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Luminescence and photoionization processes of Yb$^{2+}$ in CaF$_2$, SrF$_2$ and BaF$_2$

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1. Introduction.

The main spectroscopic features introduced by divalent rare earth ions at substitutional sites in fluorite-structure crystals (such as SrF$_2$) are the localized transitions, namely f → f and f → d. These systems are suitable to study the photoionization of such ions in crystals. Indeed, an ion such as Yb$^{2+}$ at a Sr$^{2+}$ site in SrF$_2$ is situated in a region of high negative electrostatic potential, on the order of $-20$ eV, and this reduces its energy of ionization from its vacuum
value of about 25 eV, to about 5 eV. Thus, within this energy range, photoionization thresholds may be evaluated from photoconductivity measurements using a simple electrostatic model which gives a reasonable agreement with the observed values [1-3]. Usually the ground and the lowest excited states of a rare earth impurity ion lie in the band gap of the host crystal and so localized transitions are observed. When all the excited states of the impurity lie in the conduction band there are at least two channels for loss of energy by the excited ion: ionization is one and luminescence the other. Luminescence may occur even though ionization is taking place. Normally the lowest excited localized level would be the emitting level but when this level lies above the exciton energy it may decay into it, and then the delocalized exciton may emit instead.

Most of the spectroscopic data on the systems CaF\(_2\), SrF\(_2\), BaF\(_2\) : Yb\(^{2+}\) and SrF\(_2\), BaF\(_2\) : Eu\(^{2+}\) were published in a series of papers by Reut [4], Kaplianskii [5], Loh [6] and Piper [7]. These systems are well known for their «anomalous» emission. Without the photoconductivity data however, no satisfactory interpretation of this feature could be reached. We now believe that the «anomalous» emission band is the radiation from an impurity-trapped exciton which consists of a bound electron-hole pair with the hole localized on the impurity and the electron on a nearby lattice site and which is the lowest excited state of the impurity-crystal system [8-9].

In a previous paper we reported results concerning the BaF\(_2\) : Eu\(^{2+}\) system and compared its anomalous red emission band with the normal blue emission band of SrF\(_2\) : Eu\(^{2+}\) [10]. The present paper deals with CaF\(_2\), SrF\(_2\), BaF\(_2\) : Yb\(^{2+}\) systems. New experimental results of absorption, emission, photoconductivity and lifetime measurements are interpreted in terms of configuration coordinate curve diagrams and confirm our impurity-trapped exciton model previously reported.

2. Experimental.

The crystals of CaF\(_2\), SrF\(_2\), BaF\(_2\) doped with 0.01 % - 0.1 % Yb\(^{2+}\) which we have studied, were grown by Prof. H. Bill in Geneva using a Bridgman technique. The absorption measurements were made by using a CARY UV-VISIBLE-NIR spectrophotometer model 2300, equipped with a cryostat (4.2-300 K) from SMC. The synchrotron ACO of LURE in Paris was used as a light source when energy up to 10 eV was required to perform excitation spectra. For emission spectra (4.2-300 K) the samples were cooled with a helium transfer cryostat. The exciting source was either the third harmonic of a Q-switched Nd : YAG laser (Quantel), or the output beam from a pumped dye laser which could be mixed with fundamental (1.06 \(\mu\)m) or frequency doubled and mixed with fundamental. The excitation wavelength may thus be scanned from 230 to 420 nm with energy up to several tens of millijoules. Emitted photons were collected and focused on the entrance slit of a Hilger 1 m monochromator. Emission spectra were obtained by using a computer-scannable monochromator and detecting the dispersed emission with a cooled EMI 8852 or RCA AsGa PMT followed by an amplifier/discriminator and a photon counter. They were afterwards corrected for the apparatus sensitivity. Decay time measurements were recorded either with a multichannel analyzer (Intertechnique IN90) with a maximum resolution of 2 \(\mu\)s per channel for the long lifetimes, or a model 8100 waveform recorder (Biomation) with a minimum sample interval of 10 ns for the short lifetimes. Photoconductivity measurements were made using blocking electrodes. The sample mounting geometry was a sandwich configuration. Light from a 450 W xenon lamp was passed through a small monochromator to select the desired wavelength and came through the transparent front electrode collinearly with the applied electric field. The photocurrent was measured with a vibrating reed electrometer.
CARY 401 which was sensitive to $10^{-17}$ A. The previous experimental set-up [1-4] has been modified in order to improve the quality of very low intensity photocurrent measurements. A highly stabilized 6522A DC power supply from Hewlett-Packard gave a much lower noise level, a new electrode arrangement allowed us to increase the electric field up to 20 kV/cm and automatic repetitive measurements and data treatments by a microcomputer ensured better reproducibility of the results.

