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De-excitation processes of optically excited Nd^{3+} pairs in CsCdBr_3 (*)

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Résumé. — Des cristaux de $\text{CsCdBr}_3 : \text{Nd}^{3+}$ ont été étudiés à l'aide des techniques d'excitation sélective par laser pulsé et de spectroscopie en temps résolu. Du fait de la compensation de charge résultant de la substitution de Cd^{2+} par Nd^{3+} , la proportion des ions Nd^{3+} associés en paires est très grande et ne suit pas les lois de la statistique. Cette proportion a été mesurée, sa variation avec la concentration a été mise en évidence et l'effet d'un codopage avec un ion monovalent a été observé. Par comparaison entre les propriétés des ions isolés et des paires, les transferts d'énergie ont pu être analysés. Les chemins de désexcitation depuis quelques niveaux excités ont été déterminés grâce à la dynamique et aux intensités relatives des raies de luminescence. Un comportement inhabituel, pouvant conduire à des applications, a été observé : la luminescence du niveau $^4\text{F}_{3/2}$ est favorisée pour les paires par rapport aux ions isolés. Il est très bien expliqué.

Abstract. — $\text{CsCdBr}_3 : \text{Nd}^{3+}$ crystals have been studied by laser selective excitation and time resolved spectroscopy. Due to the charge compensation resulting from the $\text{Nd}^{3+}/\text{Cd}^{2+}$ substitution, the proportion of Nd^{3+} pairs is very large and does not follow the statistical laws. This proportion has been measured, its variation with concentration has been established and the effect of codoping with a monovalent metal observed. From a comparison between the properties of single ions and pairs, energy transfers have been analysed. De-excitation channels have been determined for some excited levels from the dynamics and the relative intensities of luminescence lines. An unusual behaviour, which can lead to applications, has been observed : the $^4\text{F}_{3/2}$ luminescence of pairs is favoured with respect to that of single ions. This behaviour is well explained.

1. Introduction.

Previous investigations of rare earth ion pairs in insulators have shown the interest of studying their properties for identification and characterization of the ion-ion interaction mechanisms. Based on selective excitation of a given ion species, single ion or ion involved in a pair, these studies were conducted on weakly doped crystals in order to attain the intrinsic properties of these species [1-4]. Indeed, in a random distribution an ion pair is spatially distant from other ions and its behaviour depends only on the interaction between its two ions.

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As shown many years ago by McPherson and Wai-Ming Heung [5] and McPherson and Henling [6] the distribution of trivalent rare earth ions in compounds of the AMX_3 series, where X is an halide, A a monovalent metal and M a divalent metal, is not random. The charge compensation needed by the substitution of M by a trivalent ion produces the association of two rare earth ions around a M vacancy. A few years ago, these doped compounds attracted additional interest for use in luminescence or laser research fields [7-9]. It appeared worthwhile to apply the methods recalled above to compare single ion and pair properties.

$\text{CsCdBr}_3 : \text{Nd}^{3+}$ has been chosen for this study. As only few spectroscopic results are known, a comprehensive analysis of energy level positions has been completed. It will be published elsewhere [10]. In this work we present two types of results. In section 3, the optical properties are used to discuss the problem of the

proportion of clustered ions and the effect of codoping with a monovalent ion. In section 4 energy transfer processes are studied. It will be shown how time resolved techniques are powerful for comparing de-excitation channels for single ions and clustered or pair ions.

2. Experimental procedures.

2.1 CRYSTAL GROWTH. — $\text{CsCdBr}_3:\text{Nd}^{3+}$ powder has been prepared by slow evaporation of HBr aqueous solutions having the correct proportion of CsBr , $(\text{CdBr}_2, 4 \text{H}_2\text{O})$ and NdBr_3 . The obtained powder is then dried under vacuum at 200°C for 24 hours and then introduced into a quartz crystallization ampul. This ampul whose internal diameter is 9 mm or 12 mm and whose length is 150 mm, is then translated at a speed of 1 to 4 mm/h to a region where the temperature is 300°C . This temperature is then slowly reduced (5°C/h) to the room temperature. The temperature gradient in the growing zone is of the order of 30°C/cm . Crystals as large as $20 \times 10 \times 7 \text{ mm}^3$ can be obtained in the ampul.

An alternative method consists in directly mixing CsBr , NdBr_3 and dried CdBr_2 in the quartz ampul. CsCdBr_3 is then produced *in situ* before the growing process starts.

