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Exciton dynamics and energy transfers in pure CsMnF₃

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Résumé. — Les caractéristiques spectrales et temporelles de la fluorescence du composé CsMnF₃ sont présentées. L'analyse de la faible émission intrinsèque du matériau pur par la technique de la spectroscopie résolue dans le temps montre l'existence du transfert d'énergie de l'exciton vers les pièges fluorescents. On fait varier l'efficacité de ce transfert en appliquant : soit une contrainte uniaxiale suivant une direction Mn₂-Mn₁, soit un champ magnétique intense dans le plan des spins. On observe en outre que la non-exponentialité de la décroissance de fluorescence excitonique augmente pour des densités d'exciton allant jusqu'à 10¹⁸ cm⁻³. En supposant un mécanisme d'interaction exciton-exciton, le paramètre de collision p_b nous permet d'évaluer un coefficient de diffusion effectif

\[ D \sim 10^{-8} \text{ cm}^2 \text{s}^{-1}. \]

La validité du modèle excitonique est montrée et les résultats ainsi obtenus sont comparés aux données connues sur MnF₂. Enfin, en accord avec les mesures sous contrainte ou champ magnétique, on propose une description de la propagation de l'énergie d'excitation faisant intervenir l'interaction d'échange entre ions Mn₂ troisièmes voisins de spins parallèles.

Abstract. — We report the spectral and time characteristics of the fluorescence of CsMnF₃. The weak intrinsic fluorescence in nominally pure samples is analysed with time resolved techniques showing the energy transfer processes from exciton to fluorescing traps. By applying either a uniaxial stress along the Mn₂-Mn₁ direction or a high magnetic field in the basal plane we are able to monitor the efficiency of this energy transfer. Moreover a non linear exciton decay channel is observed for exciton densities up to 10¹⁸ cm⁻³. Assuming an exciton-exciton interaction mechanism, the collision parameter p_b is used to estimate an effective diffusion coefficient

\[ D \sim 10^{-8} \text{ cm}^2 \text{s}^{-1}. \]

The validity of the exciton model is then discussed, and the results obtained on CsMnF₃ are shown to be consistent with the ones known on MnF₂. Finally a description of the propagation of the excitation involving the exchange interaction between third nearest neighbour Mn₂ ions having parallel spins is proposed, in agreement with the stress and high magnetic field data.

1. Introduction. — In the recent years, an abundant literature has been devoted to the luminescence of the concentrated manganese fluorides. However, the results show that at least two questions of fundamental interest remain:

1. In a magnetic crystal such as MnF₂ and AMnF₃ — with A = K, Rb, Cs —, numerous experimental observations cannot be fully interpreted without including a non negligible effect of the exciton dispersion. However, to our knowledge, no direct measurement of it has been achieved so far. In particular, this can result, in some circumstances, in the difficult task of deciding between a « wave like » or a « diffusive » description of the exciton motion.
2. In the « high » temperature domain (T > 5 K) the processes of intrinsic exciton decay and of energy transfer to the various fluorescing traps agree fairly well with a model of rapid exciton diffusion and trapping [1]. At very low temperature, however, being non exponential and nearly independent of the impurity concentration in the crystals, the dominant decay mode of the exciton fluorescence is attributed to...
an intrinsic deexcitation process which depends non-linearly on the initial exciton density [2, 3]. Unfortunately, no particular physical mechanism could be concluded from the present experiments.

This research is motivated by both its practical aspect (applications often need highly concentrated materials) and its theoretical interest. In addition, the numerous works which have been performed in this field well illustrate the necessity of investigating various systems by using conventional methods such as optical absorption or emission as a function of an external perturbation (pressure, magnetic or electric field, ...) as well as recent techniques such as high power pulsed dye laser excitation and time resolved spectroscopy.

In that sense, our interest has been addressed to the antiferromagnet CsMnF₃ in which, by contrast with the other three dimensional manganese fluorides MnF₂, K₃MnF₄ and RbMnF₃, exist non centrosymmetric ion sites resulting in the observation of electric-dipole allowed electronic transitions and also a six magnetic sublattice structure.

Two articles have been recently devoted to the study of the optical absorption of lower energy 6A₁g(6S) → 4T₁g(4G) and, more precisely, the optical fine structure which appears in the spectrum below the ordering temperature [4, 5].

In the present paper, we analyse the fluorescence characteristics of CsMnF₃ over a large temperature range. In particular, the following section (section 2) is devoted to a presentation of the crystallographic and magnetic properties of the compound, and to a short summary of the above absorption data. We give then in section 3 a description of the materials, apparatus and techniques which have been used here more specifically. In section 4, we describe the general fluorescence properties of CsMnF₃, for example, the thermal behaviour of the various impurity induced lines and the importance of the magnons, the slowing down of the energy transfer due to uniaxial stress or its enhancement by an applied magnetic field. In section 5, a detailed analysis of the intrinsic exciton at very low temperature is given, in particular, as to the effect of the optical pump power on its fluorescence decay mode, and to its thermal variation. In the last section, we discuss our results in connection with those already obtained in the other manganese fluorides.

2. Preliminary information. — CsMnF₃ is characterized by its hexagonal structure [6] and the presence of two types of manganese sites, one third being centrosymmetric labelled Mn1, site group D₃dn, and two thirds being non centrosymmetric labelled Mn2, site group C₃v. Below the Néel temperature \( T_N = 53.6 \) K, the crystal orders antiferromagnetically and the spins align in ferromagnetic planes, which alternate along the main axis \( C_6 \) [6]. This is shown in figure 1. The neutron diffraction results [7] indicate exchange constants for nearest and next-nearest neighbour magnetic ions given by \( J_1 = -3.13 \) cm⁻¹, \( J_2 = -4.46 \) cm⁻¹ (antiferro.) and \( J_3 = +0.46 \) cm⁻¹ (ferro) respectively.

As in the case of the other three dimensional manganese fluorides, the optical absorption of CsMnF₃ is entirely attributed to the Mn²⁺ ions. Of particular interest here, the 6A₁g(6S) → 4T₁g(4G) absorption is characterized by a broad band peaking around 5 100 Å, with a series of sharp lines appearing on its low energy side for temperatures below \( T_N \). More precisely, at very low temperatures, in its low energy and less intense portion, the spectrum is formed of two \( \pi \) polarized features noted A₂ (5 522.75 Å) and A₃ (5 521.25 Å) which are attributed to pure excitonic transitions characteristic of Mn₂ ions essentially, and six other lines, broader than the latter, noted A₁ (5 527.25 Å), A₄ (5 517 Å), A₅ (5 512 Å), A₆ (5 509 Å), A₇ (5 502.75 Å) on one hand and A₈ (5 498.5 Å) on the other hand, that are attributed to magnon and phonon assisted transitions. The lines A₅, A₇ and A₈ have been associated [4, 5] to the exciton A₂ and the line A₆ to the exciton A₃; the lines A₁ and A₄ have been attributed to hot and cold absorption magnon sidebands, the involved magnon being mainly localized on a Mn₁ sublattice — with a characteristic frequency interval of \( \sim 15 \) cm⁻¹ (case of A₁) or on a Mn₂ sublattice — with a characteristic frequency interval of \( \sim 38 \) cm⁻¹ (case of A₃).

