Optical analysis of X-ray effects in Ag+-doped Strontium fluoride crystals

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Optical analysis of X-ray effects on Ag\textsuperscript{+}-doped strontium–fluoride crystals

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Abstract

The optical and paramagnetic properties of X-irradiated silver doped SrF\textsubscript{2} crystals were investigated. The freshly irradiated crystals show a complex absorption spectrum between approximately 200 and 650 nm. Subsequently, systematic heat treatments were applied and absorption, photoluminescence and its polarization dependence, thermo- and radio-luminescence experiments have been undertaken. The resulting experimental data were mutually correlated with the aid of the factor analysis technique and six different origins of the observed spectra were identified. Models of the underlying silver-defect structures are discussed and crystal preparation is further presented. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Monovalent silver-doped alkaline-earth fluoride crystals are very attractive materials for potential applications such as tunable solid state lasers operating in the UV range [1,2]. These systems were shown to contain several kinds of Ag\textsuperscript{+}-related photoluminescent centers, including single Ag\textsuperscript{+} ions in cubic environment, which are a substitute for the lattice cation or interstitial sites [2] and two species of (Ag\textsuperscript{+})\textsubscript{2} pairs with different geometries [3]. The single silver (I) ion centers were found to be predominant in these crystals and they were expected to be laser active [4]. However, the optically induced appearance of various light-absorbing centers is a main limitation for solid state laser applications. These undesirable centers limit severely the applicability of otherwise promising laser materials. Besides the fundamental interest of such studies regarding their luminescent properties, the detailed investigation of these centers may help to determine whether there is some chemical way to reduce, or even to eliminate their formation. This paper follows previous investigations [4] on X-irradiated Ag\textsuperscript{+}-doped CaF\textsubscript{2} and SrF\textsubscript{2} crystals using ESR [5] and optical absorption [6] spectroscopy. The former method allowed us to demonstrate the existence of a cubic Ag\textsuperscript{2+} ion subjected to a trigonal Jahn–Teller effect. The optical absorption studies led us to the discovery of three stable optical centers labeled A, A\textsuperscript{′} and B. Thereby the factor analysis technique [6–8] was applied to the absorption spectra.

The present paper presents new optical results on X-irradiated SrF\textsubscript{2}:Ag\textsuperscript{+} crystals. In particular, the photoluminescent centers have been singled out by their main spectral characteristics. Several energy transfer processes have been identified and will be discussed, especially those involving the silver (I) ions. Different models will further be presented for these silver-related centers on the basis of additional data, including luminescence dynamics, luminescence polarization properties as well as radio and thermoluminescence (TL) characteristics.

2. Materials and experimental techniques

The procedure for the growth of oxygen-free Ag\textsuperscript{+}-doped strontium fluoride crystals is reviewed in Ref. [6]. Only a few specific points will be given. The crystals were grown in a homemade computer controlled Bridgman furnace. A stoichiometric mixture of silver fluoride (AgF or AgF\textsubscript{2}) and pre-crystallized SrF\textsubscript{2} powder contained in a carbon crucible was heated to 1455°C under 0.2 atm of ultrapure Ar or along
with a low percentage of fluorine gas. The solidification isotherm was then moved vertically through the crucible with a typical speed of 15–20 mm h\(^{-1}\). The as-grown crystal rods generally exhibit a large transparent and colorless part in the center (containing monovalent silver) and their extremities are yellow. The bottom part is usually opaque being as it contains silver droplets and colloidal precipitates, whereas the top part remains transparent. The coloration is probably due to a silver concentration above saturation that is a direct consequence of the high thermal instability of the silver fluorides.

Plates typically 2 mm thick were extracted from the colorless part of the crystal rod. They were separated into two categories according to their optical properties: those labeled \(\alpha\) contained mainly the single Ag\(^+\) ions, whereas those labeled \(\beta\) had a much larger concentration of (Ag\(^+\))\(_2\) pairs, as ascertained by their characteristic absorption and luminescence spectra. The plates were X-irradiated at room temperature (typically 40 kV, 35 mA, W anode, 30 min) and then annealed at about 100\(^\circ\)C for 15 min to remove the unstable color centers. They were denoted XR\(\alpha\) and XR\(\beta\), respectively. After this treatment, the crystals exhibited a characteristic yellow coloration and the examination by ESR systematically revealed the presence of divalent silver [5]. Several of these samples were at first annealed at 350 and then at 500\(^\circ\)C, under vacuum, for 1 h. This treatment rendered the crystals colorless. They are denoted in the following XR350 and XR500, respectively.

