2}$ Er^{3+} level) excited at 0.9–1-μm region and down-conversion (Yb^{3+} emission) excited via Er^{3+} at 514.5 μm (Ar laser).

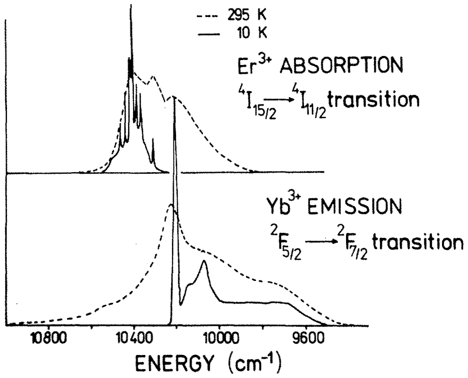

FIG. 4. Absorption spectrum of Er^{3+} and emission spectra of Yb^{3+} in CdF$_2$ crystals in the vicinity of 10 000 cm^{-1} at 295 K (——) and 10 K (– – –).

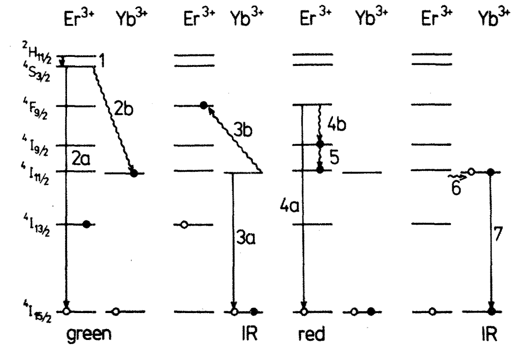

FIG. 5. Deexcitation route at the Er-Yb pair after laser excitation of the $^2H_{11/2}$ Er^{3+} level. Circles denote the status of the pair after each step (○-*na*, ●-*nb*).

An explanation of the low-temperature increase of the Yb^{3+} emission during the down-conversion experiment (excitation was achieved by 514-nm Ar laser line almost resonant with the position of the $^2H_{11/2}$ Er^{3+} level) is less straightforward. Deexcitation of the Er^{3+} ions in the presence of Yb^{3+} takes place with the energy transfer of Yb^{3+}. This holds true especially for the green emitting $^4S_{3/2}$ Er^{3+} level, whose lifetime dramatically decreases when Yb ions are present.[17] The deexcitation route of the laser excited $^2H_{11/2}$ level is shown in Fig. 5. All three energy transfers (2*b*, 3*a*, and 6) proceed with phonon emission and are thus relatively weakly temperature dependent. In heavily doped crystals the energy migration among Yb^{3+} ions is very fast. Thus the energy received by Yb from Er during its deexciation may be either radiatively emitted (3*b* and 6) or may participate in the up-conversion process decreasing the efficiency of the Yb emission. At temperatures below 100 K the up-conversion process is stopped and therefore the only deexcitation path remains that illustrated in Fig. 5 and Yb^{3+} emission should increase. The more than twofold increase indicates a speed of the back transfer from Yb to Er at higher temperatures which is high in comparison with the radiative emission rate of Yb^{3+}. This is consistent with the high efficiency of the light up conversion at temperatures above 100 K as well as the estimates of the energy-transfer probability inferred from an analysis of the kinetics up conversion, discussed in the first part of this Communication.

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