3. Experimental results.

3.1 ABSORPTION. — The ground state of Yb$^{2+}$ ion corresponding to $4f^{14}$ configuration in an $O_h$ symmetry site is $A_{1g}$. The first excited configuration is $4f^{13}5d$ which is split into $4f^{13}5d(e_g)$ and $4f^{13}5d(t_{2g})$ by the cubic field with (e$_g$) the lowest. The absorption spectra at $T = 6$ K for the three crystals are shown in figure 1. These spectra had been extensively studied in the past [6]. The lowest energy bands, below 40 000 wavenumbers, shift towards higher energy when the cation size increases, while the highest energy bands, above 40 000 cm$^{-1}$, shift in the opposite direction. The former corresponds to the e$_g$ orbital and the latter to the t$_{2g}$ orbital, and the relative displacement is due to the decrease of the crystal field. The parameter 10 $D_q$ is approximately equal to 16 000 cm$^{-1}$ and the energy difference between the two main e$_g$ bands ($\approx 10^4$ cm$^{-1}$) is close to that of $^2F_{5/2}-^2F_{7/2}$ of the $4f^{13}$ core [11].

The hyperbolic cotangent law which describes the temperature dependence of the absorption bandwidth $\sigma$ is given by:

$$\sigma^2(T) = \sigma^2(0) \cdot \coth (h\omega / 2kT)$$  \hspace{1cm} (1)
where $\hbar \omega$ is the average phonon frequency of the totally symmetric or breathing mode of the \((\text{YbF}_8)_6^-\) cluster. The data shown in figure 2 are from the first absorption band \((A_{1g} \rightarrow T_{1u})\) which is well separated from the other bands. Best fits are obtained for $\hbar \omega = 314, 250$ and $220 \text{ cm}^{-1}$ for CaF$_2$, SrF$_2$ and BaF$_2$, respectively, in good agreement with the main frequencies previously obtained in the same lattices doped with other rare-earth impurities (see for example Ref. [12]).

\[ \text{Arg} \left( \frac{\alpha^2(0)}{\alpha^2(T)} \right) \]

![Graph showing variation of bandwidth](image)

**Fig. 2.** — Variation of the bandwidth of the first absorption band of Yb$^{2+}$ as a function of temperature.

### 3.2 EMISSION.

The intensity of the normally expected emission, as the inverse of the absorption process to the lower states of Yb$^{2+}$ in the three crystals should be maximum around $23 \, 000 \text{ cm}^{-1}$ and the bandwidth should not exceed $10^3 \text{ cm}^{-1}$. The actual emission of CaF$_2$: Yb$^{2+}$ peaks at $17 \, 400 \text{ cm}^{-1}$ and is $4 \, 000 \text{ cm}^{-1}$ in width at half height and that of SrF$_2$: Yb$^{2+}$ is maximum at $12 \, 000 \text{ cm}^{-1}$ and is approximately $4 \, 800 \text{ cm}^{-1}$ wide, as for BaF$_2$: Yb$^{2+}$ no emission was detected as far as $1.5 \mu\text{m}$ even under strong laser excitation. Figure 3 shows both emissions from CaF$_2$: Yb$^{2+}$ and SrF$_2$: Yb$^{2+}$. The dashed part (below $11 \, 000 \text{ cm}^{-1}$) of the SrF$_2$: Yb$^{2+}$ spectra is extrapolated as the mirror image reflection of the higher energy side about the maximum since our detection system was not sensitive in this energy range. These very large Stokes shifts suggest that these «anomalous» emissions are not due to localized transitions. The temperature dependence of the luminescence intensity under $355 \text{ nm}$ laser excitation of both crystals are shown in figures 4 and 5. The fluorescence intensity is maximum at $20 \text{ K}$ in SrF$_2$ and at $110 \text{ K}$ in CaF$_2$. Increasing the temperature leads to the quenching of the fluorescence respectively at $140 \text{ K}$ and $180 \text{ K}$. In figure 6 are shown the temperature dependences of the bandwidth (left scale, (+) points) and of the energy of the maximum of the emission band of CaF$_2$ (right scale, (*) points). In the very low temperature range (below $6 \text{ K}$) the bandwidth and the band maximum do not change.
Fig. 3. — Emission spectra at $T = 4.2$ K corrected from the detection system sensibility. The dashed part of the SrF$_2$: Yb$^{2+}$ emission is deduced as the mirror image reflection of the high energy side of the spectrum about the maximum.