The absorption spectra were recorded on a Cary 2300 equipped with an Oxford Instruments bath cryostat. The luminescence spectra were obtained by using a home-assembled computer controlled spectrometer. The excitation light of a Varian 300 W xenon lamp was filtered by a H20 Instrument SA monochromator (including a step motor) and focused onto the sample. The luminescence was analyzed at right angle with the aid of the monochromator of a Cary 16 (including a step motor). It was detected with a Hamamatsu R928 PMT, followed by a SR 530 lock-in amplifier. The low-temperature measurements were achieved on a Cryo-Industries 8CC bath cryostat. The excitation and emission spectra were systematically corrected for the spectral response of the source, the monochromator and the PMT, respectively. The programs we developed to command this spectrometer allowed us to record usual excitation and emission spectra and to produce ASCII-data files, containing the setup parameters in their header. In addition, a subroutine was included which allowed us to automatically perform a 2D excitation/emission scan. Thereby a fixed high energy limit of the excitation spectrum, a pre-determined low energy limit of the emission spectrum and a step are specified at the beginning of the execution. The program will then perform a series of excitation/luminescence scans while the lower limit of the excitation is set to remain 10 cm\(^{-1}\) higher than the high energy limit of the emission scan.

The lifetime measurements were carried out as a function of temperature. A xenon flash lamp (Hamamatsu 30 W, 10 Hz repetition rate) filtered by appropriate combinations of band-pass filters was focused onto the sample. The detection was realized by the setup described above with the exception of a computer controlled LeCroy 9420 digital oscilloscope that replaced the SR 530 lock-in amplifier. The polarization dependence of the intensity of the luminescence signal was studied at room temperature with the aid of an assembly described in Ref. [3]. Care was taken to focus the excitation light (of a deuterium lamp) onto the crystal plate as a circular spot smaller than 2 mm in diameter. The incident beam was selected by the appropriate filters and linearly polarized with the help of a fused-silica Glan polarizer. The sample plates were mounted onto a laboratory built rotator, such that either the (111), (110) or the (100) crystal face be oriented perpendicularly to the direction of the light propagation. The origin of the rotation angle was chosen to coincide with a highest order symmetry axis of the crystal. The luminescence intensity was measured with the analyzer parallel \((I_\parallel)\) and perpendicular \((I_\perp)\) to the incident electric vector as a function of the crystal plate’s angle of rotation \(\theta\). A dichroic UV Polaroid filter (HNPB) was thereby used as the analyzer. The \(I_\perp\) intensity was corrected in order to compensate for the monochromator’s and the PMT’s dichroism.

The radioluminescence spectra were obtained at room temperature by using X-rays as the excitation source (15 kV, 10 mA, W anode). A 10 mm thick lead glass was placed as a protection shield before the collection quartz lens. The 180\(^\circ\) luminescence arising from the crystal was focused onto the entrance of the H20 monochromator. It was detected by the R928 PMT followed by a pre-amplifier and a laboratory built computer-controlled photon counting card. TL data were recorded between 300 and 825 K with the help of a laboratory built assembly. It consisted in a heating element of a soldering iron provided with a central copper conductor that formed at the same time the sample holder. A temperature controller (Omega 76000) was used in conjunction with a NiCr–Al thermocouple to produce a constant rate of the temperature increase \((\beta = 10^\circ\text{C min}^{-1})\). The sample temperature was recorded by a second thermocouple, maintained in close contact with the surface of the crystal plate. The luminescence was selected with a high pass filter (wavelength cut off at 650 nm) and analyzed by the PMT, positioned as closely as possible to the sample.

3. Experimental results

The optical absorption and emission results of several silver-related optically active impurities will be presented in the following sections. To simplify the discussion they will be designated by ‘\(A\) center’, ‘\(A\) center’ etc. No model is at the moment associated with the term \(center\) unless otherwise stated explicitly.
3.1. Absorption

The absorption spectra of the X-irradiated crystals were studied under various conditions and some of the results have already been published in Ref. [6]. After X-irradiation, numerous new absorption bands appeared in the range 20 000–40 000 cm$^{-1}$ as illustrated by the liquid nitrogen temperature (LNT) absorption spectrum of a XR$\alpha$ crystal shown in Fig. 1. This spectrum was decomposed into a group of 14 individual gaussians with a fit of over 99%. Each one of them is characterized by an absorption coefficient that was about 50 times greater than those measured for silver (I) ions in the as-grown crystals. The choice of gaussians is justified because the bands show large Stokes shifts and because electron–phonon coupling is strong to numerous phonon modes. Further, it would have been possible to use a smaller number of bands only if some of them had an exceptionally large width. The main spectral characteristics of these bands can be seen in Table 1.

3.2. Photoluminescence

As there is a large number of centers which contribute to the total luminescence it was necessary to record the extensive excitation/emission spectra using the setup described in Section 2. Excitation spectra were obtained at a starting point of 180 nm, while the lower limit of the emission energy was set at 800 nm with a step of 50 nm. This systematic investigation generated a substantial amount of data which was best presented with the aid of 3D contour plots (see Figs. 2 and 3). The emission frequencies were thereby plotted on the horizontal axis ($\chi$), and the excitation frequencies vertically ($\gamma$). The heights ($z$) represented the corrected intensities. The data points were interpolated with the help of a mathematical interpolation program (Matlab). The validity of the procedure was checked against additional experimental data. The correction function, which was applied, included the radiation source intensity,
the spectral response of all optical components and the spectral detector sensitivity. Note that a symbolic representation scheme of the data is briefly discussed at the beginning of the discussion section.

