Scintillation Properties of and Self Absorption in SrI₂ : Eu²⁺

Mikhail S. Alekhin, Johan T. M. de Haas, Karl W. Krämer, and Pieter Dorenbos, Member, IEEE

Abstract—The scintillation properties of pure SrI₂ and SrI₂ doped with 0.5%, 0.86%, 2%, and 5% europium were studied. Different techniques were used to measure γ-ray excited pulse-height and scintillation decay time spectra, and to perform X-ray excited and optically excited emission spectroscopy. Eu²⁺ emission and trapped exciton (TE) emission was observed in SrI₂ : Eu²⁺ samples. These emissions were studied as a function of temperature, Eu concentration, and sample size. A spectral overlap was observed between Eu²⁺ excitation and emission spectra, the amount of overlap depends on temperature. The light yield, energy resolution and luminescence decay profiles reveal also a dependence on temperature, sample size, and Eu concentration. The observations were analyzed and interpreted in terms of two separate models. One model consists of the relation between TE and Eu²⁺ emission and the other deals with self absorption processes.

Index Terms—Gamma-ray spectroscopy, scintillators, self-absorption, SrI₂, strontium iodide.

I. INTRODUCTION

PATENTED in 1968 by Hofstadter [1], the recently re-discovered scintillator SrI₂ : Eu²⁺ is a material with a reported very high light yield of 120,000 photons/MeV, good energy resolution of 2.8% at 662 keV gamma excitation, excellent non-proportionality, and a decay time of 1.2 µs [2], [3]. SrI₂ has a calculated density $\rho$ of 4.5 g/cm³ and an effective atomic number $Z_{eff}$ of 50.2. Several studies were performed by Glodo et al. [4] on the dependence of scintillation decay time and light yield on Eu²⁺ concentration and crystal size. The results were interpreted by a scintillation model based on a radiation trapping effect.

In this paper a research on pure, 0.5%, 0.86%, 2%, and 5% Eu²⁺ doped SrI₂ is presented. The light yield, scintillation decay time and emission spectrum were studied as function of temperature, Eu concentration, and sample size. The data were analyzed employing two separate models. One model relates to the scintillation process. It deals with trapped exciton (TE) emission and Eu²⁺ emission, and how that changes with temperature and concentration. Self absorption of scintillation light by europium appears a very important factor influencing scintillation properties of SrI₂ : Eu²⁺. The second model therefore concerns self absorption from which the observed scintillation properties can be explained fairly well.

II. EXPERIMENT

SrI₂ crystals with 0%, 0.5%, 0.86%, 2% and 5% Eu²⁺ concentration were grown from commercially available SrI₂ and EuI₂ starting material with a conventional crystal growth method from the melt. Eu²⁺ concentration is assumed equal to the ratio of EuI₂ to SrI₂ in the starting material. Crystals with sizes from 5 cm³ to 10 cm³ were cut from the original boules. Fig. 1 shows pictures of SrI₂ doped with 2% and 0.86% Eu, made in a glove box after cutting. Irregularly shaped pieces with sizes ranging down to 0.5 mm³ were cleaved from these crystals for size-dependence studies.