Fig. 4. — Temperature dependence of the fluorescence intensity of CaF$_2$: Yb$^{2+}$ under 355 nm excitation.

Between 6 and 40 K the band maximum strongly shifts towards the blue by an amount of 1 200 wavenumbers, simultaneously the bandwidth slightly increases first and then drastically decreases from 4 000 to 3 015 cm$^{-1}$. For further increase of temperature (higher than 40 K) the band shifts backward and its width increases again to its initial value. These strange temperature dependences which contribute to the anomalous character of the Yb$^{2+}$ fluorescence, will be interpreted later.
3.3 PHOTOCONDUCTIVITY. — The photoconductivity spectra are represented in figures 7 and 8 and are compared to the absorption spectra for both crystals. One observes a strong modulation of the photoconductivity curves by the absorption of the Yb$^{2+}$ impurity, even in the low energy range for SrF$_2$ and contrary to previous results [8] which were obtained with another photoconductivity set-up less efficient. In particular then we had to work with a spectral resolution of about 8 nm to detect the signals instead of 1 nm as in the present work. The photoconductivity spectra per incident photon are basically the same above 35 000 cm$^{-1}$.
and bear the same relationship to the absorption spectra. The photoconductivity rises abruptly at about 4.3 eV in each case, as the second major band begins to rise. In SrF$_2$, as the absorption is weaker in the second and third bands than in the first one, the photocurrent is
relatively much more important. This feature clearly indicates that electron ejection occurs from the upper levels without prior relaxation. It is clear also that in the energy regions where the systems do not or only weakly absorb \((\hbar \omega < 25 \, 000 \, \text{cm}^{-1} \text{ and } 32 \, 300 < \hbar \omega < 34 \, 300 \, \text{cm}^{-1})\) no photocurrent can be detected. This means that photoionization, i.e. direct transition from the impurity ion to the conduction band, as for \(\text{Cu}^+\) in \(\text{CdCl}_2\) \cite{13}, is not observed. In \(\text{SrF}_2: \text{Yb}^{2+}\), the photoconductivity threshold is found around \(25 \, 000 \, \text{cm}^{-1}\) (3.10 eV) and corresponds to the onset of the first absorption band of \(\text{Yb}^{2+}\) while no photocurrent is detectable below \(35 \, 000 \, \text{cm}^{-1}\) (4.34 eV) in \(\text{CaF}_2\). If these thresholds are considered as the photoionization energies of \(\text{Yb}^{2+}\) ion, they are very well accounted for by our electrostatic model which predicts 3.34 eV and 4.22 eV for \(\text{Yb}^{2+}\) in \(\text{SrF}_2\) and \(\text{CaF}_2\), respectively \cite{3}. These results suggest that all the excited states and all but the first excited state of \(\text{Yb}^{2+}\) lie in the conduction band of \(\text{SrF}_2\) and \(\text{CaF}_2\) respectively. It should be noted that the photosensitivity, which is proportional to the photoconductivity per absorbed photon, is very different at low or high excitation energy in \(\text{SrF}_2: \text{Yb}^{2+}\). This is probably due to the fact that the coupling with the conduction band is weaker for the low energy than for the high energy levels of \(\text{Yb}^{2+}\). This and the anomalous emission may be explained by introducing another energy level in our system: a self-trapped exciton-like state which is now going to be described.