We have investigated the luminescence properties of the XRα crystals in the liquid helium temperature range (LHT), at LNT and at room temperature (RT). Fig. 2 shows the data obtained at \( T = 3 \text{ K} \) (under pumped He). The three most intense excitation bands (37 595, 32 260 and 27 400 cm\(^{-1}\)) gave rise to a unique emission, centered at 18 020 cm\(^{-1}\). These bands were attributed to the same center, labeled A, with reference made to the notation used in Ref. [6]. The intensity of the remaining bands was comparatively weak at this temperature, making it difficult to find their precise location. Warming the crystal to LNT (Fig. 3) gave rise to strong modifications of the pattern and other peaks distinctly appeared. Two excitation bands (peaking at 35 335 and 29 585 cm\(^{-1}\)), in particular, appeared, both of which produced the same emission frequency at 15 430 cm\(^{-1}\). This set of lines, called the A\(^0\) center in the following, had been identified previously on absorption [6]. In addition, we obtained an excitation/emission profile at the bottom left of the diagram (\( \nu_{\text{exc}} = 23 750 \text{ cm}^{-1} \) and \( \nu_{\text{em}} = 14 755 \text{ cm}^{-1} \)). In our terminology this is the B1 center, responsible for the yellow coloration of the crystals. The remaining two bands (at 35 715 and 26 595 cm\(^{-1}\)) belonged to another center referred to below as the B2 center. Only one of the emission bands connected to the 26 595 cm\(^{-1}\) excitation was observed (and is plotted in the diagram at the right vertical limit of the pattern). The other peak was too weak to be seen. The B1 and the B2 bands actually formed two independent components of the B absorption system reported in Ref. [6]. Excitation of the 24 690 cm\(^{-1}\) band produced additional luminescence at 19 800 cm\(^{-1}\) which arose from a supplementary center.
called C. The remaining three weak excitation bands (39 060, 33 220 and 28 655 cm\(^{-1}\)) were similar to those of the A center in the 3 K pattern, but shifted slightly towards the high energy side. These bands correspond to a sixth center hereto called A1. Excitation of these bands at 3 K produced two emission bands, at 20 835 and 18 020 cm\(^{-1}\), respectively. The former belonged intrinsically to the A1 center, whereas the latter resulted from the energy transfer from the A1 to A center.

The dashed horizontal lines at 35 460 and 29 850 cm\(^{-1}\) in Fig. 2 represent all the A\(^0\) related bands. Their projection onto the emission axis by vertical lines passing through the peaks yielded three emission frequencies at approximately 15 250, 18 050 and 20 000 cm\(^{-1}\). The first emission belonged genuinely to the A\(^0\) center, whereas the two others arose out of the transfer of energy to centers A and C, respectively. Similarly, energy transfers occurred from C to B1 and from B1 to A\(^0\). At LNT, the energy transfer between C and B1 was still active and an additional excitation transfer was also observed from A1 to C (see Fig. 3). The A center emission was weak and barely noticeable in the LNT diagram, but the center still existed in the crystal.

### Table 2

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>Center</th>
<th>Excitation energy (cm(^{-1}))</th>
<th>(\lambda_{ex}) (nm)</th>
<th>Emission energy (cm(^{-1}))</th>
<th>(\lambda_{em}) (nm)</th>
<th>Stokes shift (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>A</td>
<td>37 595/32 260/27 400</td>
<td>266/310/365</td>
<td>18 020</td>
<td>555</td>
<td>9380</td>
</tr>
<tr>
<td></td>
<td>A1</td>
<td>38 910/33 110/28 170</td>
<td>257/302/355</td>
<td>20 835</td>
<td>480</td>
<td>7335</td>
</tr>
<tr>
<td></td>
<td>A(^0)</td>
<td>35 460/29 850</td>
<td>282/335</td>
<td>15 250</td>
<td>655</td>
<td>14 600</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>23 865</td>
<td>419</td>
<td>15 040</td>
<td>665</td>
<td>8825</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>35 090/26 955</td>
<td>285/371</td>
<td>2 2470</td>
<td>445</td>
<td>4485</td>
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<tr>
<td></td>
<td>C</td>
<td>24 875</td>
<td>402</td>
<td>20 410</td>
<td>490</td>
<td>4465</td>
</tr>
<tr>
<td>80</td>
<td>A</td>
<td>37 455/32 680/27 320</td>
<td>267/306/366</td>
<td>13 950</td>
<td>717</td>
<td>13 370</td>
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<tr>
<td></td>
<td>A1</td>
<td>39 060/33 220/28 665</td>
<td>256/301/349</td>
<td>18 020</td>
<td>555</td>
<td>10 635</td>
</tr>
<tr>
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<td>A(^0)</td>
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<td>283/338</td>
<td>15 430</td>
<td>648</td>
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<td>B1</td>
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<td>14 755</td>
<td>678</td>
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<tr>
<td></td>
<td>B2</td>
<td>35 715/26 595</td>
<td>280/376</td>
<td>2 1835</td>
<td>458</td>
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<td>24 690</td>
<td>403</td>
<td>19 800</td>
<td>505</td>
<td>4890</td>
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<tr>
<td>300</td>
<td>A</td>
<td>36 900/32 360/27 400</td>
<td>271/309/365</td>
<td>15 040</td>
<td>665</td>
<td>12 360</td>
</tr>
<tr>
<td></td>
<td>A(^0)</td>
<td>35 970/30 395</td>
<td>278/329</td>
<td>16 800</td>
<td>595</td>
<td>13 595</td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>23 865</td>
<td>419</td>
<td>15 750</td>
<td>635</td>
<td>8115</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24 940</td>
<td>401</td>
<td>–</td>
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</tr>
</tbody>
</table>
One should note that at this temperature its luminescence had shifted to the low energy side by some 3200 cm$^{-1}$. As shown in Fig. 4 two distinct emission bands with relative intensities, which are dependent on temperature, were connected with this center. At $T = 13$ K, the 18 000 cm$^{-1}$ band was predominant but it disappeared upon warming. At LNT, only one band which peaked at approximately 13 950 cm$^{-1}$ remained. We have assumed that the A1 center has behaved similarly being as its emission also shifted considerably, from 20 835 to 18 020 cm$^{-1}$, on warming (see Table 2). At room temperature, the X-irradiated crystals exhibited only a red luminescence signal. Its peak value moved somewhat as a function of the excitation energy. As shown in Fig. 5, some of the signals appeared to be asymmetric and therefore consisted of several overlapping emission bands. Likewise, the RT excitation spectra were found to be a superposition (in various proportions) of the elementary spectra that had been isolated at low temperature. Assuming that there were gaussian line shapes for both, the excitation and emission spectra, spectral decomposition revealed contributions from the A, A', B1 and C centers.