662 keV γ-ray excited pulse-height spectra at room temperature (RT) were recorded with a Hamamatsu R1791 photomultiplier tube (PMT) connected to a Cremat CR-112 pre-amplifier and an Ortec 672 spectroscopic amplifier with 10 µs shaping time. The bare crystals were mounted on the window of the PMT and covered with several Teflon layers; all pulse-height measurements were performed inside an M-Braun UNILAB dry box with a moisture content less than 1 part per million. The yield expressed in photoelectrons per MeV of absorbed gamma ray energy (phe/MeV) was determined without an optical coupling between the scintillator and the PMT-window. The yield was obtained from the ratio between the peak position of the 662-keV photpeak and the position of the mean value of the so-called single photoelectron peak [5] in pulse-height spectra. Single photoelectron spectra were recorded with a Hamamatsu R1791 PMT connected to a Cremat CR-110 pre-amplifier. The absolute light yield expressed in photons per MeV (ph/MeV) was determined by correcting for the quantum efficiency and reflectivity of the PMT as outlined in [5].
X-ray excited luminescence spectra were recorded using an X-ray tube with Cu anode operating at 60 kV and 25 mA. The emission of the sample was focused via a quartz window and a lens on the entrance slit of an ARC VM504 monochromator (blazed at 300 nm, 1200 grooves/mm), dispersed and recorded with a Hamamatsu R943-02 photomultiplier tube. The spectra were corrected for the monochromator transmission and for the quantum efficiency of the PMT. X-ray excited luminescence measurements were performed between 80 and 600 K using a Janis VPF-800 Cryostat operated with a LakeShore 331 Temperature Controller. Each time after selecting another temperature we waited until the crystal reached its thermal equilibrium. The waiting time varied from 15 minutes to several hours. The PMT was outside the cryostat and remained always at room temperature.

UV optical excitation and emission spectra were recorded using a 450 W xenon lamp (FL-1039) in combination with a double-grating monochromator (Gemini-180, HORIBA J. Y., USA) and a deuterium lamp (Hamamatsu L1835) in combination with an ARC VM502 monochromator as excitation sources. The emission light from the crystal was dispersed with a Macam MCG 910 monochromator and detected by a single photon counting module with a channel photomultiplier (CPM, MP-1993, PerkinElmer). Excitation spectra were corrected for the background counts of the CPM and for the lamp spectrum. Emission spectra were not corrected for the transmission of the monochromator and the quantum efficiency of the CPM. UV excited luminescence measurements were performed between 80 and 600 K using a Janis cryostat.

Scintillation time profiles were recorded by the delayed co-occurrence single photon counting method [7], with a setup described by Bizarri et al. [6]. A 662 keV γ-ray source was used for excitation. The same setup without 'stop' PMT was used for temperature dependent pulse-height measurements. Smaller than 5 mm thick crystals were pressed by a needle spring to the bottom of the sample holder inside the cryostat. Larger samples were additionally embedded into Al foil for better thermal contact. Due to the high moisture sensitivity of SrI₂:Eu the used cryostat was baked out to remove all water from the system prior to sample mounting.

III. RESULTS

A. Excitation and Emission Spectra

X-ray excited emission spectra of SrI₂ doped with 0.5%, 0.86%, 2%, and 5% Eu²⁺ at 80 K and 300 K are shown in log-ln scale in Fig. 2. Spectra are normalized to each other by their maximal intensities. The europium 5d → 4f emission peak is observed for all the samples. For SrI₂ : 0.5% Eu²⁺ at 80 K the maximum is located at 430 nm. For the samples with other Eu concentrations it is shifted by 2–5 nm towards longer wavelength. In addition, a 300 nm broad emission band is present peaking at 550–600 nm. The same emission is observed for pure SrI₂ in Fig. 3. The broad nature of the emission indicates that much lattice relaxation is involved. This suggests that it originates from self-trapped or impurity-trapped or defect-trapped exciton like states. Although the true origin is not known we will call it Trapped Exciton emission (TE). A similar broad emission was observed in BaI₂:Eu single crystal [3] and SrI₂:Eu ceramics [10], and was tentatively assigned to an impurity-mediated recombination transition.

Fig. 2 shows that with increase in the Eu concentration the intensity of the TE band decreases relative to that of the Eu emission band. The Eu emission and TE emission were fitted with two Gaussian bands and the integrated emission intensities determined. The relative contribution of the TE emission to the total emission is compiled in Table I.

At 80 K the contribution of the TE emission decreases from 40% to 2% with increase in Eu concentration, and at 300 K it decreases from 34% to less than 1%.