![Configuration coordinate curve diagram of CaF2:Yb2+](image-url)
4. The impurity centered exciton model.

The model used to explain the fluorescence properties of Yb$^{2+}$ in CaF$_2$ and SrF$_2$ is the same as that already developed by us for BaF$_2$: Eu$^{2+}$ [10] and uses configuration coordinate diagrams illustrated in figures 9 and 10. In both cases we assume that the breathing mode is the main vibrational mode which all the electronic states are coupled with. Its value is taken from the temperature dependence of the absorption bandwidth. The $X$ axis scale corresponds to the relative displacements of the ligands. The lower parabola represents the ground state of Yb$^{2+}$. Two excited state parabolas of Yb$^{2+}$ are shown, corresponding to the $T_{1u}$ and $T_{2u}$, $E_u$ states. They are located on the energy scale so as to explain the peaks ascribed to the transitions to these states. The size of Yb$^{2+}$ in its excited states is not known, but the position of the minimum of the absorption bands allows us to estimate the equilibrium distances for those excited states. The expansion of Yb$^{2+}$ found this way, is about 0.07 Å in SrF$_2$ and 0.05 Å in CaF$_2$ and is consistent with the metal ion site size. The third parabola corresponds to the impurity exciton, the geometry of which is that expected for a trivalent ion, Yb$^{3+}$ in our case, at a divalent site with an electron delocalized over the next neighbor metal-ion sites. The impurity-trapped exciton state is supposed to be the lowest excited state and thus the emitting level responsible of the «anomalous» fluorescence observed. The collapse of the F$^-$ cube around the Yb$^{3+}$ reduces the equilibrium distance of the (YbF$_8$)$^{5-}$ cluster and accounts for the large Stokes shift. The position of this parabola is not defined very well, but the decrease of the impurity-fluoride distance is of the order of magnitude of the difference.

Fig. 10. — Configuration coordinate curve diagram of SrF$_2$: Yb$^{2+}$. 
between the ionic radii of \( \text{Yb}^{3+} \) and \( \text{Yb}^{2+} \), i.e. 0.2 Å. Pedrini et al. had shown in a previous paper [3] that for a given impurity, the bigger the metal ion, the larger the relaxation of fluorine and that for a given crystal, the smaller the impurity ion, the larger the relaxation. Thus, the expected negative shift of the exciton curve increases from \( \text{CaF}_2 \) to \( \text{SrF}_2 \) and even more for \( \text{BaF}_2 \). This accounts for the red shift of the emission band in the various crystals and may even explain why no fluorescence at all is detected in \( \text{BaF}_2 \). In figures 9 and 10 the exciton curves are drawn assuming that the energy of the symmetric vibrational mode is the same as in the other excited states and their positions are deduced from the value of the maximum and of the high energy tail of the emission bands. This gives a shift equal to \(-0.17 \) Å and \(-0.27 \) Å in \( \text{CaF}_2 \) and \( \text{SrF}_2 \), respectively. If we apply a very rough proportionality law between the metal ion size and the exciton curve shift this leads to \(-0.34 \) Å for \( \text{BaF}_2 \) and a maximum of emission band beyond 2.5 \( \mu \)m. In those figures the fifth parabola corresponds to an \( \text{Yb}^{3+} \) ion plus a free electron in the conduction band. The gap between the minimum of these curves and the exciton curve in both cases represents the binding energy \( E_b \) of the impurity trapped exciton. Its value is not known but can be estimated from photoconductivity measurements. The bottom of the conduction band is at most at energy around 25 000 cm\(^{-1}\) for \( \text{SrF}_2 : \text{Yb}^{2+} \) and between 29 000 and 34 000 cm\(^{-1}\) for \( \text{CaF}_2 : \text{Yb}^{2+} \). It should be noted that \( E_b \) could be more accurately determined by a two-step photoconductivity experiment now in progress. This binding energy is likely smaller in \( \text{SrF}_2 \) than in \( \text{CaF}_2 \), the electron-hole distance being larger in the former crystal. In our crude configuration curve diagram \( E_b \) is estimated to be less than 5 000 cm\(^{-1}\) (0.6 eV) in both crystals. This value is in reasonable agreement with the one calculated using a Bohr model for the electron-hole pair which gives a good first approximation to the binding energy (0.35 eV in \( \text{SrF}_2 \)) as shown by Eisenberger and Pershan [14]. With this model, it is now possible to interpret the relatively low photosensitivity recorded in \( \text{SrF}_2 : \text{Yb}^{2+} \) in the low energy range and the «anomalous» emission. When we excite \( \text{Yb}^{2+} \) in the \( T_{1u} \) level with the 355 nm third harmonic of the YAG laser, the electron quickly relaxes into the lower energy levels, i.e. the