Under excitation at 330 or 280 nm (resp. at 30 300 and 35 715 cm$^{-1}$)—through the A' excitation bands—the red luminescence contained contributions from both the A' and A centers; meanwhile the A emission appeared at the low energy wing of the luminescence signal. This behavior can be explained by the existence of an energy transfer between A' and A (as mentioned above) and by the fact that the A and A' excitation bands mutually overlapped.

Excitation of the crystal through the B1 excitation band at 420 nm (23 810 cm$^{-1}$) produced an intense luminescence, consisting essentially of two overlapping emission bands centered at approximately 595 and 635 nm, respectively (resp. 16 800 and 15 750 cm$^{-1}$). According to the excitation spectra, the first band is produced by A and the second luminescence band by B1. This confirms the existence of an energy transfer between B1 and A'. Finally, the luminescence generated by excitation at 360 nm (27 780 cm$^{-1}$), i.e. into one of the A excitation bands, consists of a single emission from B1 centered at around 635 nm. The A emission is in this case nearly quenched which demonstrates the existence of an efficient energy transfer from A to B1 centers. At this temperature, the A1 and B2 centers seemed to have completely disappeared. Table 2 summarizes the main spectral properties of all of these photoluminescent centers at various temperatures.

As a note of comparison, the spectral properties of XR350a and XR350b sample plates were studied at LNT. After thermal treatment at 350°C, the relative intensities of the luminescence signals changed radically: the B1 center vanished almost completely whereas the magnitude of the B2 and C centers increased significantly. In addition, a new peak appeared at 31 200 cm$^{-1}$. Moreover, at this temperature, the A' center remained dominant. After having annealed the crystal at 500°C we observed that the B1 and B2 luminescence were completely quenched. Further, the A bands’ intensity significantly increased with respect to the same quantity of the A' bands. The examination of the XRβ...
Fig. 6. Emission spectra obtained under 221 nm (45 250 cm\(^{-1}\)) excitation for an XR\(_\alpha\) crystal at \(T = 3\) K (---) and \(T = 80\) K (----) and for an XR500\(_\alpha\) crystal at \(T = 80\) K (---).

Fig. 7. Glow curves of an XR\(_\alpha\) crystal (solid line) and XR\(_\beta\) crystal (broken line).
samples revealed mainly the presence of $A'$ and B1 centers, whereas the A, A1 and B2 bands appeared much weaker than in the XR$\alpha$ treated samples.