3. Materials and techniques. — All the samples used here were of good optical quality. The purest one (crystal 1) is characterized, after chemical analysis, by the following impurity concentrations : 0.8 ppm Zn²⁺, 13 ppm Mg²⁺, less than 20 ppm Cu²⁺, 9.2 ppm Ni²⁺, 19 ppm Fe²⁺, 0.6 ppm Co²⁺ and 0.5 ppm Cu²⁺. Two other samples were also studied, one (crystal 2) overconcentrated in Cu²⁺ ions, 150 ppm after analysis, and the other (crystal 3) overconcentrated in Zn²⁺ ions, 600 ppm after analysis. Each of the crystals was oriented with a possible error on the crystallographic axis of about 1 degree; their size was typically of the order of \( 4 \times 4 \times 4 \) mm³.

The emission spectra were recorded continuously.
by exciting the sample with an all lines argon laser (5 W maximum) from SPECTRA PHYSICS, then by analysing and detecting the fluorescence output signal at right angle with respect to the axis of excitation, with the aid of a 1 m HILGER and WATTS high resolution (8 Å/mm in first order) scanning monochromator, an E.M.I. 9816 fast photomultiplier with a S 20 response, an ORTEC photon-counting system and an ordinary stripchart recorder. The temporal analysis of the fluorescence intensities (decay times) and spectra (Time Resolved Spectroscopy) was realized by using the 10 Hz pulsed radiation from either a one stage amplifier dye laser pumped by a MOLECTRON Model UV 12 nitrogen laser (pulses of 7 ns duration and 250 µJ maximum at 5 400 Å), or a frequency doubled QUANTEL Model 481 infrared YAG : Nd³⁺ laser (pulses of 10 ns duration and 380 mJ maximum at 5 320 Å), or a three stage amplifier dye laser pumped by the previous one (pulses of 10 ns and 75 mJ maximum at 5 650 Å). With the help of the ORTEC photon counting and sampling systems, we were able to resolve the emission and excitation spectra as well with a minimum time delay after the laser pulse of less than 500 ns. Moreover, using a fast INTERTECHNIQUE Model IN90 multichannel analyser, the fluorescence decay data could be recorded and processed over 256 channels with a maximum resolution of 2 µs per channel.

For the thermal measurements, we used a helium bath AIR LIQUIDE cryostat equipped with carbon and platinum probes and a temperature regulating device which allowed us to experiment from 1.6 K up to ambient temperature. A second helium bath ARDIN cryostat, of larger diameter, was also used to experiment under uniaxial stress or magnetic field at 2 K.

The uniaxial stress could be varied continuously up to about 2 500 kg/cm². A BITTER type split coil electromagnet allowed us to get fields continuously up to about 125 kOe.

4. General fluorescence properties of CsMnF₃. -
The emission spectrum of a nominally pure sample of CsMnF₃ at T = 1.6 K is presented in figure 2. This spectrum is characterized by a broad band peaking around 5 820 Å, with a width at half maximum of about 450 Å, accompanied by a series of sharp lines, more or less intense, on its high energy side.

As in absorption, a number of these lines can be attributed to exciton type intrinsic transitions — pure and magnon/or phonon assisted transitions —, within the bulk Mn²⁺ ions. However, most of the sharp lines have been found [1] to be due to the presence of perturbing impurities such as Ca²⁺, Mg²⁺ and Zn²⁺. They are present even in the purest samples, and the Mn²⁺ ions in their vicinity have their first excited level ⁴T₁₋(⁴G) depressed in energy below that of the unperturbed bulk Mn²⁺ ions. These impurity perturbed ions act as localized traps for the excitation and emit their own sharp line fluorescence — pure electronic and magnon/or phonon assisted transitions. Since these induced fluorescence lines are strongly dependent on the nature and the concentration of the relevant impurities, and also, on the position of these impurities with respect to the manganese ions, their number and their intensities are highly sample dependent. This is illustrated in figure 3: by comparing the spectra of crystal 2 and crystal 3, for example, the respective positions of the trap levels characteristic of ions Ca²⁺ and Zn²⁺ are clearly evidenced.

The origin of the broad band emission is not so straightforward. It is generally attributed to over-
lapping phonon sidebands of the above structures. This assumption can be supported by the decay time measurements. However, the shape as well as the overall intensity of this band are independent of the samples. This discrepancy remains a matter of discussion and still motivates current research [8].

From a dynamical point of view, it is usually assumed that all the emitting levels are populated from the intrinsic exciton band formed by the unperturbed Mn\(^{2+}\) ions, since all the corresponding excitation spectra correlate with the absorption spectrum of the crystal. In particular, the efficiency of the energy transfer which is responsible for the feeding of the fluorescing traps is usually expressed by a notable shortening of the intrinsic fluorescence decay with respect to the radiative lifetime \(\tau_R\). In addition, this radiative lifetime is generally assumed to be the same for the perturbed and unperturbed manganese sites as well. In the case of CsMnF\(_3\), the fluorescence decay time of the impurity-induced lines and of the broad band at \(T = 1.6\) K is \(\sim 15\) ms. The effective decay time of the intrinsic exciton is measured at the maximum of the line which coincides with the absorption exciton of lower energy noted A\(_2\) (552.75 Å).

A value of \(\sim 700\) μs is found, which is more than one order of magnitude shorter than the actual radiative lifetime. From that observation may be seen how to separate the intrinsic fluorescence from that of the traps : the spectra are time resolved either at short or long time delay after the laser pulse. The results are shown in figure 4.

Three important pieces of information are then derived :

1. The intrinsic fluorescence (spectrum 1) is composed essentially of two lines; the higher energy one is resonant with the A\(_2\) absorption line and thus is confirmed as a pure exciton transition; the lower energy one is attributed to an associated magnon satellite of the latter with a characteristic frequency interval of \(\sim 38\) cm\(^{-1}\).

2. By comparing spectrum 1 with spectrum 3, the above intrinsic magnon satellite is seen to overlap with an impurity-induced fluorescence line of comparable magnitude.

3. The overall trap fluorescence is much more intense than the intrinsic one. This is indicative of very efficient exciton to trap energy transfer which leads conclusively to the assignment of the broad band to the trap fluorescence.

4.1 EFFECT OF UNIAXIAL STRESS. — In a previous article [5] we have shown the effect of uniaxial stress and high magnetic field on the absorption spectrum of CsMnF\(_3\).

Experimental evidence was reported there for the attribution of the pure exciton lines A\(_2\) and A\(_3\) to optical transitions within Mn\(_2\) ions essentially associated with orbitally non degenerate components of an E like sublevel (of the excited cubic term T\(_{1g}\)) coming from an additional local site distortion [5].