As usual, a segregation occurs in the melt and Nd^{3+} concentration in the crystal is not the same as the starting one. A chemical analysis of one crystal was performed after an absorption spectrum had been recorded. The concentration of every crystal was deduced from a comparison of its absorption spectrum with the reference spectrum.

2.2 EXPERIMENTAL METHODS. — To benefit from the narrowness of the optical lines and reduce phonon effects, experiments have been done at liquid helium temperatures between 1.5 K and 2.1 K. At these low temperatures, the population of $^4\text{I}_{9/2}^{(1)}$ (located at 8 cm^{-1} above the ground state) is negligible [11].

Excitation spectra have been obtained with a modified Sopra dye laser pumped with a Quantel YAG. The pulse duration is 10 ns and the spectral width is 0.1 cm^{-1} . Four different dye mixings have been used to excite various multiplets. A HR-1000 Jobin Yvon monochromator has been used for absorption and luminescence spectra. It was monitored by an Apple II^e microcomputer. For excitation spectra, this monochromator plays the role of a 3 nm wide filter. Such a resolution allows us to select the various luminescence lines emitted by the different Nd^{3+} species and corresponding to a well defined transition. The detectors used were a photomultiplier EMI-9635QB, a GaAs Hamamatsu photomultiplier, type R636, and a North Coast Scientific C^o germanium detector, type EO-8172, respectively for UV, visible and IR ranges. Time resolved spectra were obtained using an ATNE boxcar

having a 5 ns gate. For lifetime measurements a Lecroy TR8818 transient recorder having a temporal resolution of 10 ns has been used. Boxcar and transient recorder were also interfaced with the Apple II^e microcomputer for averaging, signal treatment and fitting.

3. Single ions and pairs.

The emission spectra of $\text{CsCdBr}_3:\text{Nd}^{3+}$ upon excitation of $^2\text{G}_{7/2}$ or $^4\text{G}_{5/2}$ level are very rich and contain lines from IR to UV spectral ranges. Detailed spectra will be given in another paper devoted to the spectroscopic results and their interpretation [10]. For the present work, it is sufficient to know approximately the position of some energy levels which are shown in figure 1a.

Fig. 1. — a) scheme of Nd^{3+} energy levels in CsCdBr_3 . The luminescent levels are indicated by half-circles. b) double arrows show the two quenching processes for $^4\text{G}_{5/2}$; single arrows show the second step of one of the quenching processes. c) double arrows show the quenching process for $^4\text{F}_{9/2}$. d) short arrows (resp. long arrows) show the quenching process for $^4\text{F}_{7/2}$ (resp. $^4\text{F}_{5/2}$). In b, c and d wavy lines represent multiphonon relaxations.

Most of the results discussed here are deduced from excitation spectra of a few luminescence lines. These spectra are time resolved and recorded with different time constants as indicated in the figure captions. Figure 2 shows excitation spectra of the luminescences emitted from $^4\text{G}_{5/2}$ and $^4\text{D}_{3/2}$ (located respectively at $16\,573 \text{ cm}^{-1}$ and $27\,445 \text{ cm}^{-1}$) following an excitation around $^2\text{G}_{7/2}$. The first occurs after a fast relaxation from the level excited by the laser; the second is an up-conversion or antiStokes luminescence in the UV range. Excitation spectra of other luminescences and the absorption spectrum around the $^4\text{I}_{9/2}^{(0)} \rightarrow ^2\text{G}_{7/2}^{(1)}$ transition are given in figure 3. Figure 4 presents the

Fig. 2. — Time integrated excitation spectra for $^4\text{G}_{5/2}$ (a) and $^4\text{D}_{3/2}$ (b) luminescences for excitation near the $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{7/2}$ transition at 2 K and for the 0.02 at. % Nd^{3+} doped crystal. (a) luminescence is produced after a fast relaxation from the $^2\text{G}_{7/2}$ pumped level; (b) luminescence results from a transfer, shown by the curved arrows, between two excited ions A and B. Lines 1, 2 and 3 of (a) are assigned to pairs and 1', 2' and 3' to single ions.

Fig. 3. — a) absorption spectrum corresponding to the $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{7/2}$ transition (linear scale). b, c, d, e) excitation spectra of the luminescences indicated in the figure. The gate of the boxcar was located at the maximum of the signal for each level emission. Centres of pair line 1 and of single ion line 1' are shown on spectrum (e). Spectral resolutions for the absorption spectrum and for the excitation spectra are given. All these spectra were obtained at 2 K with the 0.02 at. % crystal.