### 3.3. Energy transfers involving monovalent silver

There was monovalent silver in various proportions present in all of the SrF$_2$:Ag$^+$ crystals, as accredited by the systematic observation of the five excitation bands at 50 000, 48 310, 45 250, 43 860 and 42 550 cm$^{-1}$ associated with the silver (I) luminescence at 31 750 cm$^{-1}$ (315 nm) of Ref. [3]. Under excitation at 45 250 cm$^{-1}$ (at LHT) the X-irradiated crystals exhibited two emission bands in the visible range, at around 450 and 550 nm (at 22 200 and 18 200 cm$^{-1}$), in addition to the silver (I) luminescence (Fig. 6). These additional emission bands were connected with the B2 and A centers, respectively. The latter was by far predominant. At LNT, three new emission bands appeared at approximately 390, 555 and 635 nm (25 640, 18 020 and 15 750 cm$^{-1}$). The first band corresponded to silver pairs [3] and the two others were attributed to A1 and $A'$, respectively. The UV luminescence of silver (I) was extremely weak in the latter case. However, we were able to restore it by heating the XR$\alpha$ crystal to 500°C (see Fig. 6). With regards to the XR$\alpha$ crystals, the UV luminescence of silver (I) exhibited a structure that had not been observed in the as-grown systems [2]. More specifically, this structure was comprised of three distinct transitions at 296, 315 and 335 nm (resp. 33 780, 31 750 and 29 850 cm$^{-1}$). All of the visible emission signals ($\lambda > 400$ nm) produced by excitation at 45 250 cm$^{-1}$ resulted from the energy transfers from silver (I) to the other optical centers. At LHT, the Ag$^+$ $\rightarrow$ A energy transfer was consistent with the resonant re-absorption of the silver (I) luminescence since the frequency of this emission coincided with the frequencies of the A excitation bands. The participation of $A'$ was negligible at this temperature. At LNT the A emission disappeared whereas the intensity of the $A'$ and A1 emission bands grew. Moreover, at this temperature, the energy transfers seemed rather efficient since they resulted in the near quenching of the silver (I) emission. After the thermal treatment of these crystals at 500°C, the optical centers that participated in the energy transfers were partly destroyed, which had two main consequences. First of all part of the single silver (I) ions was restored and secondly, energy transfers became less efficient. As a result, the intensity of the silver (I) luminescence in the UV domain was found to have increased (see the solid curve in Fig. 6).

### 3.4. Thermoluminescence

TL experiments were performed on XR crystals of both types, $\alpha$ and $\beta$. In all samples alike, the glow curves exhibited 2 maxima at 382 and 453 K, respectively (Fig. 7). The half-width at mid-height of the TL bands was $\delta_{1}^{(1)} = 18.5$ K for the low temperature band and $\delta_{1}^{(2)} = 24$ K for the other one. The 382 K peak was much stronger in XR$\alpha$ than in XR$\beta$ samples whereas the 453 K peak was much stronger in the XR$\beta$ crystals. The TL parameters (i.e. the trap depth $E_{\phi}$ and the frequency factor $A$) were estimated by using the following expressions [18]:

$$E_{\phi} = 2kT_{\text{peak}}/\delta$$

and

$$A = \beta \exp(T_{\text{peak}}/\delta),$$

where $\delta$ represents the half-width at mid-height of the TL bands and $\beta$ the heating rate ($1/6$°C s$^{-1}$). The results are tabulated in Table 3. They demonstrate that in both types of crystals, two kinds of electron traps were present, at 1.36 and 1.47 eV, respectively, beneath the lower border of the conduction band (CB) of the strontium fluoride host.

### 3.5. Radioluminescence

Under X-irradiation at RT, the Ag$^+$-doped crystals exhibited an intense red luminescence, which depended strongly on the sample. A typical $\alpha$-type crystal presented a very broad luminescence with a maximum shifting from 648 to 670 nm (15 430 cm$^{-1}$ to 14 930 cm$^{-1}$) as the X-irradiation time was increased from 6 to 60 min. This luminescence consisted of two overlapping bands: one belonged to the B1 center (635 nm, 15 750 cm$^{-1}$) and the other, to the A center (665 nm, 15 040 cm$^{-1}$). The red-shift of the luminescence probably resulted from the increase in proportion of the A center concentration, with respect to the concentration of the B1 center, as the X-irradiation time grew. The $\beta$-type crystals presented luminescence, which contained once again contributions from both, B1 and A centers. However, in this case the ratio between the emissions from B1 and A was found to be independent of the X-irradiation time interval. In the latter crystals, there was always a greater proportion of B1 centers than of A centers.

### 3.6. Luminescence dynamics

It proved to be difficult to accurately analyze the temperature dependence of the photoluminescence decay times considering that there was important overlap between the various emission bands. In addition energy transfers were taking place between the photoluminescent centers. For these reasons, only partial results concerning XR$\alpha$ crystals are presented here. According to our apparatus, all of the temporal decays we have recorded were single exponentials. The time-constant of the $A'$ luminescence was found to be $530(\pm 10)$ µs at $T = 3$ K. It was nearly temperature independent up to 200 K, at which point it began to decrease. This is a typical evolution for a single emitting level whose emission starts to quench at 200 K because of thermal

| Table 3: TL: parameters estimated for XR$\alpha$ and XR$\beta$ crystals |
|--------------------------|--------------------------|--------------------------|
| TL maximum (K) | Frequency factor (Hz) | Trap depth (eV) |
| $T_{\text{peak}}^{(1)} = 382$ | $A_{(1)}^{(1)} = 8.4106$ | 1.36 |
| $T_{\text{peak}}^{(2)} = 453$ | $A_{(2)}^{(2)} = 1.1106$ | 1.47 |
effects or energy transfer. Concerning the A luminescence, the decay-time was constant at approximately $840(\pm 20)$ ms up to 60 K, then increased to $1050(\pm 20)$ ms between 60 and 130 K and finally decreased to $750(\pm 10)$ ms between the latter temperature and room temperature. This behavior is consistent with two emitting sublevels in mutual thermal equilibrium between 60 and 130 K with the upper level possessing a probability for radiative relaxation smaller than that of the lower level. Above 130 K, either the A centers partially transfer their energy through a phonon-assisted process, or their emission begins to be quenched.