Moreover, when a stress was applied along an intermediate direction joining nearest neighbour ions Mn1 and Mn2, it was shown that the lines A\(_2\) and A\(_3\) split into two components arising from the distinct excitonic contributions of the adjacent Mn2 ions having antiparallel spins. Indeed, by choosing the system of local coordinates \(x, y\) and \(z\) as shown in figure 5, a strain of type \(\sigma_{xz} > 0\) for the upper site Mn2 will correspond to a strain of type \(\sigma_{xz} < 0\) for the site below. Consequently the associated residual magnetic sublattice degeneracy of the exciton states is lifted.
Exciton localization effect induced by a stress directed along adjacent Mn1 and Mn2 ions on the short wavelength portion of the emission spectrum of CsMnF3 at $T = 2$ K: 1. continuous emission $\cdots$ and 2. time resolved emission at short time delay ($d = 0.5$ ys, $p = 50$ µs) $\cdots$ for zero stress; 3. continuous emission for an applied uniaxial stress $P = 1180$ kg/cm² $\cdots$.

1. At zero stress, both continuously (spectrum 1) and time resolved at short time (spectrum 2) in order to separate the respective contributions of the intrinsic and trap emissions.

2. Continuously again, with the crystal being submitted to an intermediate stress, as indicated above, of about 1180 kg/cm² (spectrum 3); at this pressure the lower energy components of the split absorption excitons are separated by $\simeq 1.3 \text{Å}(4.3 \text{cm}^{-1})$ — see insert of figure 6.

It is found that the intensity ratio of the lines noted A (intrinsic exciton) and B (intrinsic magnon sideband + impurity induced exciton) compares favourably in the spectra 2 and 3 ($I_B/I_A \simeq 5.4$ for spectrum 2 and $I_B/I_A \simeq 4.4$ for spectrum 3) but strongly contrasts with that of spectrum 1 ($I_B/I_A \simeq 8.6$). This means that the applied stress decreases the overall efficiency of the exciton to trap energy transfer.

Such an observation was also reported in KMnF3 [9]. It was subsequently proposed that the exciton diffusion might become anisotropic, thus resulting in a reduction of the probability to find a trap [10].

It should be noted that in MnF₂, each of the absorption exciton lines noted E₁ and E₂ splits into two components which are attributed to the two inequivalent magnetic sublattices of the structure. Then, two emission lines corresponding to the two stress-induced sublattice components of E₁ appear in the emission spectrum indicating a negligible relaxation between them within the time scale of the exciton decay [11]: this agrees with negligible inter-sublattice excitation exchanges for which a change of spin angular momentum of $\pm 2$ is required. In CsMnF₃, the higher energy component of the stress induced splitting of the exciton A₂ does not appear in fluorescence. However, the lower energy component of the stress induced splitting of the exciton A₃, noted A', clearly appears. We propose the following explanation.

Let us introduce the $E_+$ and $E_-$ components of the excited state, noted E in the group representation, responsible for the A₂ and A₃ transitions (see insert of Fig. 6). If 1 and 2 stand for the up and down adjacent manganese ions labelled Mn2 (antiparallel spins), the applied stress shifts the energy levels by the quantities:

$$a = \langle E_+(1) | V_s | E_+(1) \rangle \quad \text{and} \quad b = \langle E_+(2) | V_s | E_+(2) \rangle$$

for level $E_+$

$$c = \langle E_-(1) | V_s | E_-(1) \rangle \quad \text{and} \quad d = \langle E_-(2) | V_s | E_-(2) \rangle$$

for level $E_-$

where the strain Hamiltonian $V_s$ is diagonal because of the linear line-shifts with pressure (see Fig. 3 of Ref. [5]).

When the condition $b = c$ and $a = d$ is fulfilled we get the dynamical scheme shown in figure 6. After being transferred (magnon or phonon assisted process) to levels $E_-(2)$ and $E_+(1)$, the excitation can only relax on levels $E_-(2)$ and $E_-(1)$ respectively (relaxation between excited levels of the same ion, namely between states with parallel spins), the excitation exchange between the lower energy components labelled $A[E_+(2)]$ and $A[E_-(1)]$ (states with antiparallel spins) being forbidden. Since, the lines $A/A'$ and $A_2/A_3$ observed in emission and absorption have comparable intensity ratios, the inter-ion energy transfers for ions belonging to antiparallel spin sublattices can be neglected within the time scale of the exciton decay as in MnF₂.

4.2 MAGNETIC FIELD EFFECT. — The emission spectra of CsMnF₃ have been observed at very low temperature for continuous or pulsed laser excitation in the magnon sideband noted A₅. A portion of these spectra, calibrated to display the same exciton intensity (line A), is shown in figure 7 for fields $H \perp C₅$ up to 120 kOe. As shown on this figure, the trap fluorescence (lines B, C and D) increases significantly with the applied magnetic field. Thus, as opposed to the effect of a uniaxial stress, the application of a magnetic field
Increased exciton delocalization effect induced by a magnetic field $H \perp C$ on a short wavelength portion of the emission spectrum of CsMnF$_3$ at $T = 2 \, \text{K}$ for $H = 0$ (---), $H = 70 \, \text{kOe}$ (-----) and $H = 120 \, \text{kOe}$ (-----).

in the basal plane of the crystal is seen to favour the overall efficiency of the exciton to trap energy transfers. This observation is further verified through the decay time measurements and the time resolved spectra. In particular, both the intrinsic exciton decay and the trap fluorescence rise are shortened — by a factor of $\sim 1.2$ in a field of $70 \, \text{kOe}$ for example. —

The results are explained as follows : the pure (no magnon no phonon) exciton transitions are characterized by a unit change in the ion spin projection which leads, in collinear antiferromagnets, to a rigorous spin exclusion on the intersublattice exchange of excitations. However, in materials which present a weak anisotropy, magnetic field induced spin-flop transitions can be easily achieved. A weak ferromagnetic component then appears along the applied magnetic field and a new spin configuration corresponding to a mixing of the different magnetic sublattices takes place; thus, the above interdiction is partially lifted and the overall efficiency of the energy transfer is increased.

Knowing that the critical field value corresponding to the basal plane anisotropy in CsMnF$_3$ is of the order of $700 \, \text{Oe}$, the above argument applies for fields at least as high as this value, which is the case in the present experiment.