Fig. 4. — a) absorption spectrum around the $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{9/2}$ transition for the 0.6 at. % crystal (linear scale). b) and c) excitation spectra of $^4\text{F}_{9/2}$ luminescence observed at 0.1 μs (b) and 0.1 ms (c) after the laser pulse for 0.6 at. % crystal. The sensitivity for (c) is about 200 times larger than for (b). d) and e) excitation spectra of $^4\text{F}_{9/2}$ luminescence observed at 0.1 μs (d) and 0.1 ms (e) after the laser pulse for 0.02 at. % crystal. The sensitivity for (e) is about 10 times larger than for (d). The larger noise of spectrum (d) with respect to that of (e) results from the use of a shorter integration time. Spectral resolutions for absorption spectrum and for excitation spectra are given. All these spectra were obtained at 2 K.

absorption spectrum for the $^4\text{I}_{9/2}^{(0)} \rightarrow ^4\text{F}_{9/2}^{(0)}$ transition and the excitation spectra of $^4\text{F}_{9/2}$ luminescence observed with 0.6 at. % or 0.02 at. % doped samples.

Figure 2 shows that $^4\text{G}_{5/2}$ excitation spectrum has twice as many lines as the up-conversion excitation spectrum. Two lines for each transition have also been observed on the absorption spectrum [10]. This observation has been interpreted as arising from two Nd^{3+} species: i) ions having a nearby Nd^{3+} ion and forming a pair with it; ii) other ions [12]. Only pair ions can produce, when they are both excited, an antiStokes luminescence after an energy transfer process has redistributed energy between them.

The existence of such pairs has been first proved by McPherson *et al.* [5, 6]. Their structure results from the necessity of a charge compensation when Nd^{3+} is substituted to Cd^{2+} and corresponds to a chain $-\text{Cd}^{2+} - \text{Nd}^{3+} - \text{V}^0 - \text{Nd}^{3+} - \text{Cd}^{2+} -$ where two Nd^{3+} are on both sides of a Cd vacancy and at about 6 Å from each

other. Ions associated to the line for which up-conversion is not observed will be called single ions since they have not a nearby Nd^{3+} with which they can easily exchange energy.

The proportion of ions forming pairs can be deduced from the absorption spectrum of figure 3a. The pair line has an area 13 times larger than the area of the line of single ions for a 0.02 at % doped sample. This ratio 13:1 is equal to the ratio between the two Nd^{3+} species if the oscillator strengths for the $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{7/2}$ transition are the same for the two species. Three arguments are given to support this equality: i) lines for pairs and single ions associated with the same optical transition being separated by only a few cm^{-1} , the crystal fields and thus the wave functions cannot be very different; ii) the lifetimes of $^2\text{H}_{11/2}$ and $^4\text{F}_{3/2}$, given below in table I, which are certainly radiative lifetimes and thus representative of the oscillator strengths of the various radiative transitions, have nearly the same value for pairs and single ions; iii) absorption spectrum 3a and excitation spectrum 3b show roughly the same ratios between pair and single ion line areas (13 and 16 respectively). Spectrum 3b being observed with a 0.15 μs delay, very short as compared to the lifetimes of the two ion species, this ratio is meaningful; since different oscillator strengths are involved in these two spectra, it would be very surprising that their change from single ion to pair ion would be the same for the two involved transitions. Thus, it can be concluded that for the 0.02 at % doped crystal, 93 % of Nd^{3+} are involved in pairs; if the distribution were at random the proportion of Nd^{3+} associated in pairs would be only 4×10^{-4} !

The proportion of pair ions present in a 0.6 at % doped crystal has also been measured. For this measurement, neither the absorption spectrum (Fig. 4a) nor the $^4\text{F}_{9/2}$ luminescence excitation spectrum (Fig. 4b) can be used since the single ion line is not visible. A comparison with the spectrum of figure 4d, obtained with a 0.02 at %, shows that the proportion of single ions is lower in the 0.6 at % crystal. To get an estimation of this proportion, the time resolved excitation spectra observed after a long delay were used because, as shown in table I, the pair ion lifetime for $^4\text{F}_{9/2}^{(0)}$ level is much shorter (due to quenching as explained in section 4) than that of single ions. Thus, with a long delay, only Nd^{3+} having not a nearby Nd^{3+} are detected. Figure 4c shows such a spectrum recorded with a sensitivity about 200 times larger than that of spectrum 4b. The line located at the pair line position is attributed to « special single ions » having a crystal field perturbed nearly in the same manner as that of pair ions. The shape of this line results from the strong absorption of the laser by pairs near its centre which reduces the volume of the crystal pumped by the laser and thus reduces, with respect to the wings of the line, the number of special ions excited. The fact that the volume pumped by the laser changes with the

Table I. — Lifetimes of some luminescent levels for single ions and ion pairs.