The temperature dependence of X-ray excited emission of pure SrI₂ shown in Fig. 3 reveals a wide TE emission band.
peaking at 570 nm. In addition at low temperature there are two emission bands observed peaking at 360 nm and 430 nm. Multiple exciton bands in pure compounds are frequently observed [16]. With increase in temperature the 570 nm emission decreases and shifts towards shorter wavelength until it is totally quenched at 500 K. This quenching is further illustrated in Fig. 4 which is derived from the results in Fig. 3. The broad emission at 360 nm is almost totally quenched at 200 K, and seems to shift to longer wavelength. The emission at 430 nm is totally quenched at 300 K.

Fig. 5 shows the temperature dependence of X-ray excited emission for SrI₂ : 5% Eu²⁺. Eu²⁺ emission shifts towards longer wavelength, gets broader in the process, and its intensity decreases with increase in temperature. Fig. 6 shows that the integral light yield (LY) at 600 K is about 75% of the LY at 80 K and 83% of the LY at 300 K. Note that this is the scintillation intensity under steady rate X-ray excitation and therefore it includes all decay and afterglow components. Note that such afterglow, has been reported both in single crystals [2] and ceramics [10] of SrI₂ : Eu⁺.

SrI₂ : 0.5% Eu²⁺ emission spectra as function of temperature are shown in Fig. 7. They reveal both Eu²⁺ and TE emission. Eu emission demonstrates similar behavior as in SrI₂ : 5% Eu²⁺, i.e., it shifts towards longer wavelengths, gets broader, and its intensity decreases with increase in temperature. The TE band decreases continuously with temperature as in pure SrI₂.

The light yields derived from the spectra in Fig. 7 are shown in Fig. 8. The total light yield of curve 1) is the sum of Eu and TE emissions. Curve 2) is the contribution from Eu emission and does not reveal strong temperature quenching similar to what was observed for SrI₂ : 5% Eu²⁺. The TE contribution shown by curve 3) is completely quenched at 500 K like observed in Fig. 4 for pure SrI₂. Because of this quenching TE contribution, the total light yield of SrI₂ : 0.5% Eu²⁺ quenches stronger than that of 5% Eu doped SrI₂. Similar results were obtained for SrI₂ : 0.80% Eu²⁺.

The Eu emission spectral shape as a function of temperature, sample size, and concentration was studied. Fig. 9 shows the position of the maximum of the Eu emission peak versus temperature for 5% Eu doped crystals with three different sizes, and for the 0.5% Eu doped crystal with the smallest available size. In 5% Eu doped samples, the peak position shifts by 10–11 nm towards longer wavelengths with increase in temperature from 80 to 600 K. In the 0.5 mm thick 0.5% Eu doped crystal the emission shifts slightly towards shorter wavelengths in the same temperature range.

Fig. 10 shows the full width at half maximum (FWHM) intensity of the Eu²⁺ emission band as function of temperature. The
band broaden with temperature increase for all studied samples, and it narrows with increase in sample size and Eu concentration.

Fig. 11 shows excitation and emission spectra of 1 mm thick pure SrI₂ and SrI₂ : 0.5%Eu²⁺ at 80 K. Excitation spectra (curves 1 and 3) were measured by monitoring 545 nm TE emission. They reveal multi-peak excitations in the 225–250 nm region near the band gap of SrI₂. We attribute it to the creation of trapped excitons of the pure lattice and near defects. The presence of different type of TE states is further evidenced by exciting SrI₂ at 234 nm. We then observe (curve 4) several overlapping broad emission bands. By exciting SrI₂:0.5%Eu²⁺ at 220 nm we observed Eu emission and weak broad TE emission (curve 2) similar to the X-ray excited emission shown in Fig. 7.

Fig. 12 shows excitation and emission spectra of the 0.5 mm thick crystal measured at various temperatures. Excitation spectra reveal the 225 nm TE creation peak and a broad excitation continuum from 270 to 400 nm which we attribute to Eu²⁺ excitation. The excitation continuum shows an overlap with the Eu emission band near 415 nm. The amount of overlap increases with temperature. Similar type of overlap is reported for Eu doped in other iodide compounds [8], [9].