This delocalization process can be related to the magnetization data as follows. Within a fast diffusion model the exciton decay rate $p = \tau^{-1}$ is directly proportional to an isotropic diffusion coefficient, this diffusion coefficient being proportional to the square of the matrix element for the resonant transfer of excitation between adjacent ions belonging to the different sublattices. Taking into account the spin orientation of ions $\alpha$ and $\beta$ this matrix element transforms as [12] :

$$M_{\alpha,\beta}^{f} = \mathfrak{M}_{\alpha,\beta} \cos^{2} \theta$$

where $\mathfrak{M}_{\alpha,\beta}$ is an amplitude value independent of the orientations of the spins, $f$ is the involved electronic excitation and $\theta$ stands for the angle between the equilibrium positions of the spins on the ions $\alpha$ and $\beta$ i.e. $\theta = \frac{\theta_{\alpha} - \theta_{\beta}}{2}$. For fields higher than the spin-flop transition one can write :

$$\cos \theta \simeq \left( \frac{M}{M_{0}} \right)$$

where $M$ is the magnetic field induced magnetization and $M_{0}$ its saturation value. In the end, we get the following relationship :

$$p \equiv \left( \frac{M}{M_{0}} \right)^{4}$$

The exciton decay rate increases as the fourth power of the induced magnetization. For example, a change in the value of $\tau$ by a factor 1.2 will correspond to a change in magnetization of about 1.04. This model has been checked by assuming that $H_{E_{2}}$, the exchange field on the ions Mn$^{2+}$, is roughly proportional to $M$, then by using the expressions for $H_{E_{2}}$ versus $H$ given in the literature [13]. For an applied field of $\sim 70 \, \text{kOe}$, we find that $H_{E_{2}}$ is increased by a factor of $\sim 1.015$, which is close to the variation of $M$ reported above. In a field of $120 \, \text{kOe}$, it is predicted that $H_{E_{2}}$ will increase by a factor $\sim 1.1$ by assuming $p$ to be proportional to the trap fluorescence intensity $I_{T}$ (which is correct within a fast diffusion model) an augmentation of $I_{T}$ of $\sim 1.45$, now in perfect agreement with the observation (see Fig. 7 and table below).

<table>
<thead>
<tr>
<th>$H$ (kOe)</th>
<th>$I_{D}/I_{A}$</th>
<th>$I_{C}/I_{A}$</th>
<th>$I_{D}/I_{A}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.22</td>
<td>3.78</td>
<td>9.67</td>
</tr>
<tr>
<td>70</td>
<td>8.44</td>
<td>4.22</td>
<td>11.22</td>
</tr>
<tr>
<td>120</td>
<td>10.33</td>
<td>5.33</td>
<td>14.00</td>
</tr>
</tbody>
</table>

Remark : we may ask why the line D splits in magnetic fields and the other lines do not. The absence of splitting of the lines A, B and C is perfectly understandable since, whether they are intrinsic or impurity induced, pure or magnon or phonon assisted transitions, no Zeeman components can be involved for fields higher than the critical field (the magnetic sublattice structure is destroyed). As a consequence, the apparent splitting of line D is attributed to a complex intensity increase of several overlapping impurity induced lines.

4.3 THERMAL BEHAVIOUR OF THE TRAP FLUORESCENCE. — At short times after the laser pulse, i.e. for times $t \leq 2 \, \text{ms}$, the decay mode of the impurity-induced lines is dominated by a fluorescence rise characteristic of the exciton feeding function. This will be analysed in the following section. The present subsection is devoted to the study of the long time
portion of the decays which, with characteristic time constants of 12 to 15 ms at low temperature, carry most of the observed integrated fluorescence intensity.

In general, for sufficiently high temperatures, the intensities and decay time constants of the various impurity induced lines undergo similar temperature variations, i.e. exponential decreases supported by an activation-type or « boil back » process where the energy barrier $\Delta E$ stands for the energy mismatch of the various trap levels with the intrinsic exciton band. For example, the thermal behaviour of the decay rate $\tau_T$ of the T-trap fluorescence is given by [1]:

$$\frac{1}{\tau_T} = \frac{1}{\tau_0} + C e^{-\Delta E/kT} \quad (4)$$

where $\tau_0$ is the residual lifetime recorded at very low temperature and $C$ measures the coupling strength between the exciton and the trap. In particular, relation (4) can be transformed as follows:

$$\ln \left( \frac{1}{\tau_T} - \frac{1}{\tau_0} \right) = \ln C - \frac{\Delta E}{kT}. \quad (5)$$

Figures 8 and 9 show semilog-plots of the inverse time constants of the fluorescence decays of the lines located at 5 547 and 5 627 Å as a function of the inverse temperature. In the case of line 5 627 Å the fitting of the data to relation (5) works fairly well. It results in values of:

$$\tau_0 = 15 \text{ ms}, \quad C = 4 \times 10^6 \text{ s}^{-1}$$

and

$$\Delta E = 332 \text{ cm}^{-1}$$

(for a measured spectral separation of 333 cm$^{-1}$).

In the case of the shallower trap located at 5 547 Å, the agreement is not so good. In particular, the fluorescence decay is no longer exponential: it is formed of two components with two distinct time constants noted $\tau_{fast}$ and $\tau_{slow}$. Using the data given by $\tau_{slow}$ the fitting to relation (5) brings us to the following values:

$$\tau_0 = 14 \text{ ms}, \quad C = 8 \times 10^6 \text{ s}^{-1}$$

and

$$\Delta E = 100 \text{ cm}^{-1}$$

(for a measured spectral interval of 77 cm$^{-1}$).

The observed discrepancy is attributed to the additional assistance of magnons. Indeed, in CsMnF$_3$, a number of lines are made of juxtapositions of a particular impurity induced transition, with a specific trap depth, and a magnon sideband of an upper exciton. As a consequence, the deactivation of the latter which occurs at lower temperature, may strongly affect the deactivation of the former. As indicated before, by the time-resolved spectra (see Fig. 4) it is the case, for example, of the line located at 5 535 Å and the intrinsic exciton. It is also the case between the lines located at 5 547 and 5 535 Å. In the end, for shallow traps, the existence of hot magnon excitation may also contribute significantly to the above discrepancy.
In any event, in the high temperature regime ($T > 10$ K), the above mechanism of exciton diffusion, trapping and thermal detrapping, previously described, seems to apply satisfactorily again.

5. Intrinsic fluorescence dynamics at low temperature. — 5.1 EXCITON DECAY MODE AT 1.6 K. — In concentrated manganese fluorides, adopting a localized phase incoherent exciton description, a rapid diffusion of the optical excitations among the donor system formed by the bulk active ions is generally assumed [1]. In this case, at any time of the decay, all donors have an equal probability of being excited which considerably simplifies the configurational averaging problem arising in the calculations [14]; in particular, when starting with microscopic rate equations one needs an exact analytical description of the whole donor fluorescence versus time. Such a situation gives rise to an overall transfer rate $\Gamma$ which is time independent and proportional to the acceptor concentration.

Writing $\Gamma = q + p_T$, where $q$ is the sum of all the transfer rates except those which refer to traps $T$ i.e. $p_T$, the rate equations governing the populations $n_e$ and $n_T$ of the intrinsic and trapped excitons transform as:

\[
\dot{n}_e(t) = -[\gamma_R + q + p_T] n_e(t) \quad (6)
\]
\[
\dot{n}_T(t) = -\gamma_T n_T(t) + p_T n_e(t) \quad (7)
\]

where $\gamma_R$ and $\gamma_T$ represent the respective radiative probabilities.

The form of these equations leads to the following remarks:

- The integration of (6) gives rise to an exponential exciton decay with time constant $\tau_R = [\gamma_R + q + p_T]^{-1}$.
- The feeding term of the trap fluorescence i.e. $F(t) = p_T n_e(t)$ is directly proportional to the exciton population.