Excited level	Luminescent level	Lifetime (μs)	
		Single ions	Ion pairs
$^2\text{G}_{7/2}$	$^4\text{G}_{5/2}$	5.6 ± 0.2	2.6 ± 0.2
$^2\text{G}_{7/2}$	$^2\text{H}_{11/2}$	1200 ± 50	900 ± 30
$^4\text{F}_{9/2}$	$^4\text{F}_{9/2}$	670 ± 20	1.3 ± 0.1
$^4\text{F}_{7/2}$	$^4\text{F}_{7/2}$	< 5	1.8 ± 0.2
$^4\text{F}_{7/2}$	$^4\text{F}_{5/2}$	48 ± 5	48 ± 5
$^4\text{F}_{7/2}$	$^4\text{F}_{3/2}$	600 ± 20	630 ± 20
$^2\text{G}_{7/2}$	$^4\text{G}_{7/2}$ ◆	—	43 ± 3
$^2\text{G}_{7/2}$	$^2\text{P}_{1/2}$ ◆	—	180 ± 10
$^2\text{G}_{7/2}$	$^4\text{D}_{3/2}$ ◆	—	15 ± 1
$^2\text{G}_{7/2}$	(*) ◆	—	1.0 ± 0.2

◆ Up-conversion luminescence.

(*) This luminescent level, located at $32\,250\text{ cm}^{-1}$, has not been identified.

wavelength makes difficult a precise comparison between the number of pairs, single ions and special ions. Since spectra 4b and 4c are observed with delays short as compared to respectively pair and single ion lifetimes (see Table I), the areas of pair line in 4b and single ion line in 4c are representative of the number of these two Nd^{3+} species. Taking into account the different sensitivities for 4b and 4c spectra, one can deduce that the number of single ions is less than 1/200 of that of pair ions, therefore an increase of Nd^{3+} concentration produces a greater proportion of pair ions. In addition, spectrum 4e, obtained with the same experimental conditions as those for spectrum 4c, shows a smaller proportion of « special ions » in the low doped crystal.

Previous estimations can be found in the literature. Henling and McPherson [13] said that, in a 0.3 at % nominally doped crystal, at least 90 % of Gd^{3+} form pairs. Berdowski *et al.* [7] found, for a 0.6 at % measured concentration, that 95 % of Tb^{3+} form pairs. The more precise results reported here are not in contradiction with these estimations but nevertheless they show a larger proportion of pair ions. Growth conditions can perhaps be important.

To get complementary information on the pair formation, crystals doped with both Nd^{3+} and monovalent ions like Li^+ , Na^+ and Ag^+ have been grown. Figure 5 presents the excitation spectra for delayed luminescence observed with a 1 at % Nd^{3+} and 0.1 at % Li^+ crystal (spectrum a) and with a Nd^{3+} - Ag^+ codoped crystal (spectrum b). For comparison, the excitation spectrum 4c of a 0.6 at % Nd^{3+} crystal has also been given. For all these crystals, the pair line, observed at short time after the laser pulse, remains the largest line by two orders of magnitude. Spectrum (b) and specially spectrum (a) show that the proportion of single ions is strongly reduced. These spectra also show that « new lines » appear at different positions for the two crystals. Peaks observed on these spectra do not

Fig. 5. — Excitation spectra around the $^4I_{9/2} \rightarrow ^4F_{9/2}$ transition observed 0.1 ms after the laser pulse at 2 K. a) 1 at. % Nd^{3+} and 0.1 at. % Li^+ . b) Nd^{3+} and Ag^+ codoped crystal (concentrations not measured). c) 0.6 at. % Nd^{3+} (identical to spectrum 4c).

represent the centres of the new lines because, as explained above, the volume excited by the laser in the crystal is lower at the very centre of the pair line and the lineshape is complex. Nevertheless, it seems that $\text{Nd}^{3+}\text{-Li}^+$, $\text{Nd}^{3+}\text{-Ag}^+$ and $\text{Nd}^{3+}\text{-Nd}^{3+}$ lines are at slightly different positions.