B. Photoelectron Yield

Data on the photoelectron yield and energy resolution of pure SrI₂ and SrI₂ doped with 0.5%, 0.86%, 2%, and 5% Eu²⁺ are shown in Figs. 13 and 14. Data were obtained from 137Cs 662 keV γ-ray pulse height spectra recorded with a shaping time of 10 μs at room temperature. We observed the highest photoelectron yield of 30000 phe/MeV for 5% Eu and of 31000 phe/MeV for 2% Eu in 1 mm thick samples. These values correspond to
Fig. 13. Photoelectron yield as a function of Eu concentration in SrI$_2$. Black squares correspond to 1 mm thick samples. Red circles correspond to 10–25 mm thick samples. The numbers below the red points are sample thicknesses.

Fig. 14. Energy resolution at 662 keV as a function of Eu concentration in SrI$_2$. 85000 photons/MeV and 90000 ph/MeV, respectively. Note that in [4] the maximum photon yield was reported for 5% and 6% Eu doped crystals.

The best energy resolution at 662 keV in Fig. 14 is 3.1% for 5% Eu and 2.8% for 2% Eu doped samples of 1 mm thickness. Figs. 13 and 14 show that the photoelectron yield is lower and the energy resolution is poorer for the 10–25 mm thick samples as compared to the 1 mm thick ones.

SrI$_2$:5%Eu$^{2+}$ is the most interesting material. First of all, the difference in photoelectron yield between 1 mm and 10–25 mm thick samples is most pronounced for the 5% doped samples as can be seen in Fig. 13. Secondly, the emission is almost exclusively from Eu as can be seen in Table I. Thirdly, the light yield is close to the maximum for 5% Eu doping.

This motivated us to study SrI$_2$:5% Eu$^{2+}$ further, and eight crystals with various thicknesses were selected. Data on the photoelectron yield and energy resolution derived from 662 keV pulse height spectra recorded with a shaping time of 10 $\mu$s at room temperature are shown in Figs. 15 and 16. The photoelectron yield decreases with increase in sample thickness, and the 15 mm thick sample shows 40% less yield than that of the 1 mm thick one. A discussion on the ballistic deficit can be found below. The energy resolution worsens from 3% to 6.8% with increase in sample thickness.

The 1, 3.3, and 7.3 mm thick samples of SrI$_2$:5% Eu$^{2+}$ crystals were selected for further temperature dependence studies.

The photoelectron yield as a function of temperature relative to the yield at room temperature was derived from pulse-height spectra on samples in a cryostat recorded with a shaping time of 10 $\mu$s under $^{137}$Cs 662 keV $\gamma$-ray excitation. The absolute values of photoelectron yield at room temperature for 1, 3.3, and 7.3 mm thick samples were taken from Fig. 15. Using these values the relative light yield curves were normalized to each other at 300 K.

Due to prolonged exposure to X-rays the 3.3 mm thick sample gained a slight yellowish color. Probably this resulted in a somewhat decreased 662 keV gamma-ray excited photoelectron yield which may then explain the displaced data point in Fig. 15. Our first correction was to shift this data point to a value that coincides with the solid curve in Fig. 15. Another error originates from the ballistic deficit. The decay time constant may range up to 7 $\mu$s for various SrI$_2$:5% Eu$^{2+}$ samples as shown below in Fig. 19. Since the electronic shape time was 10 $\mu$s this leads to an underestimation of the photoelectron yield due to the ballistic deficit. To correct for this we measured the photoelectron yield as a function of shaping time and extrapolated the yield towards infinite shaping time. After correcting for these two errors we obtained the photoelectron yield data presented in Fig. 17.