In connection with the latter, when going through the integration of equation (7), assuming $\gamma_R + q + p_T \gg \gamma_T$, conditions which prevail at very low temperature (in the previous section we assumed that the residual radiative rate of the traps, i.e. $\gamma_T = \tau_T^{-1} = \tau_0^{-1}$ is equal to $\gamma_R = \tau_R^{-1}$) the trap fluorescence is found to rise at short times with the same time constant that the exciton decay.

In figure 10 we have reported the fluorescence decay of the intrinsic exciton $A_2$ at $T = 1.6$ K after pulsed laser excitation in the absorption magnon sibeband $A_5$. The semilogarithmic scale used here clearly shows the non exponential behaviour of the exciton decay at short and also long times, in strong disagreement with the above formulation.

At this point the exciton decay mode was tentatively assigned to a situation where the donor-trap energy transfers may compete efficiently with diffusion. This is seen essentially at short times when the excitation goes preferentially to nearest neighbour acceptor sites (traps) this giving rise to an increased deactivation of the donor system. At long times the situation goes back asymptotically to a diffusion regime and the exciton decay becomes slower.

Such a « diffusion-limited » situation [15-19] does predominate in samples which have been voluntarily overdoped with known impurities [20]: the feeding of the trap fluorescence no longer tracks with the exciton population and the resulting transfer rate decreases at short times as expected for a multipolar or an exchange mechanism in the so-called « static » limit [21, 22]. In nominally pure samples containing few parts per million of impurities, it is thought that the diffusion limited energy transfers, though they cannot be fully disregarded, are generally very weak. This agrees with our observation in CsMnF$_3$: by extracting the feeding function $F(t)$ from the risetime behaviour of a particular trap fluorescence and dividing it by the intrinsic fluorescence intensity $I_e(t)$, we find that the energy transfer rate $p_T = F(t)/I_e(t)$ remains constant at short times.

Two other sources of non exponential exciton decay were also considered: laser induced local heating and magnon (or phonon) — assisted energy transfers.

As will be shown in the next section, the exciton decay rate increases with temperature. So, depending
on the intensity of the exciting beam, this decay rate (and the local temperature) may happen to be greater at short times after the laser pulse than later on. This effect has been avoided in our experiments by controlling the ratio of $A_3$ to $A_2$ emission (because of the fast relaxation between these states no $A_3$ emission is observed at very low temperature for moderate pump powers; the $A_3$ line appears for temperatures higher than $\sim 3.5$ K and/or for excitation levels above $\sim 7 \times 10^{19}$ photons/cm$^3$).

The non exponential decay mode might also be attributed to a magnon (or phonon)-assisted energy transfer process [20]. In this case, the associated transfer rate would strongly depend on the excitation wavelength. This process can be ruled out too since, all exciton densities being kept equal, no significant variation of the intrinsic fluorescence decay has been noted by moving the excitation across the immediate absorption magnon (or phonon) sidebands.

Following recent findings in MnF$_2$ [2] and KMnF$_3$ [3], the dominant exciton decay mode in CsMnF$_3$ (at very low temperature and short times after the laser pulse) is finally attributed to a non linear process, resulting in the following rate equation:

$$\dot{n}_e(t) = -p_1 n_e(t) - p_B n_e^2(t)$$

where the quantities $p_1$ and $p_B$ stand for the respective single and pair decay rates.

The solution of this equation can be written as:

$$n_e(t) = \left[ \frac{p_B}{p_1} + \left( \frac{1}{n_e(0)} + \frac{p_B}{p_1} \right) e^{-p_1 t} \right]^{-1}.$$  

(9)

The efficiency of radiative two exciton decay is further described in the final expression of the exciton emission intensity:

$$I_e(t) = \alpha p_1 n_e(t) + \beta p_B n_e^2(t)$$

(10)

where $\alpha$ and $\beta$ are the branching ratios of the one and two « particle » processes.

We end with a non exponential decay mode which depends non linearly on the exciton population $n_e(0)$, that is on the excitation pump power. In particular, the higher the intensity of the pump laser beam the faster the decay is at early times. This is illustrated in figure 11. No $n^2$ dependence of the emission intensity is found and the best fits to the decays (dotted lines in Fig. 11) are obtained for a negligible two exciton branching ratio $\beta$, i.e. for $I_e(t)$ proportional to $n_e(t)$ and:

$$I_e(t) \approx \left[ -\frac{p_B}{p_1} + \left( \frac{1}{I_e(0)} + \frac{p_B}{p_1} \right) e^{+p_1 t} \right]^{-1}$$

(11)

with

$$p_B n_e(0) = p_B I_e(0).$$

(12)

The initial exciton population $n_e(0)$ is estimated from the laser pump power ($10^{14}$-$10^{16}$ photons per pulse),

$$p_1 = (1.4 \pm 0.1) \times 10^3 \text{ s}^{-1}$$

and

$$p_B = (5.3 \pm 2.5) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}.$$

We also have shown the theoretical prediction of this model in figure 10. The fit to the data is excellent over two orders of magnitude. However, a slowing down of the exciton decay with respect to the predicted asymptotic approach to purely exponential is taking place in the long time limit. B. Wilson et al. [2, 20] have already mentioned such a discrepancy in the case of MnF$_2$. This discrepancy was then tentatively assigned to « various back transfer mechanisms and limited diffusion rates across macroscopic faults » which prevail at long times.

The physical mechanism itself responsible for the non linear deexcitation of the excitons at very low temperature can be interpreted as follows : as in the kinetic theory of gases, the exciton migration is described in terms of particle trajectories, a model which can be only applied if the considered exciton gas is sufficiently diluted (low enough optical pumping) to allow only pairwise exciton collisions; such a process would lead to a red shifting and a broadening of the energy levels which would depend linearly on the exciton density. This seems to apply to the behaviour of the exciton $E_1$ in KMnF$_3$ [3]. No such shifting and broadening have been observed on the exciton $A_2$ in CsMnF$_3$, except those which are related to the laser local heating.

5.2 THERMAL BEHAVIOUR OF THE INTRINSIC EMISSION. — 5.2.1. Extinction of the exciton fluorescence. — Above 4 K, the $A_2$ exciton decay becomes exponential and the decay rate increases significantly.
with increasing temperature. Specifically, we start with a situation of dominant non-linear biexcitonic decay at 1.6 K to end with a situation of dominant rapid exciton diffusion (see § 5.1) above 4 K. This result is generally attributed to a thermal deactivation process involving the absorption (step-up) of a phonon (or a magnon) with energy equal to \( \varepsilon \), and producing a variation of the form:

\[
\frac{1}{\tau} = \frac{1}{\tau_1} + K\bar{n}
\]

(13)

where \( \tau_1^{-1} \) stands for the residual transfer rate governing the exciton decay at very low temperature \( (\tau_1^{-1} = p_1) \), \( K \) is an interaction constant measuring the probability of the process and \( \bar{n} \) the mean population of bosons (phonons-magnons) with energy \( \varepsilon \), i.e. \( \bar{n} = \left[ \exp(\varepsilon/kT) - 1 \right]^{-1} \).