A tentative interpretation of these results can be proposed. The so called « single ions » are Nd^{3+} ions having not a nearby charge compensation and thus are submitted to the « normal » crystal field produced mainly by the 6 Br^- ligands. Pairs, whose structure has been recalled above, have ions in a different crystal field since, due to the vacancy, the two Nd^{3+} are shifted from the Cd^{2+} site, and their ligand neighbouring modified. The new lines in codoped crystals are assigned to Nd^{3+} for which the charge compensation is produced by a Li^+ or Ag^+ giving an environment described by $-\text{Cd}^{2+}\text{-M}^+\text{-Nd}^{3+}\text{-Cd}^{2+}$. It is more difficult to give a precise description of the « special ions ». The proximity of their associated line with that of pair ions leads to conclude they are perturbed in a similar manner. They could be for instance near a vacancy or a trivalent ion with which energy transfer would not be possible. The relative positions of $\text{Nd}^{3+}\text{-Nd}^{3+}$, $\text{Nd}^{3+}\text{-Li}^+$ and $\text{Nd}^{3+}\text{-Ag}^+$ lines show that the crystal field perturbation seen by Nd^{3+} is almost the same when the nearby Cd^{2+} is replaced by monovalent ion or by a vacancy. In both cases, Nd^{3+} is probably off centre. This behaviour does not seem to be the one observed for Cr^{3+} by McPherson and Devaney [14] in their comprehensive work. Using codoped crystals, they show that the crystal field of Cr^{3+} pairs (whose structure is the one given above) is strongly different from that of Cr^{3+} having a nearby Li^+ ion. But the difference between the crystal fields seen by this latter species and by a Cr^{3+} having no nearby charge compensation depends on the crystals : weak for CsCdBr_3 , it becomes larger for CsMgCl_3 and

CsMgBr_3 . Blasse *et al.* [8] have also discussed the problem of charge compensation. Their results suggest that Ce^{3+} having a nearby Li^+ is more similar to single Ce^{3+} than to Ce^{3+} in a pair. All these results, as well as those reported here, show that the ionic radii play probably a major role in this process. They also show that considerable work remains to be done before a good understanding can be obtained. It must nevertheless be pointed out that combined selective excitation and time resolved excitation spectra are powerful tools for such studies.

4. Luminescence dynamics.

4.1 LIFETIMES. — By selective excitation with a spectrally narrow pulsed laser, it is possible to observe the luminescence dynamics of various levels for pairs and single ions. Table I gives the results for some decay time measurements. To be sure that the decay displays the decay time of a level, it is necessary to directly pump this level by the laser or possibly to pump a slightly more excited level from which ions will decay to the observed level by very fast relaxation. In table I, pumped and observed levels have been given. It can be seen that decay times τ of pairs and single ions are very similar for some levels and very different for others. The shortening of pair decay time is of course a result of the ion-ion interaction which induces an energy transfer between the excited ion and its neighbour. The decay time can be written as

$$1/\tau = W_r + W_p + W_t \quad (1)$$

where W_r , W_p and W_t are respectively the radiative, phonon relaxation and transfer rates. From a comparison between single ion and pair lifetimes, it is possible to deduce W_t if W_r and W_p are supposed to be equal for the two Nd^{3+} species. This point has already been discussed for W_r in section 3. Similar arguments can be used for W_p to reach the same conclusion. A possible change of the ion phonon coupling induced by the pair structure could however make this hypothesis less sound.

Because CsCdBr_3 is composed of heavy ions, the cutoff frequency of its phonon spectrum must be relatively low. From an observed vibronic sideband [10], this limit is found at 90 cm^{-1} . In a Raman experiment, the higher peak has been observed at 162 cm^{-1} [15]. Although different, due to the fact that phonons involved in these experiments are not the same, these values confirm that CsCdBr_3 has no high frequency phonons, a property which, of course, has consequences for relaxation and phonon assisted processes. For instance, it is clear from figure 1a that relaxation of the lowest state of all multiplets will be multiphonon, except for $^2G_{7/2}$, $^2H_{9/2}$ and $^4S_{3/2}$. Since the efficiency of multiphonon processes decreases rapidly with the number of phonons emitted, the lifetimes of these states will strongly depend on their gap with the

next lower lying state. It is the reason why ${}^4G_{5/2}$ and ${}^4F_{7/2}$ have the shortest lifetimes although ${}^2H_{11/2}$, ${}^4F_{9/2}$ and ${}^4F_{3/2}$ have very long lifetimes which are probably radiative lifetimes. The low value of the phonon cutoff frequency explains why so many levels produce a luminescence in this crystal [10]. It also explains the weak efficiency of quenchings needing emission of more than one phonon. For instance the 25 % reduction of the ${}^2H_{11/2}$ pair lifetime with respect to that of single ions is the proof of a quenching having a weak efficiency because at least 3 phonons must be emitted; ${}^4F_{3/2}$ shows approximatively the same lifetime for pairs and single ions because about 10 phonons should be emitted.

