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ENERGY TRANSFER IN  $\text{CsCdBr}_3:\text{Nd}^{3+}$  SYSTEM \*R.B. Barthem\*\*, R. Buisson, J.C. Vial and J.P. Chaminade<sup>†</sup>*Laboratoire de Spectrométrie Physique (L.A. du CNRS), Université Scientifique et Médicale de Grenoble, BP 87, 38402 Saint Martin d'Hères Cedex, France**†Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 33405 Talence Cedex, France*

**Résumé** - Les cristaux du type  $\text{CsCdBr}_3$  dopés avec des ions terres rares trivalents sont bien adaptés pour étudier les transferts d'énergie. Les ions trivalents peuvent se grouper en paires autour d'une vacance de  $\text{Cd}^{2+}$ . Les relaxations coopératives doivent alors être très efficaces. Une comparaison des spectres d'absorption et d'excitation montre que, même à très faible concentration, les ions sont presque tous groupés en paires d'un seul type.

**Abstract** -  $\text{CsCdBr}_3$  doped with trivalent rare earths is an attractive system to study energy transfer phenomena. Trivalent rare earths substituted to  $\text{Cd}^{2+}$  can be associated in pairs close to a  $\text{Cd}^{2+}$  vacancy. In these systems, cooperative relaxation (up conversion and cross relaxation) are very efficient. A comparison between  $\text{Nd}^{3+}$  absorption and excitation spectra shows that the great majority of  $\text{Nd}^{3+}$  are associated in one kind of pairs even in low doping crystals.

## I - INTRODUCTION

$\text{CsCdBr}_3$  belongs to a series of  $\text{AMX}_3$  halides which have structures similar to that of  $\text{CsNiCl}_3$ . In this hexagonal lattice the  $(\text{CdBr}_6)^{4-}$  distorted octahedra share opposite faces to form infinite linear chains. These compounds are accommodating host materials: a large variety of divalent or trivalent metal ions can be introduced as impurities into the chains. Since trivalent ions are substituted to  $\text{M}^{2+}$  ions a charge compensation is required. Mc Pherson /1/ has demonstrated the tendency of trivalent ions to enter a chain in pairs. Two trivalent ions are located on either side of a vacant divalent ion site, the  $\text{M}^{3+}$  - vacancy -  $\text{M}^{3+}$  complex being electrostatically equivalent to three divalent ions.

Previous experiments in other systems /2,3/ have shown it is possible to study non radiative energy transfer between the two ions of specific classes of pairs even if the ion distribution is random on the crystal sites. Among the various possibilities of pair relaxation, the up conversion is of particular interest. Since it needs the double excitation (i.e. the excitation of both ions) the excitation spectra of up conversion can reveal the nature of some optical lines.

With these views we decided to study absorption and time resolved excitation spectra of luminescence of weakly doped  $\text{CsCdBr}_3:\text{Nd}^{3+}$  crystals. It appeared that, due to slow multiphonon relaxation, luminescence and energy transfer are very efficient in this system.

## II - SAMPLE PREPARATION

The compounds  $\text{CsCdBr}_3:\text{Nd}^{3+}$  was prepared by dissolving  $\text{CsBr}$ , the stoichiometric amount of Cd salt and 0.1% (or 1% for one sample)  $\text{Nd}^{3+}$  in an aqueous solution of  $\text{HBr}$ . The compound obtained was dried under vacuum and crystalized by the Bridgman method. Large ( $\approx 20 \times 10 \times 7 \text{ mm}^3$ ) non hygroscopic single crystals were obtained.

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## III - RESULTS AND DISCUSSION

In first approximation the crystal field symmetry about the cadmium ion is octahedral ( $O_h$ ). Many levels of  $Nd^{3+}$  should be degenerated and intraconfigurational optical electric dipole transition are forbidden. In fact, structural studies have shown it exists a slight trigonal distortion along the C axis and the point symmetry at the  $Cd^{2+}$  site is lowered to  $D_{3d}$ . In addition, for trivalent ions located at  $Cd^{2+}$  sites the charge compensation can lower the symmetry to  $C_{3v}$ . Consequently the invariance by inversion is removed and electric dipole transitions are allowed. For  $Nd^{3+}$  in  $CsCdBr_3$  the above perturbations seem to be small. As we can see in fig. 1, the absorption spectrum from the fundamental  $4I_{9/2}(o)$  to  $4G_{5/2}$  and  $2H_{11/2}$  multiplets can be explain, in first approximation, in the frame of octahedral ( $O_h$ ) point symmetry:  $2H_{11/2}$  gives four lines between 5890 Å and 6050 Å but two of them (near 5940 Å) are nearly degenerate doublets. This is conform to the reduction of  $J = 11/2 \rightarrow \Gamma_7 + \Gamma_6 + 2 \Gamma_8$  in the  $O_h$  point symmetry.  $4G_{5/2}$  (which gives lines near 5840 Å) can be interpreted in the same manner but the trigonal distortion effects seems to be more important. The spectral behaviour of other transitions (not shown here) can be explain by the same approximation. This trigonal distortion is also responsible for the strong polarization of the observed lines.