The semi-logarithmic plot of \( \left( \frac{1}{\tau} - \frac{1}{\tau_1} \right) \) versus inverse temperature, shown in figure 12, indicates by its straight-line behaviour that the boson population \( \bar{n} \) can be approximated by a single exponential. The slope of this line gives rise to the activation energy gap: \( \varepsilon = (5.4 \pm 0.5) \text{ cm}^{-1} \); this value is in close agreement with the measured spectral interval of \( \sim 4.9 \text{ cm}^{-1} \) between the exciton lines \( A_2 \) and \( A_3 \). Thus the thermal extinction of the exciton fluorescence might be attributed to a step-up phonon (or magnon) process from \( A_2 \) to \( A_3 \).

5.2.2. Magnon-assisted hot transitions. — The excitation spectra of several emission lines (intrinsic or impurity induced lines) have been recorded as a function of the temperature. Except for their relative intensities, all these spectra are identical. Figure 13 illustrates the results obtained with the emission line located at \( \sim 5618 \text{ Å} \) for \( T = 1.7 \text{ K} \) and \( T = 13-14 \text{ K} \). Two « antistokes » excitation lines (arrows on Fig. 13) clearly appear in the spectra, the one at \( \sim 17 \text{ cm}^{-1} \) from \( A_3 \) (and at about the same position that the absorption line \( A_1 \)) and the other at \( \sim 39 \text{ cm}^{-1} \) from \( A_3 \), in close agreement with the zone-edge magnon frequency intervals deduced from the absorption and neutron scattering data. These lines are attributed to magnon-assisted hot transitions associated with the excitons \( A_3 \) and \( A_2 \) respectively.

6. Discussion and interpretation of the results. — In a magnon-assisted cold emission process the annihilation of the exciton and the creation of the magnon on equivalent sublattices do not coexist in time [11]. Thus, the band shape of a magnon assisted cold emission satellite is theoretically stripped of the effects induced by the exciton-magnon interaction [23] (shift and distortion of the band) and this band shape can be expressed by a convolution of the exciton and magnon densities of states. The comparison of the experimental profile of this band with the theoretically predicted magnon density of states allows then to evaluate the size of the excited state dispersion. This method is examined in § 6.1.

The data obtained in absorption clearly demonstrated the delocalized character of the excitations [4, 5]; though the ion-ion interactions are certainly much weaker than in the case of molecular crystals, we noted
that the exciton theory was perfectly adapted to the
description of the observed phenomena in CsMnF₃.
However, the usefulness of the exciton model in
fluorescence still has to be proved. We deal with this
problem in § 6.2 by comparing the data obtained in
MnF₂ and CsMnF₃.

In § 6.3, a discussion is developed concerning the
nature of the excited state interactions and the effects
of dimensionality on the energy transfer efficiency.

6.1 Evaluation of the excited state dispersion
from the magnon density of states. — The
magnon density of states, calculated in the basal plane
\((k_x, k_y)\) of the first Brillouin zone by inserting the
antiferromagnetic exchange constants

\[ J_1 = -3.1 \text{ cm}^{-1} \quad \text{and} \quad J_2 = -4.4 \text{ cm}^{-1} \]

between the first (Mn₂ - Mn₂) and second
(Mn₁ - Mn₂) nearest neighbours given by
D. Khatamian et al. [7] and the anisotropy parameter
\( A = 0.096 \text{ cm}^{-1} \) in the energy branch expressions
given by A. J. Belyaeva et al. [24], is shown on figure 14
(dashed band) along with the intrinsic exciton and
magnon sideband emissions recorded at short time
delay after the laser pulse. The magnon density of
states extends over 39.5 cm⁻¹, thus ~1.5 cm⁻¹
more than the energy gap measured between A₂
and A₂ₗ. In other words this discrepancy (0.5 cm⁻¹
in MnF₂ [11], 2 cm⁻¹ in KMnF₃ [3]) might be attributed
to the exciton dispersion.

Thus, the size of the excited state dispersion which
can be deduced from that method is very uncertain.
The observed discrepancy might be due to an imperfection
of the magnetic model or to a residual exciton-
magnon interaction effect.

Remark. — The knowledge of the exciton-magnon
interaction allows us to evaluate the antiferromagnetic
exchange integral in the excited state \( J' \). It is obtained
by taking the energy mismatch of the energy gaps
observed between the exciton A₂ and the associated
magnon sidebands A₅ and A₅ₗ in absorption and
emission.

Within a simple Ising model, neglecting the anisotropy
interactions, the energy required to produce a
spin reversal in a given site is \( zJ' S \) where \( z \) stands for the
number of nearest neighbours ions coupled by the
antiferromagnetic exchange \( J \), and \( S \) for the spin
component in the ground state. Following J. B. Par
kinson et al. [23] the energy gap between the absorption
lines A₂ and A₅ takes the form:

\[ \Delta = |J| S(z + \rho) \approx 35 \text{ cm}^{-1} \quad (14) \]

with \( \rho = z \frac{S'}{S} - 1 \) and \( z = \frac{J'}{J} \), where \( J' \) and \( S' \)
are the exchange integral and the spin component in the
excited state.

If \( A^* \) stands for the energy gap of the emission
lines A₂ and A₅ₗ, it can be approximated by:

\[ A^* = 3 J_{12} S + J_{22} S \approx z |J| S \approx 38 \text{ cm}^{-1} \quad (15) \]

where we assume \( z = 4 \) nearest neighbours coupled by
\( |J| \approx 3.8 \text{ cm}^{-1} \). The comparison of \( \Delta \) and \( A^* \) gives the parameters:

\[ \rho = -0.32 \quad \text{and} \quad z = \frac{J'}{J} = 1.13. \]

The value for \( \rho \) compares remarkably well with that
obtained in MnF₂ through the thermal variation of the
pure excitonic absorption line noted E₁ [25].

6.2 Validity of the exciton model in fluorescence. — If the spin states of the fundamental and
excited levels are good quantum numbers (negligible
effect of the spin orbit mixing), the exchange interaction,
when it is the dominant mechanism responsible
for the resonant energy transfers, is restricted to the
nearest neighbour ions having parallel magnetic
moments. Indeed, in the case of optical transitions of type \( ^6A_1 (M_S = \pm \frac{3}{2}) \rightarrow ^4T_1 (M_S = \pm \frac{3}{2}) \) for which
\( \Delta M_S = 1 \), the matrix elements describing these resonant
energy transfers are given by:

\[ \langle M_S \phi'_a \phi'_b | \mathcal{H}^{\text{ex}} \phi_a \phi_b \rangle \quad (16) \]

where \( \mathcal{H}^{\text{ex}} \) is the exchange part of the inter-ion interaction Hamiltonian, \( \phi'_a \) and \( \phi'_b \) the vibronic eigenfunctions of the ground and excited states on a given site \( a \).