Fig. 11. — Absorption tail of exciton state in \( \text{SrF}_2 : \text{Yb}^{2+} \) at \( T = 6 \) K. The small hump at 26 000 cm\(^{-1}\) corresponds to the absorption of \( T_{2u} \), \( E_u \) level.
The exciton level and \( T_{2u}, E_u \) results in the complete quenching of the fluorescence from \( T_{1u} \) level. Then \( T_{2u}, E_u \) loses its energy by a tunnel effect toward the exciton state, which is more likely than the radiative transition to the ground state, leading in turn to the total quenching of the fluorescence from \( T_{2u}, E_u \) level and to the strong emission of the exciton. Autoionization of an energy level is very likely when the coupling between this level and the conduction band is strong. In our diagram this coupling corresponds to the overlap between the localized states and the \((Yb^{3+} + e^- \text{ free})\) state, the bottom of which corresponds to the bottom of the conduction band. It is clear in \( \text{SrF}_2 : \text{Yb}^{2+} \) that, although the \( T_{1u} \) level is above the bottom of the conduction band, the coupling with the \((Yb^{3+} + e^- \text{ free})\) state is weak leading to the low photosensitivity in this energy range. Furthermore, we believe that the absorption shoulder observed on the higher energy side of the \( T_{1u} \) absorption band corresponds to the direct excitation of one electron in the exciton state. The exciton absorption band is expected to be very wide and we do observe an absorption tail stretching down to 20,000 cm\(^{-1}\) (Fig. 11). The residual background below 20,000 cm\(^{-1}\) is likely due to reflection losses on the sample surface that the baseline of the spectrophotometer cannot take into account. The large overlap of the exciton and the \((Yb^{3+} + e^- \text{ free})\) state explains the higher photosensitivity observed around 30,000 cm\(^{-1}\).

5. Fluorescence lifetime.

We now move beyond the simple configuration coordinate curve diagram to a more detailed analysis of the exciton structure which might explain the observed lifetime. The ground state of \( \text{Yb}^{2+} \) is an \( A_{1g} \) state. According to the «corrected» band structure proposed by Albert \textit{et al.} [15], the lowest point of the conduction band is made up of Ca 4s wave functions. Although this calculation deals with CaF\(_2\), the result is certainly also valid for SrF\(_2\). The impurity trapped exciton is made of \( \text{Yb}^{3+} \) core in its ground state \( 2F_{7/2} \) which is split by the cubic field into three levels \( \Gamma_6 + \Gamma_7 + \Gamma_8 \) with probably \( \Gamma_7 \) the lowest and one «s» electron which corresponds to \( \Gamma_6 \) according to the double group notation. The hole-electron coupling gives \( \Gamma_6 \times \Gamma_7 = A_2 + T_2 \), both forbidden as electric dipole transitions to the ground state.

![Fig. 12. Temperature dependence of the lifetime of CaF\(_2\) : Yb\(^{2+}\). Below 50 K left scale, above 50 K right scale.](image-url)
Fig. 13. — Temperature dependence of the lifetime of SrF$_2$: Yb$^{2+}$. Below 30 K left scale, above 30 K right scale.

