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Trivalent europium in x-irradiated NaCl:Eu

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In the present paper evidence has been gathered to show for the first time that the room-temperature x irradiation of an europium-doped NaCl crystal produces the conversion of doubly valent europium ions to the tripositive state. This conversion occurs in both well-aged and fast-quenched samples. However, it is considerably enhanced in the former crystals in which precipitates with the $EuCl_2$ structure are present before irradiation. If one takes advantage of this fact, the optical absorption, emission, and excitation spectra of the Eu^{3+} ions can be obtained. In particular, transitions between the different Stark levels of the various ^7F manifolds and the excited levels $^5D_2$, $^5D_1$, and $^5D_0$ of Eu^{3+} have been identified in the visible region of the absorption, emission, and excitation spectra of the x-irradiated samples.

I. INTRODUCTION

To date, alkali-halide single crystals doped with divalent cation impurities have been extensively studied with the use of many techniques such as optical absorption, photoluminescence, thermoluminescence, electron paramagnetic resonance (EPR), ionic thermocurrents, etc. Much less work has been performed with trivalent impurity ions mainly because of the difficulty of introducing the trivalent ion into the alkali-halide host, due to the charge compensation required to maintain the overall charge neutrality of the crystal. Radhakrishna and Sharma[1] studied Pr^{3+} ions in various alkali-halide crystals, and their results indicate that the trivalent impurity ion is bound to two charge-compensator vacancies occupying both nearest-neighbor and next-nearest-neighbor sites. Cook and Smith,[2] analyzing the EPR spectra of trivalent ytterbium, erbium, and dysprosium in AgCl, also arrived at the conclusion that the trivalent ion is compensated by two cation vacancies. However, Hay *et al.*[3] found that Fe^{3+} occupies an interstitial position in AgCl in association with four cation vacancies at the corners of a tetrahedron.

The tripositive state of various divalent cation impurity ions in alkali-halide single crystals has been observed after exposing the doped samples to ionizing radiation. Mel'nikov *et al.*[4] have reported that heating $KCl:SnCl_2$, $NaCl:SnCl_2$, and $NaCl:PbCl_2$ after x irradiation at 77 K results in the capture of holes by the Sn^{2+} and Pb^{2+} and that this process transforms them into Sn^{3+} and Pb^{3+}. It is also possible that the ionizing radiation may result in the trapping of electrons by the divalent cation impurities (M^{2+}) converting them to the M^+ and M^0 valence states.[5-9]

The effects of the x irradiation in KCl doped with Eu^{2+} have been studied by Chowdari and Itoh[10] and more recently by Kao and Perlman.[11] In order to interpret their experimental observations at room, dry-ice, and liquid-nitrogen temperatures, Chowdari and Itoh suggested that the Eu^{2+} ion is converted to the Eu^{3+} state by trapping a hole released by the x irradiation and that the Eu^{3+} ion is converted back to Eu^{2+} by trapping an electron released by F bleaching. Since spectroscopic evidence revealing the presence of Eu^{3+} in their irradiated samples was not found, these authors considered that the weak Eu^{3+} absorption bands peaking at 465, 526, and 578 nm were hidden under the strong F band. Later, Kao and Perlman established that the x irradiation changes the Eu^{2+} ions to the monovalent state; evidence revealing the presence of Eu^{3+} in their irradiated samples was not found. On the other hand, Parfianovich *et al.*,[12] studying the recombination processes that causes the x-ray-induced emission of Eu^{2+} in alkali-halides, arrived at the conclusion that Eu^{3+} is not produced under x irradiation, in disagreement with the hypotheses of Chowdari and Itoh.

Recently, a systematic investigation of the first-stage F coloring of europium-doped KCl as a function of the impurity concentration, as well as of the aggregation-precipitation state of the europium ions in the crystal, was performed in our laboratory.[13] During the course of a similar investigation in europium-doped NaCl, we found that the x irradiation at room temperature produces the conversion of the doubly valent europium ions to the tripositive state. Evidence of this conversion in the host NaCl is presented in this paper for the first time. It is reported that the amount of conversion of Eu^{2+} to Eu^{3+} is quite small in quenched samples where the major number of Eu^{2+} ions are in the form of I-V dipoles. However, it is considerably enhanced in those crystals in which precipitates with the $EuCl_2$ structure are present before irradiation. Taking advantage of this fact, the optical-absorption, emission, and excitation spectra of Eu^{3+} in the irradiated samples could be obtained.