Using the detailed energy level scheme [10], it is possible, considering only one phonon processes and supposing a cutoff frequency equal to 90 cm^{-1} , to find that for ${}^4G_{5/2}$ the quenching processes are :

$$[{}^4G_{5/2}^{(0)}; {}^4I_{9/2}^{(0)}] \rightarrow [{}^4F_{9/2}^{(i)}; {}^4I_{11/2}^{(j)}]$$

with 13 possibilities for (i, j) and

$$[{}^4G_{5/2}^{(0)}; {}^4I_{9/2}^{(0)}] \rightarrow [{}^4F_{5/2}^{(i)} \text{ or } {}^2H_{9/2}^{(i)}; {}^4I_{13/2}^{(j)}]$$

with 10 possibilities for (i, j) . They are illustrated in figure 1b. The high number of possibilities results from the great number of levels in the multiplets. Since each one-phonon assisted transfer rate is proportional to the energy of the phonon emitted [16], the total energy emitted by these 23 possibilities is representative of the total transfer rate if the matrix elements involved do not change too much from one possibility to another. That total energy is 800 cm^{-1} . For ${}^4F_{9/2}$, and within the same hypothesis, the quenching processes are :

$$[{}^4F_{9/2}^{(0)}; {}^4I_{9/2}^{(0)}] \rightarrow [{}^4F_{5/2}^{(i)} \text{ or } {}^2H_{9/2}^{(i)}; {}^4I_{11/2}^{(j)}]$$

with 15 possibilities for (i, j) , and the total emitted energy is 620 cm^{-1} . They are shown in figure 1c.

The conclusion of this crude model (consideration of only one-phonon processes, near equality of matrix elements) leading to a quasi equality of quenching rates for ${}^4G_{5/2}$ and ${}^4F_{9/2}$ can be tested experimentally. Interpreting the smaller values of pair lifetimes in table I as a result of quenching, and using (1), one can deduce $W_t = 2 \times 10^5\text{ s}^{-1}$ for ${}^4G_{5/2}$ and $W_t = 7.7 \times 10^5\text{ s}^{-1}$ for ${}^4F_{9/2}$. The comparison between the observed 3.8 and the predicted 0.8 values for the ratio of these rates shows simultaneously the usefulness and the limit of the model : it can be used for an estimation of transfer rates once others are known, but the estimation does not give any better than an order of magnitude. This order of magnitude can for example be estimated for ${}^4F_{5/2}$ and ${}^4F_{7/2}$ from the ${}^4G_{5/2}$ W_t observed. With respectively 7 and 6 possible processes and 310 cm^{-1} and 290 cm^{-1} total energy emitted, one finds $8 \times 10^4\text{ s}^{-1}$ and $7 \times 10^4\text{ s}^{-1}$ for the quenching rates. For ${}^4F_{7/2}$, a direct measurement of the lifetime has not been

possible for single ions due to the weakness of the signal. An order of magnitude of the quenching rate can however be deduced from the dynamics of the ${}^4F_{3/2}$ luminescence described in the next section. This dynamics shows that ${}^4F_{3/2}$ is populated by two de-excitation channels described by equation (3), the efficiencies being in the ratio 1/2. From its analysis given in the next section, one can deduce the ${}^4F_{7/2}$ quenching rate is about 1/3 of the ${}^4F_{7/2}$ decay rate, namely $1/3 \times 1/(1.8\text{ }\mu\text{s}) \approx 2 \times 10^5\text{ s}^{-1}$. This result is not too far from the above estimation of $7 \times 10^4\text{ s}^{-1}$. For ${}^4F_{5/2}$, since no difference can be observed within the experimental errors between pair and single ion lifetimes, an upper limit of $4 \times 10^3\text{ s}^{-1}$ can be deduced for the quenching rate. This result is more than an order of magnitude smaller than the value predicted by the crude model.