$A_1$. In addition, the hole-electron overlap is quite small at this distance, making both transition moment and splitting small. Thus it is reasonable to account for a long lifetime as the transition from these states. The temperature dependences of emission lifetime are shown in figures 12 and 13. The lifetimes are 15 ms at $T = 4.4$ K and $2.8 \times 10^{-3}$ ms at 180 K in CaF$_2$ and 0.65 ms at $T = 4.4$ K and $1.3 \times 10^{-3}$ ms at 140 K in SrF$_2$. The emission wavelength was monitored at the top of both bands and the excitation wavelength was 355 nm. Such temperature dependences are typical of the three level scheme in which $g_2$ and $g_3$ are the multiplicities for levels 2 and 3 (the lowest excited state), $A_{21}$ and $A_{31}$ the deexcitation probabilities, and $\varepsilon$ the energy gap between both excited levels [16]. In the low temperature range where radiationless processes are negligible the lifetime is given by:

$$\tau^{-1} = \frac{g_3 * A_{31} + g_2 * A_{21} * \exp(-\varepsilon/kT)}{g_3 + g_2 * \exp(-\varepsilon/kT)}.$$  \hspace{1cm} (2)

The best fits are obtained in both cases by considering the level $A_2$ below the level $T_2$, i.e. for $g_2 = 3$ and $g_3 = 1$, and give the following parameters gathered in table I:

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$A_{21}$ (s$^{-1}$)</th>
<th>$A_{31}$ (s$^{-1}$)</th>
<th>$\varepsilon$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>$3.8 \times 10^3$</td>
<td>66</td>
<td>40</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>$4.9 \times 10^4$</td>
<td>$1.5 \times 10^3$</td>
<td>26</td>
</tr>
</tbody>
</table>

These parameters deserve some comments: 1) The energy gap between both levels is small, as expected, and decreases when electron-hole distance increases; 2) At very low
temperature (typically below 10 K) only the $A_2$ level is populated and can emit, so the large difference (two orders of magnitude) between both $A_{31}$ parameters ought to account for an ionization process which could occur from the relaxed exciton state only in the case of SrF$_2$:Yb$^{2+}$ wherein the binding energy is weaker. This process could slightly take part in the photoconductivity signal in the low energy region. This model gives an ionization probability of the order of $10^3$ s$^{-1}$ which is quite small compared to the $4 \times 10^{13}$ s$^{-1}$ measured by Fuller et al. in BaF$_2$:Eu$^{2+}$ [17], indicating that although we observed a weak photocurrent in SrF$_2$ the hole-electron pair remains strongly bound; 3) Increasing the temperature leads to population of the upper level and, due to the small value of $e$, thermal equilibrium between both levels is reached at a relatively low temperature ($\approx$ 15 K). This explains the behavior of the fluorescence bandwidth of CaF$_2$:Yb$^{2+}$ and also can account for the drastic shift of the emission band between 20 and 40 K if it is supposed that the minima of $A_2$ and $T_2$ potential curves occurs for different impurity-ligand distances. We estimate the difference to be about 0.02 Å; 4) The parameter $A_{21}$ should correspond to the radiative lifetime at the higher temperature for which radiationless processes are negligible; this is the case in CaF$_2$:Yb$^{2+}$ where $A_{21}$ corresponds to the lifetime at 100 K, the temperature above which luminescence intensity and lifetime begin to drop off. In SrF$_2$:Yb$^{2+}$ an ionization process is always present, thus $A_{21}$ represents the sum of radiative and ionization processes and its calculated value corresponds to the observed lifetime at about 70 K. Above this temperature the coupling by phonons to the ground state induces non-radiative transitions which in turn explain the drastic decrease of lifetime as shown in figure 13.