EXPERIMENTAL

Single crystals of NaCl doped with divalent europium were grown in our laboratory using the Czochralski technique under a controlled atmosphere of dry argon. Doping was achieved by adding to the melt $EuCl_2$ which was previously reduced from $EuCl_3 \cdot 6H_2O$ using standard techniques.[14] The concentration of divalent europium in the samples employed was determined directly from the optical-absorption spectra of the doped samples following the same procedure as the one reported elsewhere.[15]

Optical-absorption measurements were made at room temperature with a Perkin Elmer model 330 double-beam recording spectrophotometer with capability to record up to the fourth-order derivative of the absorption spectrum. Luminescence measurements were also performed at room temperature with a Perkin Elmer model 650-10S fluorescence spectrophotometer using a 150-W xenon lamp.

Irradiation was performed at room temperature with a Philips stabilized dc generator with a tungsten target tube operated at 30 KV and 20 mA. The x rays were filtered through a 1-mm aluminun filter.

RESULTS AND DISCUSSION

Before x irradiation the optical absorption spectrum of the well-aged crystals of europium-doped NaCl consists of two structured bands in the uv range whose centers of gravity peak at 260 and 349 nm in agreement with previous data.[16] These bands have been interpreted as due to transition from the lowest Stark component of the $4f^7\,{}^8S_{7/2}$ ground state of the Eu^{2+} ion to the t_{2g} and e_g components of the $4f^65d$ configuration.[17] Figure 1 shows the emission spectrum of one of these samples (500 ppm) when the excitation is performed at 350 nm. It consists of three bands peaking at 410, 439, and 487 nm. The latter two emissions have been previously ascribed to the metastable precipitated $EuCl_2$-like plate zones parallel to the {111} and {310} planes of the matrix lattice, respectively, while that peaking at 410 nm has been associated with the stable dihalide-phase $EuCl_2$ in the host NaCl.[18] It should be pointed out that the sample employed to obtain the emission spectrum given in Fig. 1 had been stored at room temperature for seven years and was not subject to any previous heat treatment since it was grown.

After the crystal is exposed to room-temperature x irradiation, the optical density of the Eu^{2+} bands decreases and the F, K, R_1, R_2, and M bands are observed in the absorption spectrum. Also, a very sharp absorption band with a half-width of ~28 meV and peaking at 465 nm was found to be superimposed on the F band as it is shown in Fig. 2. The intensity of this band increases monotonically with

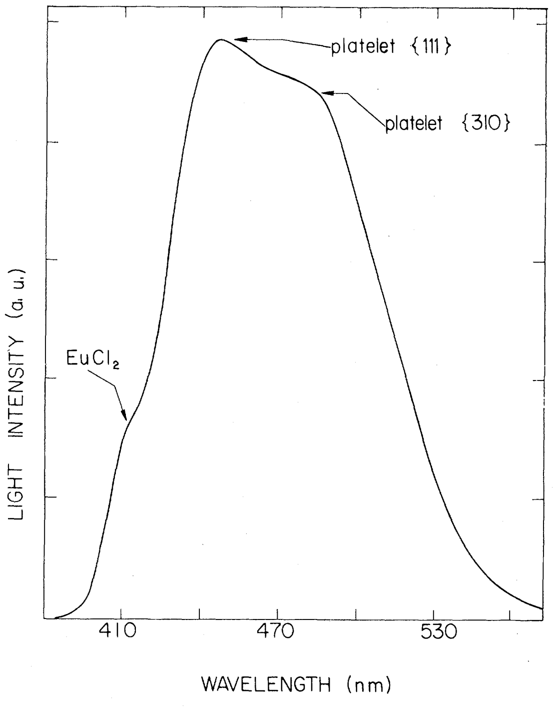

FIG. 1. Emission spectrum of Eu^{2+} in NaCl (500 ppm), excited at 350 nm. The sample employed to obtained this spectrum was stored for seven years at room temperature without any previous heat treatment.