Fig. 14. — Comparison of the short time intrinsic emission
spectrum of CsMnF₃ at \( T = 1.6 \text{ K} \) (delay time \( d = 0.5 \mu s \),
gate width \( p = 10 \mu s \)) with the magnon density of states
dashed band) in the plane \((k_x, k_y)\).
In terms of spins, these matrix elements transform like:

\[ \mathcal{M}_{1\uparrow} \equiv \left\langle \pm \frac{1}{2}, \pm \frac{3}{2} \right| U^{*}_{\alpha\beta} \left| \pm \frac{1}{2}, \pm \frac{3}{2} \right\rangle \quad \text{i.e.} \quad \Delta M_{\text{total}} = 0 \quad (17) \]

in the case of excitation exchange between ions belonging to parallel magnetic sublattices, or

\[ \mathcal{M}_{1\downarrow} \equiv \left\langle \pm \frac{1}{2}, \pm \frac{3}{2} \right| U^{*}_{\alpha\beta} \left| \pm \frac{1}{2}, \pm \frac{3}{2} \right\rangle \quad \text{i.e.} \quad \Delta M_{\text{total}} = 2 \quad (18) \]

in the case of excitation exchange between ions belonging to antiparallel magnetic sublattices.

As a consequence, exciton migration among ions having antiparallel spins is not permitted since a large change in the total spin projection \((\Delta M_{\text{total}} = 2)\) would be needed. Only excitation exchange among ferromagnetically coupled ions plays a significant role. In low dimensional antiferromagnets such as TMMC and CMC, this restriction can lead to the exciton self trapping [26].

In MnF\(_2\), the exciton would propagate essentially along directions parallel to the \(C_2\) axis of the crystal. In CsMnF\(_3\), the excitation would be shared between third nearest neighbour Mn\(_2\) ions belonging to the parallel magnetic sublattices located on both sides of the ferromagnetic planes containing the centrosymmetric ion sites Mn1. If such a scheme can be applied to the description of the effective dynamical properties, the maximum energy transfer rate \(W_{\text{max}}\) between unperturbed manganese ions and the excited state dispersion \(E_D\) can be approximated by the following expressions:

\[ W_{\text{max}} \simeq \frac{2z |\mathcal{M}_{1\uparrow}|}{\pi h} \quad \text{and} \quad E_D \simeq 4 |\mathcal{M}_{1\uparrow}| \quad (19) \]

with

\[ |\mathcal{M}_{1\uparrow}| = \chi J_{1\uparrow} S^2 \quad (20) \]

where \(J_{1\uparrow}\) represents the ground state value of the nearest neighbour ferromagnetic exchange integral \(J_{1\uparrow} = J_3 \simeq 0.46 \text{ cm}^{-1}\) in CsMnF\(_3\) [7],

\[ J_{1\uparrow} = J_1 = 0.22 \text{ cm}^{-1} \]

in MnF\(_2\) [27]) and \(\chi\) a multiplicative factor accounting for the modification of \(J_{1\uparrow}\) in the excited state. \(S^2\) is a reduction factor due to the vibronic overlap of the ground and excited state wavefunctions.

In accordance with the Born-Oppenheimer approximation, if \(\psi_0\) and \(\psi_f\) are the vibrational parts of these wavefunctions, one has:

\[ S^2 = \left\langle \psi_f^* \psi_0^0 \right| \left\langle \psi_f^0 \psi_f^0 \right\rangle = \left| \left\langle \psi_0^0 \psi_f^0 \right\rangle \right|^2 . \quad (21) \]

This reduction factor is given experimentally by the intensity ratio of the zero-phonon absorption lines over the whole vibronic spectrum corresponding to the same electronic transition.

We did not check this result. However, we can expect the exchange interaction in the excited state to be of comparable magnitude with the exchange interaction in an ion-pair. Since the latter measured in dilute crystals is found to be of the same order of magnitude as the exchange interaction in the ground state, the above relationship does make sense for \(6A_1 \to 4A_{1g}, 4E(4g)\) transitions (transitions for which the vibronic overlap is unity).

A transition to a \(4T_1\) excited state is characterized by both spin flips and orbital jumps. In that case, a simple relationship as above is hard to find. Since \(S^2\) now plays the more significant role, we shall assume that little error is introduced if the magnitude of the exchange matrix elements \(\mathcal{M}_{gf}\) for \(f \neq 4T_1\) is written:

\[ \mathcal{M}_{gf} \approx S^2 \quad \mathcal{M}_{gf}^{4T_1} \approx S^2 \quad \mathcal{M}_{gf}^{4A_{1g}, 4E} \approx -\frac{1}{2} S^2 J_{gf} \quad \text{i.e.} \quad \chi = \frac{1}{2} . \quad (23) \]

If we use this \(\chi\) value in relation (20), we get:

- in CsMnF\(_3\) \((z = 3)\)
  \[ W_{\text{max}} \simeq 1.7 \times 10^9 \text{ s}^{-1} \quad \text{and} \quad E_D \leq 2 \times 10^{-2} \text{ cm}^{-1} \]

- in MnF\(_2\) \((z = 2)\)
  \[ W_{\text{max}} \simeq 2.7 \times 10^9 \text{ s}^{-1} \quad \text{and} \quad E_D \leq 5 \times 10^{-3} \text{ cm}^{-1} \]

in good agreement with previous estimations [2, 29].

As internal strains are responsible for an inhomogeneous broadening of the lines of the order of \(1 \text{ cm}^{-1}\), it is not surprising that the excited state dispersion cannot be observed spectrally. Only indirect evidences have to be expected, such as the well known experiment from MacFarlane et al. [29] for example.

The consistency of the excitonic model has been checked here with the help of the experimental data concerning the non linear behaviour of the exciton decay and the estimated diffusion coefficients in MnF\(_2\) and CsMnF\(_3\) as well.

Assuming, as above, that the exciton migration can be described in terms of the trajectories of particles the exciton-exciton collision parameter \(p_B\) is related to the mean ion-ion transfer rate \(W\) by:

\[ p_B = \sigma \nu \quad (24) \]
and

\[ v = W \cdot r \]  (25)

where, as in the kinetic theory of gases, \( \sigma \) stands for the effective cross section for the interaction, \( v \) the average exciton velocity and \( r \) in the case of exchange energy transfers, the separation between ferromagnetically coupled nearest neighbour ions. \( p_B \) is also given by [30]:

\[ p_B = 8 \pi D \langle R \rangle \]  (26)

where \( D \) is an effective diffusion coefficient and \( \langle R \rangle \) an interaction radius related to \( \sigma \) by \( \sigma = \pi \langle R \rangle^2 \).

We obtain the final expression:

\[ D = \frac{1}{8} \left( \frac{p_B \cdot W \cdot r}{\pi} \right)^{1/2}. \]  (27)

That is, with \( W = W_{\text{max}} \):

- for CsMnF\(_3\): \( p_B \approx 5 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}; r = 5.78 \text{ Å} \)
  \[ D_{\text{max}} \approx 4.7 \times 10^{-8} \text{ cm}^2 \text{s}^{-1} \]

- for MnF\(_2\): \( p_B \approx 5 \times 10^{-13} \text{ cm}^3 \text{s}^{-1}; r = 3.31 \text{ Å} \)
  \[ D_{\text{max}} \approx 1.4 \times 10^{-7} \text{ cm}^2 \text{s}^{-1}. \]

These coefficients, characterizing the effective migration of the excitations throughout the lattice do not correlate with the size of the excited state dispersions \( E_D \) calculated above (otherwise the \( D \) coefficient in CsMnF\(_3\) would be more important). However, this evolution is in perfect agreement with the experimental value of the total decay rate noted \( p_1 \) in section (5.1).