We have found that the B1, B2 and A1 centers have an estimated lifetime of 15 ms at LHT.

3.7. Polarized luminescence

As with the previous experiments, we were confronted to problems concerning the spectral discrimination of the luminescence signals. At RT, the three emission bands of A, A’ and B1 overlapped mutually in large proportions to the extent that the polarization properties of each of the bands were more or less perturbed by those of the others. For these reasons, the azimuthal dependence of the polarization degree of the luminescence, defined as $P(\theta) = |I_0(\theta) - I_1(\theta)|/[I_0(\theta) + I_1(\theta)]$, did not always correspond exactly with the theoretical predictions [9]. The results can be seen in Fig. 8. It was found that the azimuthal variation $P(\theta)$ of the B1 luminescence correlates well with a linear dipole oriented along a $C_4$ axis of the structure, whereas the polarization dependence $P(\theta)$ of the A and A’ luminescence were both compatible with linear electric dipoles oriented along $C_3$ symmetry axes of the structure.

3.8. EPR

The samples were systematically studied by EPR after X-irradiation. Being as these results were published elsewhere [5,10] we will enumerate here only the main results of the EPR studies.

- After merely a short X-irradiation time, a rather high concentration of the cubic (Ag$^{2+}$/Sr$^{2+}$) Jahn–Teller ion was observed by EPR (typically $5–8 \times 10^{16}$ cm$^{-3}$ after 10 min irradiation).
- No spectrum of the single Ag$^+$ ion was observed in SrF$_2$ (neither before nor after X-irradiation) as opposed to the situation in BaF$_2$: Ag [11].
- We found spectra of unperturbed or perturbed $V_K$ centers, but they were annihilated after heating the crystals, typically 0.5 h, up to 100–160°C.

No other silver-related ground state EPR spectrum has been
observed between RT and LHT in both the as-grown and irradiated samples.

4. Discussion

We have represented a symbolical scheme of the data of Figs. 2 and 3 in Fig. 9, by assuming a model of optical line shapes fully determined by strong vibronic coupling to many modes and absent zero phonon lines ($S \gg 1$). The solid diagonal line ($\nu_{em} = \nu_{exc}$) represents the borderline between Stokes processes (upper left side) and anti-Stokes and up-conversion processes (lower right side). Most of the luminescence processes are located in the upper left area. The arrows pointing to the right, numbered from 1 to 4 represent the incoming excitation beam. The undulated arrows pointing downwards represent the non-radiative, dissipation processes. At their end the re-emitted light is symbolized by either one or two arrows. One of them, representing light reabsorbed through a transfer mechanism points to the left and the other, pointing downwards, represents the light escaping from the sample.

This pattern shows that an energy transfer mechanism in principle forms a characteristic rectangle (A, B, C, D). The band (A) in the upper right corner represents the primary absorption. The point B at the lower right corner is on the Stokes–anti-Stokes border and therefore is not associated with a band (no zero phonon lines were observed). This reflects the fact that within a configuration coordinate model of iso-frequency parabola the emission energy is lower than the excitation energy by the Stokes shift, as a result of non-radiative dissipating processes. The arrow pointing downwards, representing the light, which has escaped from the sample, contributes to the observed luminescence. By the same token the arrow pointing to the left representing the light which has been reabsorbed through a transfer mechanism, represents the energy transferred to another center whose excitation-emission structure corresponds to the left and bottom corner (C) of the rectangle. Finally, the peak at the top left (point D) is a consequence of the energy transfer process as two excitation peaks lined up onto the same vertical generate the same emission frequency.

Thanks to our equipment and the crystallization methods we have developed, it was possible to grow very pure alkaline earth fluorides with an unwanted residual impurity.
content well below the ppm region. In addition, Optran® quality SrF 2 which was further purified and 99.99% pure AgF 2 were always used throughout our investigation. For these reasons one can assume that our as-grown crystals contained essentially silver and intrinsic defects. According to basic arguments introducing silver (I) by substitution into the SrF 2 lattice should lead to local and/or non-local charge compensation processes in the solid (see Table 4). In particular, the as-grown crystals contain the cubic \( (\text{Ag}^+ \text{Sr}^2+)^0 \), which represents a local negative charge, compensated by a remote local positive charge. Among the many possible structures which fulfill this function, let us consider those which represent the simplest possible configurations. The \( \text{Ag}^+ \) ion on a cation lattice site associated with an anion vacancy in nearest or next nearest anion position is electrically neutral. This is also true for two mutually adjacent \( \text{Ag}^+ \) ions, one being located on a cation lattice site while the other being situated on an interstitial site at the center of an empty neighboring fluorine cube. An \( \text{Ag}^+ \) ion on a cation lattice site, associated with two (or even three) adjacent anion vacancies, is positively charged and is thus capable of distant charge compensation. This association involves several configurations. Consider the case of two vacancies in \( n3d \) neighborhood: both are on opposite corners of the \( \text{F}^- \) cube, on a common \( C_3 \) axis, with \( D_{3d} \) symmetry of the \( \text{Ag}^+ \) ion, or both vacancies are on opposite or adjacent corners of a common (100) surface of the cube containing the \( \text{Ag}^+ \) ion. In both cases the latter ion has \( C_{2v} \) site symmetry. There are undoubtedly more complex configurations possible, including, for instance, one involving the \( \text{F}^- \) vacancies in \( mnn \) position, or another with clusters of three or more silver atoms or one with more anion vacancies associated with the silver ion. But, let us consider for the time being the simplest models. Further, one should note that the silver clusters containing more than two atoms generally have low total charge states i.e. they approach metallic behavior and are not really suitable for important charge compensation purposes. In addition, being as the clusters generate an absorption band at approximately 430 nm and being as only uncoulered as-grown samples have been retained (with an emphasis on XRX type samples) we consider them to be unimportant in the present study. No absorption bands were found, prior to X-irradiation, due to F, M,… centers. They consist of intrinsic defects decorated with (an) electron(s), well separated from silver impurities.