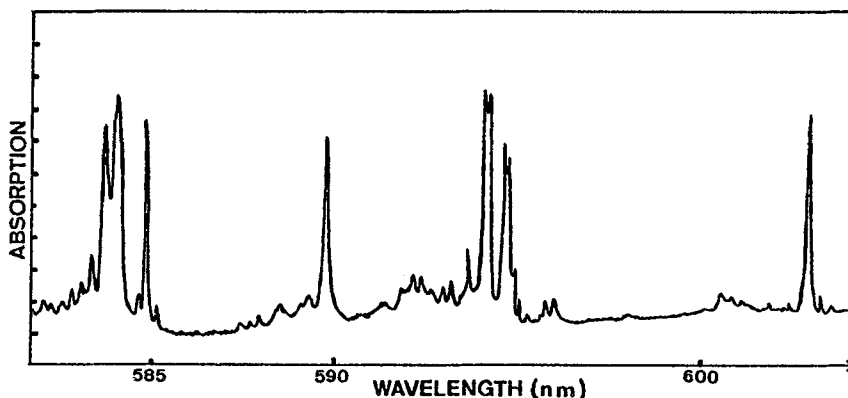
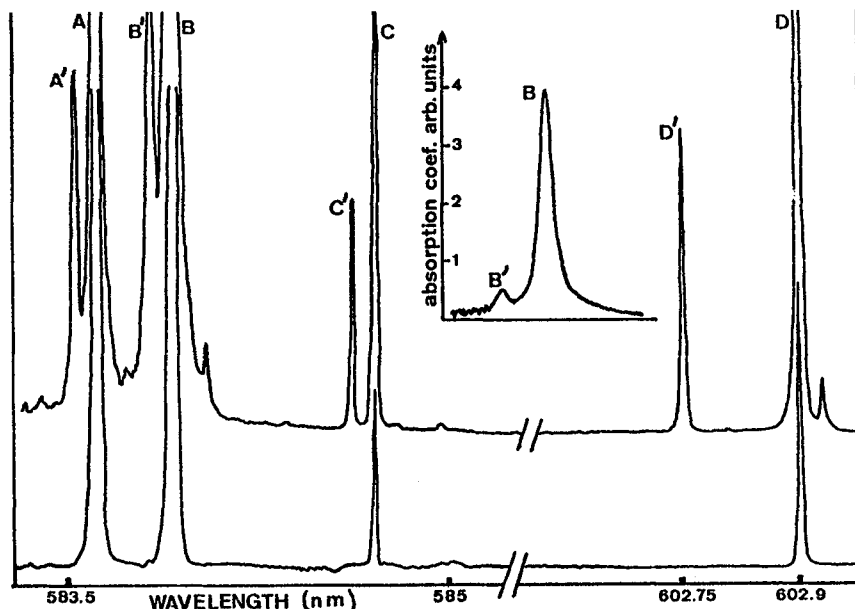


Fig. 1 - Non polarized absorption spectra of a  $CsCdBr_3 Nd^{3+}$  (1%) sample at 4 K.

The main lines are surrounded by numerous weaker lines which are not so well polarized and many of which disappear in low doping crystals. So that, in the following we do not take into account these weaker lines.

Pulse excitation of a  $4I_{9/2} \rightarrow 4G_{5/2}$  or  $2H_{11/2}$  transition is followed by a fast phonon relaxation so that the lowest level of  $2H_{11/2}$  multiplet (labelled  $2H_{11/2}(o)$  in the following) is populated after a short time. The emission from that level has two components - i) A "normal" fluorescence in the red and infrared - ii) An up conversion fluorescence in the U.V.. This fluorescence can be interpreted as the emission following a cooperative relaxation of doubly excited pairs. For the 1% sample, excitation spectra obtained by monitoring these emissions show a close correspondence with the absorption spectra of fig. 1. However this experiment is not conclusive because the optical lines are too broad. Fortunately, more accurate measurements can be done with a 0.1% sample. We can see on fig. 2 that each line is



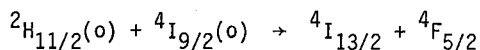
$\text{CsCdBr}_3:\text{Nd}^{3+}$  0.1% at 4 K.

Fig. 2 - Upper and lower curves are respectively the excitation spectra of normal fluorescence and up conversion for  $4I_{9/2}(o) \rightarrow 4G_{5/2}$  and  $2H_{11/2}(o)$  transitions. Insert shows the absorption spectrum of (BB') lines.

split in two components with the same polarization. As before it exists a close correspondence between the absorption spectrum and the excitation spectrum of normal fluorescence but one component of each doublet disappears in the excitation spectra of up conversion. These observations in conjunction with our previous results on  $\text{Pr}^{3+}:\text{LaF}_3$  /2/ and  $\text{Nd}^{3+}:\text{LaF}_3$  /3/ lead us to conclude that the lines A, B, C and D must be associated to pairs of  $\text{Nd}^{3+}$  while A', B', C' and D' are due to "isolated" ions. We may notice that the isolated ion line has a lower intensity than the pair line. That is just the reverse in low doped randomly distributed systems /2,3/. More precisely, as shown by the absorption spectrum of fig. 2, the ratio between the pair and isolated ion line area is  $\approx 9$ . That means that  $\approx 90\%$  of  $\text{Nd}^{3+}$  enter the  $\text{CsCdBr}_3$  crystal as pairs (as we shall see later, the isolated ion and pair cross sections are nearly the same). For the same  $\text{Nd}^{3+}$  concentration ( $\approx 0.1\%$ ) but randomly distributed the ratio should be  $\approx 10^{-4}$ . Our result is in agreement with these obtained by R.P.E. in similar systems /1/.