4.2 CHANNELS OF DE-EXCITATION. — Instead of looking at the decay of the level excited by the laser, it is interesting to observe the dynamics of the luminescence associated with a level of lower energy. One or many rise times can be measured and the decay time can be different from the one measured for a direct pumping. This dynamics, observed for pairs and single ions can thus bring information on the de-excitation

Fig. 6. — Luminescence decays after ${}^4F_{7/2}$ excitation : a) decay of ${}^4F_{7/2}$ luminescence and rising of ${}^4F_{5/2}$ luminescence for pairs. b) dynamics of ${}^4F_{5/2}$ luminescence for pairs. c) and d) dynamics of ${}^4F_{3/2}$ luminescence respectively for pairs and single ions. All these results were obtained at 2 K.

channels through the « memory » the emitting ions have kept of the dynamics of the visited levels. Figure 6 gives an example. At the top of this figure, the decay of $^4\text{F}_{7/2}$ for pairs after direct excitation is a pure exponential with a characteristic time of $1.8 \mu\text{s}$ while the dynamics of $^4\text{F}_{5/2}$ shows a rise time having the same value and a decay time of $48 \mu\text{s}$. That proves $^4\text{F}_{5/2}$ is populated by relaxation from $^4\text{F}_{7/2}$. For single ions, this $^4\text{F}_{5/2}$ decay time is found equal to the $^4\text{F}_{3/2}$ risetime (see Fig. 6d) although for pairs the luminescence rising dynamics contains an additional fast component whose characteristic time is equal to $1.8 \mu\text{s}$, the $^4\text{F}_{7/2}$ decay time. The fast and slow components contribute to this

$^4\text{F}_{3/2}$ luminescence rising with amplitudes in a ratio of 1 : 2. The starting level being the same for the two channels, this ratio also gives the proportion of the ions which decay through each channel if the $^4\text{F}_{5/2}$ lifetime is essentially non radiative since, in that case, every ion being in the $^4\text{F}_{5/2}$ state relaxes to $^4\text{F}_{3/2}$. This ratio has also been used in the previous section to calculate, within the same hypothesis, the $^4\text{F}_{7/2}$ quenching rate. The two processes are shown in figure 1d for pairs. The two sequences for single ions and pairs are summarized below. Numbers between brackets are lifetimes in μs and only the state of the more excited ion of the pair is given :

Single ions

Pairs

By similar observations, the de-excitation channels from $^4\text{G}_{5/2}$ and $^4\text{F}_{9/2}$ can be deduced for single ions and pairs. They are described here :

Single ions

Pairs

Some dynamics are less easily interpreted. For single ions, the rise time for $^2H_{11/2}$ luminescence following a $^2G_{7/2}$ excitation is equal to the decay time of $^4G_{5/2}$ showing again the feeding of $^2H_{11/2}$ by relaxation from $^4G_{5/2}$. But, for pairs, two characteristic rise times can be measured on the $^2H_{11/2}$ luminescence rising, one (80 %) $2.6 \mu s$ is the $^4G_{5/2}$ decay time for pairs while the other (20 %), of the order of $40 \mu s$ cannot be related to any known decay time. The possibility that $^2H_{11/2}$ could be fed from states populated by up-conversion processes is ruled out because the proportion of the rising component of $40 \mu s$ does not change when the laser intensity is changed. This long rise time of $40 \mu s$ cannot either be a result of a de-excitation channel through the higher levels of $^2H_{11/2}$ since a direct excitation of these levels leads to a rise time shorter than $1 \mu s$ for the $^2H_{11/2}$ luminescence (emitted from the lowest state).

Some information on the de-excitation channels for single ions and pairs can also be found in the luminescence intensities. Spectra b, c, d of figure 3 are excitation spectra of three luminescences for which the ratio between pair and single ion line areas are different. For the $^4G_{5/2}$ luminescence at $t \approx 0$, this ratio is nearly the same as that of the absorption spectrum (Fig. 3a) showing that all types of ions relax from the $^2G_{7/2}$ level pumped by the laser to $^4G_{5/2}$. The $^2H_{11/2}$ luminescence of pairs is relatively weaker than that of single ions although the $^4F_{3/2}$ luminescence is larger. It proves that the $^4G_{5/2}$ quenching process for pairs described by scheme (6) is efficient, leading to the rather unusual situation in which $^4F_{3/2}$ luminescence (of laser interest) is larger for pairs than for single ions. This exceptional situation results from the narrowness of the phonon spectrum which reduces the multiphonon relaxation rates: single ions having reached $^2H_{11/2}$ are lost for $^4F_{3/2}$ luminescence although in most of the other compounds $^2H_{11/2}$ is only a step to $^4F_{3/2}$.