C. Decay Time Measurements

Temperature dependent scintillation decay measurements were performed on the same three 1, 3.3 and 7.3 mm thick
SrI$_2$:5\%Eu$^{2+}$ samples as used in Section III-B. In addition two 0.5\%Eu$^{2+}$ doped crystals, one 2\%Eu$^{2+}$ doped crystal, and one pure SrI$_2$ crystal were studied. Scintillation decay curves were recorded under $^{137}$Cs 662 keV $\gamma$-ray excitation. The top panel in Fig. 18 shows decay curves of the 1, 3.3 and 7.3 mm thick SrI$_2$:5\%Eu$^{2+}$ samples measured at 300 K and the bottom panel shows those of the 3.3 mm thick SrI$_2$:5\%Eu$^{2+}$ sample recorded at different temperatures. The scintillation decay curves were fitted with two exponential decay components. The fast one has decay time constant in the 50–150 ns range; it contributes only about 5\% to the total photoelectron yield. A similar fast component was observed for the other SrI$_2$:Eu$^{2+}$ crystals.

The values for the main decay time constant versus temperature, sample size and Eu concentration are presented in Fig. 19. The decay time constant lengthens with temperature, sample size, and Eu concentration increase. This confirms results in [4], where also a lengthening of the decay time constant was reported as a function of sample size for a 2\% Eu doped crystals, and as a function of Eu concentration from 0.5\% to 10\%.

We observe that the decay time constant may change by an order of magnitude from 400 ns to 7 $\mu$s. They all start from 400–600 ns at temperatures below 100 K and then increase with increase of temperature. The rate of increase scales with sample thickness and Eu concentration. This is clearly demonstrated by comparing curve 1), 2), and 3) for SrI$_2$:5\%Eu$^{2+}$ samples with decreasing thickness of 7.3, 3.3, and 1 mm.

The decay time constants of the 2\%Eu$^{2+}$ 4.5 mm thick sample (curve 4) are quite close to those of the 5\%Eu$^{2+}$ 1 mm sample (curve 3), as if the effect of the size is compensated by the concentration. Curves 5) and 6) show the decay time constants observed for 4 mm thick SrI$_2$:0.5\%Eu$^{2+}$ sample. The data of curve 5) were obtained with an optical filter which transmits the Eu$^{2+}$ emission and for curve 6) without a filter. Below 300 K curve 6) deviates from curve 5) due to the contribution of TE emission to the decay curve. The emission from the 0.5\% doped sample shows a smaller increase of decay time constants with temperature than for the 2\% (curve 4) and 5\% (curves 1–3) Eu doped crystals. The scintillation decay curve of pure SrI$_2$ is exponential with decay time constant of 1.5 $\mu$s at 78 K. The decay time constant shortens to 450 ns at 300 K.

In the following section we will show that the increase in decay time constant with temperature, with sample size, and with Eu concentration is due to an increased level of self absorption of the Eu emission. To model this self absorption phenomenon we need to know the intrinsic life time of the Eu$^{2+}$ 5d-4f emission. Evidently in the sample with lowest Eu$^{2+}$ concentration and smallest size, i.e., of 0.5\% Eu and $2 \times 2 \times 0.5$ mm$^3$ size, decay time lengthening due to self absorption is minimal. By exciting this sample by 370 nm laser pulses in stead of 662 keV gamma rays one also avoids decay time lengthening due to the scintillation process. The results are shown by the data points along curve 7 in Fig. 19. The decay time constant ranges from 410 ns at 80 K to 830 ns at 600 K. It is indeed lower than all other values in Fig. 19, and it is least dependent on temperature. By extrapolation we estimate that the low temperature intrinsic radiative lifetime of the 5d state of Eu$^{2+}$ is 400 ns.
IV. DISCUSSION

The discussion is mostly devoted to the Eu emission and its self-absorption. The scintillation processes that take place prior to Eu excitation remain largely open, however several suggestions regarding the mechanism can be made based on the results in Figs. 2, 3, 11, and 12. Firstly, there are at least three emission bands observed in pure SrI₂ at 80 K, as shown in Fig. 3. Among them the high energy trapped exciton 360 nm emission is a potential source of Eu excitation in the Eu activated SrI₂. Secondly, we observed an anti-correlation between the Eu concentration and relative intensity of TE emission, as shown in Fig. 2 and Table I. This suggests the following mechanisms for Eu excitation:

— A prompt capture of electrons from the conduction band and holes from the valence band by Eu²⁺ ions. With higher Eu²⁺ concentration the probability of the prompt capture increases at the expense of TE creation.