The last point we want to discuss concerns the shape of the decay curve in the very short time limit. Indeed, by exciting both crystals in the $T_{1u}$ level (355 nm) the fluorescence decays present a risetime with an initial intensity different from zero. If we scan the excitation wavelength toward lower energies the risetime suddenly disappears without any change in the lifetime and this at any temperature (Fig. 14). This occurs at 395 nm in SrF$_2$ and 403 nm in CaF$_2$. This behavior can be explained in the framework of our exciton model. A 355 nm photon can promote an electron directly into the exciton level or, with a greater probability, into the $T_{1u}$ level. Electrons excited into the $T_{1u}$ level relax very quickly either into the

![Fluorescence decay curve](image)

Fig. 14. — Short time part of the fluorescence decay time of SrF$_2$:Yb$^{2+}$ at $T = 30$ K. The signal under 395 nm excitation is noisier because it is much weaker than the one under 355 nm excitation.
exciton or into the $E_{2u}, T_{2u}$ level leading to an equal population of both levels in first
approximation. Afterwards the risetime originates from these trapped electrons in the
$E_{2u}, T_{2u}$ metastable level which can « tunnel » into the exciton level which has a non-zero
initial population. When the photon energy becomes too weak to excite $T_{1u}$ and
$E_{u}, T_{2u}$ levels but sufficient to reach the exciton level, the risetime should disappear. This is
exactly what we observe so we can know in this way, very accurately, the position of the
$E_{u}, T_{2u}$ level in both systems, namely 25 316 and 24 814 cm$^{-1}$ in SrF$_2$ and CaF$_2$, respectively.
It is important to note that these values are in pretty good agreement with absorption spectra.
If we call $W_e$ the probability of deexcitation of exciton and $W_t$ the probability of tunneling
from the $E_{u}, T_{2u}$ level and considering that the relaxation times are faster than the laser pulse
duration we can assume that the initial populations of both levels are equal. Furthermore
since no emission from the $E_{u}, T_{2u}$ level has been detected we can say that tunneling is the
only channel to empty the $E_{u}, T_{2u}$ level. So this crude approximation leads us to the following
simple rate equations to describe our system:

$$\frac{dn_a}{dt} = -W_t \cdot n_a(t)$$  \hspace{1cm} (3)

$$\frac{dn_c}{dt} = W_t \cdot n_a(t) - W_e \cdot n_c(t)$$  \hspace{1cm} (4)

in which $n_a$ and $n_c$ are the populations of $E_{u}, T_{2u}$ and exciton levels, respectively the
resolution of the system leads to:

$$n_c(t) = A \cdot \exp(-W_e \cdot t) - B \cdot \exp(-W_t \cdot t)$$  \hspace{1cm} (5)

where $A$ and $B$ are functions of $N$, the initial population, $W_e$ and $W_t$. Moreover
$B$ is proportional to the initial population of the $E_{u}, T_{2u}$ level, and $(A - B)$ is the initial
population of the exciton level. By fitting the short time limit of decay times with equation (5)
we can evaluate $W_t$. In both crystals we find approximately the same value, $W_t = 8 \times 10^4$ s$^{-1}$,
which is temperature independent. In SrF$_2$, at high temperature (> 160 K) when $W_e$ strongly
increases and becomes comparable to $W_t$ the risetime vanishes, in agreement with the above-
mentioned equation.

6. Conclusion.

In this paper, we analyze the fluorescence and the photoconductivity properties of
Yb$^{2+}$ in CaF$_2$, SrF$_2$ and BaF$_2$. We present a new approach of the interpretation of the
« anomalous » emission usually observed in such systems by an impurity trapped exciton. We show that the excited « d » electron of Yb$^{2+}$ is delocalized in the « s » orbitals of next
neighbor Ca$^{2+}$ ions which the bottom of the conduction band is made of. Then the electron
can either autoionize and give rise to a photocurrent, or relax into the impurity trapped
exciton level which is the lowest excited state of the system and may emit in turn. The
photoconductivity spectra show that when the electron is excited into the higher energy bands
it autoionizes without any prior relaxation. When the system is in the exciton state it has a
weak probability to ionize if the binding energy is not too high as in SrF$_2$ and then to produce
a weak photocurrent if an electric field is applied to the crystal. This possibility explains the
large difference between the lifetime at $T = 4.2$ K in the two crystals. Finally, the strong
temperature dependence of lifetime shows that the exciton level is split into two close levels
and the study of the risetime of the decays allow us to calculate the energy of the
$E_{u}, T_{2u}$ level and the probability of tunneling from this level into the exciton level.
References