The samples’ X-irradiation produced the photoactive centers unambiguously connected to the presence of silver as reported above. They were characterized with the aid of the allowed optical transition in absorption, as accredited by the values of the absorption coefficients listed in Table 1. Further, most of them exhibited more or less forced transitions in emission, as can be deduced from the values of the luminescence decay times, measured at LHT. Among the six new photoluminescent centers identified in this work, three possessed a dominant role—namely A, A’ and B1—whereas the remaining three seemed to be only minor centers. This confirmed previous results obtained with the aid of the optical absorption spectroscopy [6].

It is clear that, under X-irradiation at room temperature, a host of different physico-chemical processes occurs in the crystals. These include possible displacements of atoms for a short distance as, for instance, from a cation lattice site to an interstitial position or to an empty anion lattice site, as well as the omnipresent electron transfers between species. As a direct consequence there is the possibility of forming neutral local entities in the crystals, with specific new optical properties. A first distinction can be made between single silver ions and silver pairs. In the case of single silver ions, special attention must be paid to the distance between them and the intrinsic defects of the SrF 2 lattice. If they are mutually well separated both species can be considered as independent quantities. The fact that we have observed the UV signals of the single silver (I) ions and the absorption bands, in the visible part of the spectrum, due to electron traps prior to annealing (see above), demonstrates that this is a valid situation. If the two defect species are located at a short mutual distance, their mutual interaction will then produce a perturbed silver (I) ion, characterized by a perturbed (probably red-shifted) UV luminescence. Finally, in cases where they are direct neighbors, new centers will form with original optical properties.

The intrinsic defects, which correspond to the first situation described, could be eliminated by a rather mild heat treatment with only a small modification of the \( \text{Ag}^+ \) concentration and minor changes in the UV bands. We have therefore concluded that the cubic \( \text{Ag}^+ \) ions and the silver-related defect discussed above which were in close contact with anion vacancies, formed mutually distant electron donor–acceptor systems. The cubic \( \text{Ag}^+ \) ions are important electron donors according to

\[
(\text{Ag}_{\text{Sr}}^+) + \nu \rightarrow (\text{Ag}_{\text{Sr}}^{2+})^0 + e^-
\]

The JT center results and the electron is promoted into the conduction band and trapped at some distance.

Among the likely acceptors, it is necessary to consider the possible existence of the formal valence state \( \text{Ag}^- \). This state could for instance be obtained from the \( \text{Ag}^+ \) ion associated with two \( nn \) anion vacancies. It could also be produced thanks to the silver ion moving under X-irradiation, into one of the neighboring vacancy sites, and capturing two electrons. One can also construct, at least formally, another possible structure based on this model by considering the \( \text{Ag}^+ \) ion on a host cation lattice site and associated with two fluorine vacancies, all three aligned on one single \( C_3 \) axis, the complex having trapped two electrons. An \( \text{Ag}^- \) ion results which has \( C_{6v} \) or \( D_{3d} \) point symmetry. In all of these different cases which have the same formal valence state there is the same electronic structure. The ground state is \( 4d^{10}_{\text{Sr}} 5s^2 \) (transforming as \( a_1 \)). The excited manifold is \( 4d^{10}_{\text{Sr}} 5s^1 5p^1 \) producing by descent in symmetry \( R3(\rightarrow O_h \rightarrow D_{3d}) \): \( ^2P_0(a_{1u} \rightarrow a_{1u}), ^3P_1(t_{1u} \rightarrow a_{2u} + e_u), ^3P_2 \).
Table 4
Electronic properties of some locally and non-locally compensated defects in XR SrF$_2$ crystals. Here, $\sigma_e$ and $\sigma_h$ represent the electron and hole cross-sections, respectively.