— Eu²⁺ is excited by the capture of 360 nm TE, and therefore with increase of Eu²⁺ concentration TE transfers its energy more likely to Eu²⁺ than that it is converted into the 570 nm TE.

The TE contribution to the total light yield as compiled in Table I is less than 10% for the 2% Eu doped samples and less than 2% for 5% Eu doped samples. The main factor influencing the light yield and decay time constant appears to be self absorption of Eu²⁺ emission by other Eu²⁺ ions. There are several observations that support this statement:

— The decrease in photoelectron yield with larger sample size as shown in Fig. 15 and with higher than 2% Eu concentration as shown in Fig. 13.

— The shift of the Eu emission peak position to longer wavelengths with increase in temperature as shown in Figs. 5 and 9. Part of the short wavelength Eu²⁺ emission is absorbed by other Eu²⁺ centers. Effectively it leads to a red-shifted and narrowed Eu²⁺ emission band as shown in Fig. 10.

— The lengthening of the scintillation decay time constant with increasing temperature as shown in Fig. 19. Increasing temperature broadens the Eu emission and absorption bands, see Fig. 12, leading to larger spectral overlap and consequently larger probability of self-absorption. A sequence of absorption and re-emission processes then effectively lengthens the decay time constant.

— The lengthening of scintillation decay time constant with sample size and Eu concentration as revealed in Fig. 19 is also attributed to increase in self absorption probability.

A model of self-absorption in scintillators was discussed by El-Hanay et al. [11], by Sakai et al. [12] and later further developed by Visser et al. [13], Wojtowicz et al. [14] and Drozdowski et al. [15]. The following relation applies for the effective decay time constant \( \tau_{eff} \)

\[
\tau_{eff} = \frac{\tau}{1 - a \eta}
\]

where \( \tau = 400 \text{ns} \) is the intrinsic radiative decay time constant of Eu²⁺ 5d-4f emission as determined in the previous section. \( a \) is the probability that a photon emitted by Eu²⁺ is reabsorbed by another Eu²⁺. \( \eta \) is the quantum efficiency of Eu²⁺ emission. If the transport efficiency of excitation energy from the SrI₂ host crystal to Eu²⁺ centers is much faster than \( \tau \), then the decay time constants in Fig. 19 are equal to \( \tau_{eff} \).

Self absorption also affects the scintillation yield from the sample. Suppose that after an interaction of a gamma quantum with our sample a number of \( Y \) excited states of Eu²⁺ are created and \( n \) photons are consequently emitted. Of this, a fraction of \( a \) will be re-absorbed by other Eu²⁺ ions to be re-emitted again with the probability \( \eta \). The rest fraction \( 1 - a \) will leave the crystal. The re-absorbed fraction, thus, will emit \( a \eta Y \) photons. This chain of processes continues and the effective number of photons emerging from the crystal is then given by

\[
Y_{eff} = \sum_{n=0}^{\infty} Y \eta (1-a) (a \eta)^n = Y \left( \frac{1-a \eta}{1-a \eta} \right) \frac{Y}{Y_{eff}}
\]

In the following we will treat \( Y \) and \( Y_{eff} \) as the number of photoelectrons/MeV. We will designate \( Y \) as an intrinsic yield for short. The photoelectron yield versus temperature and sample size shown in Fig. 17 is then actually the same as \( Y_{eff} \) in (2).