The dynamical properties of normal and up conversion fluorescence are summarized in fig. 3. The normal fluorescence time dependence is exponential with lifetimes:  $\tau_i = 5.5 \mu\text{s}$  for isolated ions and  $\tau_p = 2.6 \mu\text{s}$  for pairs. The shortening of the pair decay time can be explained either by an enhancement of the radiative (or

multiphonon) transition probabilities or by cross relaxation. The first possibility is ruled out because isolated and paired ions are submitted to nearly equivalent crystal fields. Indeed pair and isolated ion lines are very close. In addition, as pointed out by Wafer and Blasse /4/, paired and isolated trivalent ions are located on nearly equivalent  $\text{Cd}^{2+}$  sites because they are probably both associated to a  $\text{Cd}^{2+}$  vacancy. On the contrary, cross relaxation should be very efficient for paired ions. A transfer according to



(followed by a relaxation to  ${}^4\text{F}_{3/2}$  metastable level) is confirmed by the high efficiency of  ${}^4\text{F}_{3/2}$  fluorescence when pairs are excited into the  $({}^2\text{H}_{11/2}(0), {}^4\text{I}_{9/2}(0))$  level. Also shown in fig. 3 is the time evolution of the up conversion fluorescence. The rise time and decay time of this fluorescence can be interpreted by the model developed in ref. 2. Finally transfer rates can be extracted from the times evolutions reported in fig. 3. They are in the  $(\mu\text{s})^{-1}$  domain.

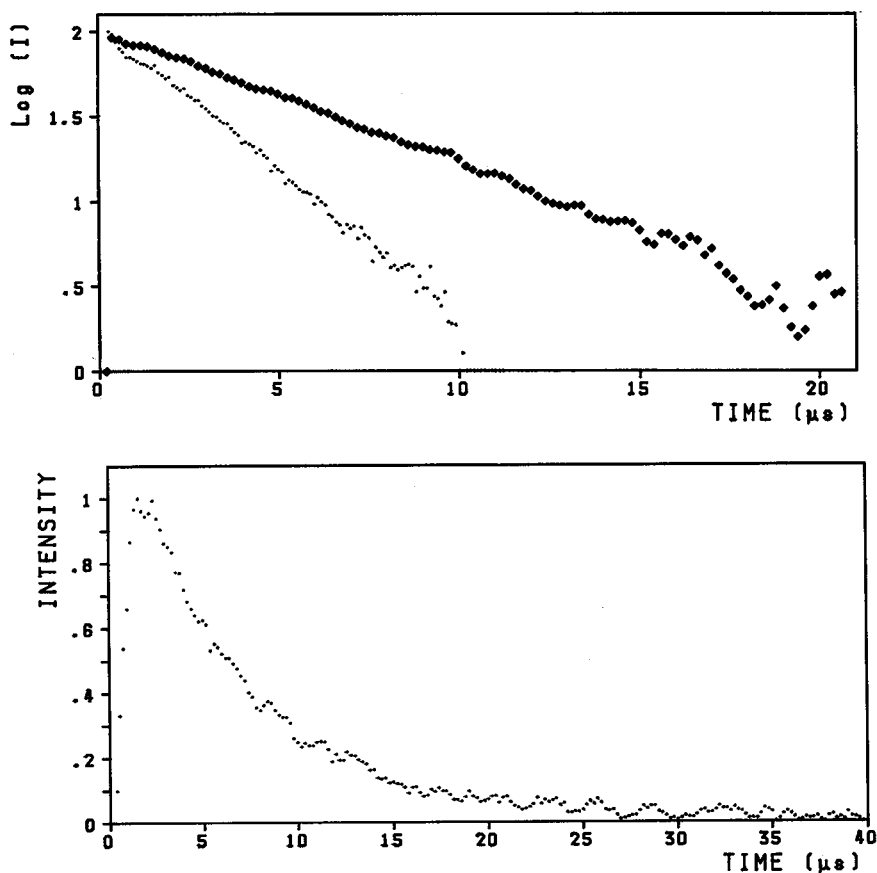


Fig. 3 - Time evolution of normal fluorescence (upper curves) and up conversion (lower curve) following excitation of isolated ions (◆) and pairs (●).

#### IV - CONCLUSION

The analysis of absorption and time resolved excitation and luminescence spectra of weakly doped  $\text{CsCdBr}_3\text{:Nd}^{3+}$  crystals provides some insights into the trivalent rare earth distribution. Our optical technique confirms the results obtained by other means. It can be generalized to similar systems doped with more than one kind of impurities between which energy transfers can occur.

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