4.3 OTHER OBSERVATIONS. — An increase of $^4F_{3/2}$ decay time has been observed with the increase of Nd concentration and the increase of the crystal volume. This results from a reabsorption process. Indeed, due to the large gap below $^4F_{3/2}$, the decay time of this level is radiative and, as can be seen in the spectrum of the luminescence emitted from $^4F_{3/2}$ (not given here), the transition to the ground state appears to have one of the strongest oscillator strength.

A stimulated emission at 612 nm from $^4G_{5/2}$ to the third excited level of $^4I_{9/2}$ has also been observed for pairs. It was still observed for the 0.6 at. % concentration crystal with a laser intensity as low as 3 kW/mm^2 (with such an intensity, only 3×10^{12} ions are excited by each laser pulse). When this stimulated emission occurs, it almost suppresses other luminescences from $^4G_{5/2}$.

5. Conclusion.

Properties resulting from two particularities of CsCdBr_3 , namely the small phonon frequency cutoff and the formation of rare earth pairs, have been studied on Nd^{3+} doped crystals. The pair formation, which results from the necessity of a charge compensation after the $\text{Nd}^{3+}/\text{Cd}^{2+}$ substitution, has been semi-quantitatively studied to determine the proportion of ions which enter the crystal as pairs and to observe the effect of codoping with a monovalent ion metal. It appears that the great majority of ions form pairs, that this proportion increases with the concentration and that the monovalent ions reduce the single ions proportion.

The small values of the phonon frequencies, besides the reduction of the multiphonon relaxation efficiency which increases the number of luminescing levels, also reduces the efficiency of phonon assisted energy transfers. Only transfers needing a relatively small emission of energy are efficient and the rate of some of them has been measured from a comparison between the single ion and pair properties. The de-excitation channels and their hierarchy have been determined for some excited levels from the luminescence dynamics. This determination shows that ions associated as pairs can have some emission intensities relatively larger than that of single ions. This is quite unusual and must be underlined because in most compounds, pairs are quenching centres and are considered as poison centres. That proves once more the great importance of the phonon properties and must be considered in future research on laser crystals.

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References

- [1] BUISSON, R. and VIAL, J. C., *J. Physique Lett.* **42** (1981) L-115.
  - [2] VIAL, J. C. and BUISSON, R., *J. Physique Lett.* **43** (1982) L-339.
  - [3] BUISSON, R., LIU, J. Q. and VIAL, J. C., *J. Physique* **45** (1984) 1533.
  - [4] BARTHEM, R. B., BUISSON, R., VIAL, J. C. and HARMAND, H., *J. Lumin.* **34** (1986) 295.
  - [5] MCPHERSON, G. L. and WAI-MING HEUNG, *Solid State Commun.* **19** (1976) 53.
  - [6] MCPHERSON, G. L. and HENLING, L. M., *Phys. Rev.* **B 16** (1977) 1889.
  - [7] BERDOWSKI, P. A. M., LAMMERS, M. J. J. and BLASSE, G., *J. Chem. Phys.* **83** (1985) 476.
  - [8] BLASSE, G., WOLFERT, A. and MCPHERSON, G. L., *J. Solid State Chem.* **57** (1985) 396.
  - [9] LAMMERS, M. J. J. and BLASSE, G., *Chem. Phys. Letters* **126** (1986) 405.
  - [10] BARTHEM, R. B., BUISSON, R., CONE, R., to be published.
  - [11] When necessary the sublevels of the multiplets are indicated by an upper index, (⁰) corresponding to the lowest sublevel.
  - [12] BARTHEM, R. B., BUISSON, R., VIAL, J. C. and CHAMINADE, J. P., *J. Phys. C* **7** (1985) 113.
  - [13] HENLING, L. M. and MCPHERSON, G. L., *Phys. Rev.* **B 16** (1977) 4756.
  - [14] MCPHERSON, G. L. and DEVANEY, K. O., *J. Phys. C : Solid St. Phys.* **13** (1980) 1735.
  - [15] LUCAZEAU, G., private communication.
  - [16] ORBACH, R. in *Optical Properties of Ions in Crystals*, Crosswhite, H. M. and Moods, H. W., Eds. (Interscience, New York) 1967, p. 455.
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