<table>
<thead>
<tr>
<th>Position in the network</th>
<th>Flourine Vacancy</th>
<th>Single silver (I)</th>
<th>Silver pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Notation</td>
<td>Subst. ($V_F$)</td>
<td>Subst. (Ag$^+$Sr$^{2+}$)</td>
<td>Interst. (Ag$^+$)</td>
</tr>
<tr>
<td>Charge compensation</td>
<td>+1</td>
<td>−1</td>
<td>+1</td>
</tr>
<tr>
<td>$\sigma_e$</td>
<td>&gt;1</td>
<td>&lt;1</td>
<td>&gt;1</td>
</tr>
<tr>
<td>$\sigma_h$</td>
<td>&lt;1</td>
<td>&gt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Presence SrF$_2$:Ag$^+$ crystals</td>
<td>Very probable</td>
<td>Very probable</td>
<td>Possible</td>
</tr>
</tbody>
</table>
(t_{2g} + e_g → a_{1u} + e_u + e_g). Within this manifold act (see Ref. [12], and references therein) the exchange interaction, spin–orbit coupling, the cubic and lower symmetry crystal field contributions as well as the electron–phonon coupling including the Jahn–Teller effect. Indeed, there remain two-dimensional irreducible representations in the axial groups. Note that pseudo-JT interactions can neither be excluded.

The experimental facts that the absorption bands tend to fall into groups of two or three, with uneven transition probabilities, favor these centers. Further, we have observed fine structure at 5 K on some of the absorption bands. Yet, basically the bands are large and clearly are the result of mutually superposing lines. This situation is reminiscent of (ns)^2 in alkali halide crystals [12–16]. These entities are expected to be stable being electrically neutral or negative locally. This may explain the population of the two trap levels lying, respectively, at 1.36 and 1.48 eV, beneath the lower CB border of the crystals and may therefore help to understand the origin of the TL signals, observed in the XR crystals.

One has to consider the question why two electrons are trapped rather than merely a single one. First of all, we have never observed Ag^0 centers by EPR. And, secondly, the pairing energy (typically 1 eV) of the two electrons may be capable of stabilizing the state. Thirdly, it is possible that the ground state is a linear combination of the electronic structures \{M center + Ag^+\} and (two empty F^- vacancies and Ag^+).

There are other possible structures, which are related to the formation of bound excitons around the anion vacancy associated Ag^+ ions, as previously considered, for example, in SrF_2:Yb^{3+} [17] and BaF_2:Eu^{2+} [18]. In this situation, the excited electron is delocalized over the nearest strontium neighbors which constitute the first cationic coordination sphere around silver (I). It is stabilized by Coulomb interaction with its hole that is localized at the silver (I) site. In this case electronic relaxation can be achieved either by radiative electron–hole recombination at the silver (I) site or by energy transfer to some excited state of another optical center. However, there must be resonance or quasi-resonance between the energy of the excitonic transition and the energy difference between the ground state and at least one excited state of the excitation acceptor. Following this energy transfer one may observe the characteristic luminescence of the acceptor center. This mechanism may possibly be applied to A and B1 since both of them exhibit the same radio and photoluminescence signals at RT.

Some of the electronic processes reviewed above can be transposed to the case of the (Ag^+)_2 pairs. In particular, electrons can be captured at a pair site to form new (Ag^+) centers. Centers of this type have already been observed: e.g. in radioluminescent Ag^+-doped phosphates used as dosimeters for ionizing radiation [19–23]. These centers exhibit allowed optical transitions, which are also formally of the type (4d^{10})5s^2 → (4d^{10})5s^15p^1. The experimental results we have reported in this study show that the presence of silver pairs in the as-grown crystals favors the observation of the A' and B1 luminescence. These two centers present, furthermore, strong anisotropic properties and rather high absorption coefficients (see Table 1), which are fully compatible with (Ag_3)^+ pairs. We suggest that the local geometry of these pairs can be deduced from the models proposed previously for the (Ag_2F_{13})^{13-} and (Ag_2F_{12})^{10-} clusters, in as-grown crystals [3]. The first cluster was described as a trigonal center, with D_{3h} local symmetry whereas the second one was tetragonal, with a D_{4h} point group symmetry. Considering the respective polarization properties of A' and B1 luminescence, we propose the attribution of these centers to, respectively, (Ag_2F_{13})^{14-} and (Ag_2F_{12})^{11-}clusters. This attribution is, moreover, consistent with the fact that the thermal modification of the A' (at around 520°C) and B1 (at around 460°C) centers, contributes to the increase in the concentration of the single Ag^+ centers [6].

5. Concluding remarks

The major photoluminescent centers in the XR SrF_2:Ag^+ crystals that are responsible for the yellow coloration and for the optical opacity, operating on the silver (I) luminescence, have been identified. The yellow coloration which appears in the XR crystals is mainly due to the B1 centers i.e. to the presence of silver pairs. The A' center seems to be also connected with the presence of silver pairs in the as-grown crystals. The concentration of such centers in SrF_2 crystals can normally be strongly reduced by using appropriate thermal treatments [3]. The A' center seems to be linked to the presence of single silver (I) ions, in close interaction with (a) defect(s) acting as a charge compensation (i.e. an electron trap), and therefore appears to be connected with the need for charge compensation in the crystals. One way to limit the formation of these latter species would be for example to focus on silver (I)-doped alkali-fluorides as, for instance, NaF, for which no charge compensation is required [24]. Further experiments will now have to be undertaken in relation with ESR spectroscopy in order to obtain new experimental data, enabling us to confirm the interpretations proposed in this paper. Such data could also furnish a basis for the explanation of the origin of the other photoluminescent centers appearing in X-irradiated SrF_2:Ag^+ crystals and the processes underlying their formation.

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References