We can solve (1) and (2) for \( a \) and \( \eta \) to obtain:

\[
a = \frac{1}{1 + \left( \frac{Y_{eff} \tau}{Y \tau_{eff} - \tau} \right)}
\]

\[
\eta = 1 - \left( \frac{1 - Y_{eff}}{Y} \right) \frac{\tau}{\tau_{eff}}
\]

To derive \( a \) and \( \eta \) we need to know the experimental values of \( Y_{eff} \) and \( \tau_{eff} \), and the intrinsic values for \( Y \) and \( \tau \). \( Y_{eff} \) and \( \tau_{eff} \) depend on temperature, sample size, and Eu²⁺ concentration, and their values can be read from the data in Figs. 17 and 19. Eqs. (3) and (4) then imply that also \( a \) and \( \eta \) should depend on temperature, sample size or Eu²⁺ concentration. The quantum efficiency \( \eta \) is an intrinsic property of the Eu²⁺ center and is assumed to be independent on sample size. It may depend on temperature and concentration due to thermal and concentration quenching mechanisms.

Most difficult is to determine the intrinsic number \( Y \) of excited Eu. We have to derive it from observed light yields \( Y_{eff} \) without prior knowledge on the quantum efficiency \( \eta \). The decrease of \( Y_{eff} \) with sample size increase as observed in Fig. 15 can be attributed to self-absorption by Eu as well as to absorption losses due to poor optical crystal quality. The decrease of \( Y_{eff} \) with temperature increase as observed in Fig. 17 may be due to decrease in \( \eta \) but also due to poorer transfer efficiency of excitation energy from the host to Eu. Therefore without proper knowledge on the energy transfer efficiency from TE to Eu as a function of temperature and Eu concentration it is not feasible to determine \( Y \) accurately. We therefore decided to analyze our data for two “extreme” cases. In the end it will turn out that the main conclusion for both cases are quite the same.

Case I. The decrease of light yield \( Y_{eff} \) when temperature and sample size increases is entirely attributed to increasing self-absorption probability \( a \) of Eu emission combined with decreasing quantum efficiency \( \eta(\text{T}) \) of Eu emission.
Case II: Self-absorption does not affect the light yield decrease at all. In other words $\eta = 1$ and the decrease of $Y_{\text{eff}}$ when temperature and sample size increases is entirely attributed to electron-hole recombination losses prior to excitation of Eu, and to poor optical quality and light collection efficiency.

Case I: The results from temperature dependent pulse-height measurements depicted in Fig. 17 show the maximum photoelectron yield of 34700 phe/MeV for the smallest sample with 5% Eu concentration at 110 K. Below 110 K the yield decreases with decrease in temperature. It can be an artifact due to a ballistic deficit. Therefore, a precise estimation of the intrinsic yield can not be made, but we can indicate a minimal and maximal value. From X-ray excited emission and $\gamma$-ray excited pulse-height measurements we estimate the intrinsic yield between 34700 and 40000 phe/MeV.

Applying (3) to the data in Fig. 17 and Fig. 19 we obtained the re-absorption probability $a$ as a function of sample thickness and temperature. The values of $a$ are shown in Fig. 20 connected by the three solid curves on the upper edge of the hatched areas. The re-absorption probability $a$ increases from the lowest value of 0.35 for the 1 mm sample at 150 K to the highest value of 0.98 for the 7.3 mm thick sample at 600 K. Using for $Y = 34700$ phe/MeV or 40000 phe/MeV changes the obtained values for $a$ by not more than 1.5%.

Applying (4) to the data in Fig. 17 and Fig. 19 we derived the quantum efficiency $\eta = 0.95 \pm 0.05$ pertaining to all sample sizes and all temperatures. The error of 0.05 originates from the defined $Y$ range and includes the variation of $\eta$ with temperature and sample size. This case analyses show that $\eta(T)$ is quite constant with $T$ and then we conclude that the decrease of $Y_{\text{eff}}$ is entirely due to the repeated self-absorption by Eu ions.

With $Y = 37000$ phe/MeV and $\eta = 0.94$ we have the best agreement between our self absorption model and our experimental data. This is demonstrated in Fig. 21 where the data points are observed photoelectron yields $Y_{\text{eff}}$ from Fig. 17 displayed against the calculated re-absorption probability $a$ in Fig. 20. The solid curve is calculated with (2) using $Y = 37000$ phe/MeV and $\eta = 0.94$.