Indeed, it is found:

\[ p_1 (\text{CsMnF}_3) \approx 1.4 \times 10^3 \text{ s}^{-1} \]

and

\[ p_1 (\text{MnF}_2) \approx 8 \times 10^3 \text{ s}^{-1} \]  [2].

Moreover, if one uses the following relationship:

\[ p_1 = 4 \pi D N_T R_T \]  (28)

where \( N_T \) represents the trap concentration and \( R_T \) the effective capture radius (diffusion model), one obtains:

- for CsMnF\(_3\) with
  \[ N_T = C_T N_E; \quad C_T \approx 5 \times 10^{-5}; \quad N_E \approx 8.6 \times 10^{24} \text{ ions/cm}^3 \]
  \[ D \approx 5.7 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}. \]

- for MnF\(_2\) with
  \[ N_T \approx 4 \times 10^{17} \text{ ions/cm}^3 \]

and \( R_T \approx 4.5 \text{ Å} \) (mean separation between nearest neighbour ions)

\[ R_T \approx 3.3 \text{ Å} \]

\[ D \approx 4.8 \times 10^{-8} \text{ cm}^2 \text{s}^{-1} \]

in accordance with the limits noted \( D_{\text{max}} \) calculated above.

These results can be explained as follows:

The values of \( p_1 \) and \( p_B \) are obtained in a time domain (above 10 \( \mu \)s in general) where the exciton coherence does not exist any more and the diffusion coefficient calculated from these parameters is proportional to an effective transfer rate \( W' \) given by:

\[ W' \approx \frac{2 \pi |\mu|}{\hbar^2} \quad \text{with} \quad D \approx W' r^2 \]  (29)

where \( \alpha \) is a damping constant characteristic of the exciton loss of phase memory [31]. This expression coincides with the form given by the Fermi Golden Rule for incoherent energy transfers. This \( |\mu|^2 \) relationship has been used in section (4.2) to correlate the magnetic field induced delocalization process to the sublattice magnetization data.

It becomes clear that the experimentally determined exciton-exciton interaction parameter \( p_B \), for example, contains implicitly this coherence damping effect: the coherence damping effect in CsMnF\(_3\) would be more important than in MnF\(_2\). This has been confirmed experimentally since no rise time behaviour of the zone edge (zone centre) emitted photons after narrow bandwidth pulsed dye laser creation of zone centre (zone edge) excitons (spectral width \( = 0.1 \text{ cm}^{-1} \), pulses of 10 ns duration and 500 \( \mu \)J unfocused) has been observed in CsMnF\(_3\) by recording the signal over 1 028 channels with 100 ns per channel (see Ref [29] for the details of the experiment).

Finally we can consider that the transfer rate \( W \) which figures for example, in the expression (27), is adequately given by the approximate excitonic relations (19) and (20). This proves the consistency of the exciton picture in fluorescence; however, this model must be used very carefully since most of the experimental parameters are obtained in a time domain where they depend not only on the inter-ion interactions and the geometry of the lattice, but also on the dimensionality of the energy migration and the scattering processes responsible for the exciton loss of phase memory (thermal phonon scattering, elastic exciton scattering by the perturbed \( \text{Mn}^{2+} \) ion traps, exciton scattering between internal strain induced macroscopic domains, exciton-exciton collisions).

6.3 Nature of the excited state interaction and dimensionality effect. — As asserted above, when the exchange interactions predominate, the exciton in CsMnF\(_3\) propagates between the two parallel Mn\(_2\) magnetic sublattices located on both sides of the ferromagnetic planes containing the centrosymmetric ion sites Mn\(_1\). In that case, the
exciton diffusion would be anisotropic and the probability to find a trap would be reduced; this might justify the low value of the $D$ coefficient found in this compound.

In particular, this interpretation is in perfect accordance with the magnetic field induced delocalization process evidenced in section (4.2). The applied magnetic field allows the excitations to propagate between nearest neighbour Mn2 ions (belonging to antiparallel magnetic sublattices when no external field is applied); the exciton diffusion becomes isotropic and the probability of finding a trap is increased.

However, the even more pronounced strain-induced effect described in section (4.1) could not be correctly interpreted. The stress effect, indeed, was used to separate the contributions of the excitations localized on each of the adjacent Mn2 ions having antiparallel spins which in case of dominant exchange interactions and from a dynamical point of view, would have changed nothing in the situation at zero stress.

Suppose that the excitation propagates throughout adjacent manganese ions Mn2 having antiparallel spins: in either the case of exchange or the case of electric multipole interactions, the spin-orbit mixing of the spins : in either the case of exchange or the case of electric multipole interactions, the spin-orbit mixing of the spins

However, this is unlikely since the resulting matrix elements would be reduced by the quantity

$$\left[ \frac{\langle \psi_{SO} \rangle^2}{\Delta E} \right] \sim 10^{-4}$$

and

$$\Delta E = E(4T_1) - E(6A_1) \sim 19,000 \text{ cm}^{-1}.$$ 

Finally, the intermediate uniaxial stress seems to act predominantly on the excitation exchange between the third nearest neighbour Mn2 ions responsible for the excited state dispersion.

We have discarded the effect of an inhomogeneous stress putting the ions out of resonance since this macroscopic effect should not perturb significantly the short range energy transfers.

The stress effect is finally attributed to a non negligible modification of the inter-ion exchange coupling. It is known, indeed, that the superexchange mechanism, involved between the manganese ions, strongly depends on the angle formed with the ligands, the largest coupling being obtained for a chain of atoms Mn-F-Mn. The stress induced modification of this angle is the more critical as the original coupling is weak, which applies here.

7. Conclusion. — This paper has been devoted to a complete description of the fluorescence properties of the nominally pure antiferromagnet CsMnF$_3$. Particular attention has been given to the intrinsic exciton decay mode and the effects of temperature, uniaxial stress and magnetic field on the energy transfer processes. The results are consistently described by a fast exciton diffusion ($D \sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and trapping, taking into account that exciton-exciton annihilation ($P_\text{ann} \sim 5 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$) predominates at very low temperature and short times after the excitation. Conclusions have been drawn in favour of the exciton picture in fluorescence even though the exciton state dispersion is too weak ($E_\text{D} \sim 0.01 \text{ cm}^{-1}$) to be measured experimentally. Excitation transfer between ions coupled by ferromagnetic exchange interactions has been pointed out. The exciton propagates in a « zigzag » between the two parallel Mn2 magnetic sublattices located on both sides of the ferromagnetic planes containing the centrosymmetric ion sites Mn1.

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