Case II: In this case analysis it is assumed $\eta = 1$ at all temperatures. From (2) $Y_{\text{eff}} = Y$ and re-absorption by $\text{Eu}^{2+}$ does not lead to yield reduction. It still leads to decay time constant lengthening, see (1). In this case the light yield $Y_{\text{eff}}$ in Fig. 17 equals Y. The light yield losses are then entirely attributed to either losses occurring at times prior to the excitation of $\text{Eu}^{2+}$ or to absorption losses in the sample other than by re-absorption in Eu centers. The re-absorption probability $a$ calculated with (3) using $Y_{\text{eff}} = Y$ is shown in Fig. 20 by the data points connected with the dotted lines at the lower edges of the hatched areas.

Fig. 20 shows that Case II values of $a$ are smaller than Case I values. However they never differ more than 10%. The hatched areas between the Case I and Case II results illustrate the maximal variation in $a$ depending on what choice is made for $\eta(T)$. For either case analysis we find that $\eta(T)$ is larger than 0.9 for all samples and temperature up to 600 K. It evidences an excellent temperature stability of $\text{Eu}^{2+}$ emission in $\text{SrI}_2$.

We conclude that self-absorption probability $a$ is a very important parameter that determines, first of all, the main decay time constant in $\text{SrI}_2:5\%\text{Eu}^{2+}$, then the shape and shift of the Eu emission band and, most likely, the light yield. Calculated with the self-absorption model presented in this work, quantum efficiency $\eta$ appears to be independent on temperature. Therefore, the light yield losses with temperature either occur during the scintillation process prior to $\text{Eu}^{2+}$ excitation or due to numerous re-absorption processes with $0.9 < \eta < 1$.

V. Conclusion

Excitation spectra, emission spectra, scintillation photon yields, and decay time spectra were measured between 80 and 600 K for pure $\text{SrI}_2$ and 0.5%, 0.86%, 2% and 5% $\text{Eu}^{2+}$ doped crystals. These data were analyzed and interpreted with two separate models. One model comprises TE emission and $\text{Eu}^{2+}$ emission and how those change with temperature and concentration. The other model concerns the self-absorption process. Of the samples studied, $\text{SrI}_2:2\%\text{Eu}^{2+}$ has the highest photon yield of 90000 ph/MeV at room temperature. Using the experimental data for 5% doped samples and the self-absorption model, the values for re-absorption probability $a$ of $\text{Eu}^{2+}$ emission and quantum efficiency $\eta$ of $\text{Eu}^{2+}$ emission were derived. The re-absorption probability appears to be quite
large in SrI\textsubscript{2} : Eu\textsuperscript{2+}. It varies from 0.35 to 0.98 depending on temperature and sample size. Quantum efficiency of Eu\textsuperscript{2+} is found to be 0.95 ± 0.05 at all temperatures. The observed change of the decay time from 400 ns to 7 μs and the shift of the Eu emission peak with Eu concentration, temperature, and sample size are related to each other. This relationship is well and consistently described with the model on self-absorption. The decrease of light yield with temperature and sample size can entirely be attributed to re-absorption, although losses due to electron-hole recombination processes prior to excitation of Eu and to poor optical quality and light collection efficiency cannot be excluded at this stage.

This work has presented a simple self absorption model that explains the observed experimental results fairly well. Nevertheless, there are several aspects that require further explanation and analysis. The self absorption model needs to be complemented with a model on the efficiency of energy transfer from the host lattice to Eu\textsuperscript{2+}. In the model we assumed that the probability of re-absorption \( a \) is the same throughout the sample volume. This is not necessarily so, and a revised model allowing for position dependent re-absorption probability may provide better results. Furthermore, the rapid 50–150 ns decay component in Fig. 18 and the light yield drop below 120 K in Fig. 17 are not yet explained.

**REFERENCES**