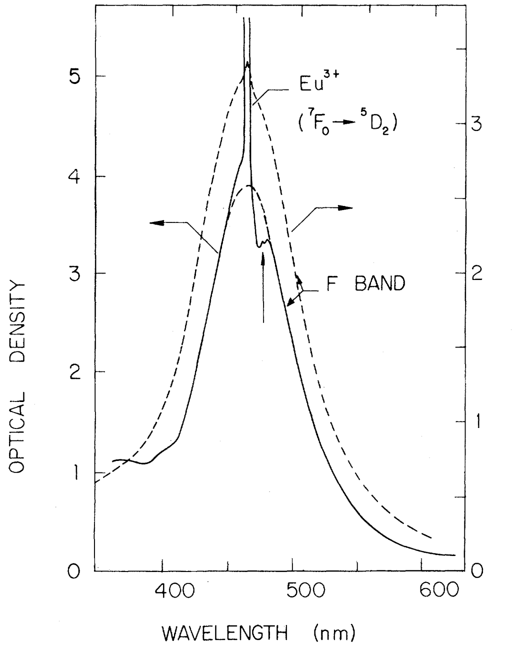

FIG. 2. Room-temperature optical-absorption spectrum in the scan range 350–650 nm of a well-aged (solid line) and a fast-quenched (dashed line) europium-doped NaCl crystal after 6 h of room-temperature x irradiation.

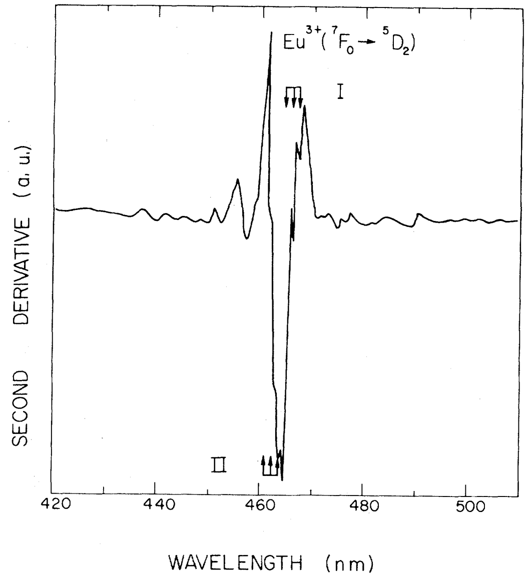

FIG. 3. Second derivative of the absorption spectrum corresponding to the well-aged crystal shown in Fig. 2.

the irradiation dose. On the other hand, the *F* absorption increases fast during the first stage of the *F*-coloring curve and then saturates during the second stage. Therefore, the 465-nm band is much better resolved during the second stage of the *F*-center growth. Figure 3 shows the second-derivative presentation of the absorption spectrum shown in Fig. 2. It reveals that the absorption at 465 nm is not single. Rather, it is composed of two sets of three sharp lines peaking at 461.5, 462.5, and 463.5 nm and 465, 467, and 468 nm. These sets have been labeled I and II in Fig. 3. It is important to note that the second-derivative presentation allowed us to measure the peak position of these sharp lines accurately.

The energy-level diagram of the trivalent europium ion has been well established in different host lattices[19–23] other than alkali halides. In particular, transitions from the ground state $^7F_0$ to the excited states $^5D_0$, $^5D_1$, and $^5D_2$ have been observed in the spectral region 17 000–24 500 cm^{-1}. Since these transitions are internal ($f \rightarrow f$), it is expected that they also occur at practically the same energy in the alkali-halide crystals. In particular, the transition $^7F_0 \rightarrow {}^5D_2$ should be composed of five sharp absorption lines due to the five Stark components of the $^5D_2$ manifold. These components have been previously observed in the absoprtion spectrum of Eu^{3+} in Y_2O_3, where the europium impurity ion occupies a C_2 symmetry site.[19] Their peak positions and relative intensities (in parenthesis) were found to be 468.3 nm (0.4), 468 nm (1), 467 nm (1), 465.4 nm (1), and 465 nm (0.4). This five-line spectrum may change into a three-line spectrum if the site symmetry occupied by the Eu^{3+} ion posseses a higher symmetry than C_2 or if the resolution in the optical-absorption spectrum is not as good as 0.3 nm, the position of the lines being ∼468, 467, and 465 nm. The peak position of these bands are quite similar to those reported above for the lines composing set I. It is possible that these three lines may be the result of a superposition of the five lines mentioned above, which are not resolved in this case in view of the fact that the resolution employed in order to take the second-derivative curve of the absorption spectrum was ∼0.5 nm. Therefore, the sharp absorption lines peaking at 465, 467, and 468 nm composing set I in Fig. 3 may be associated with the transitions $^7F_0 \rightarrow {}^5D_2$ of the Eu^{3+} ion in the irradiated samples. Also, taking into account that the relative intensities and energy separation of the absorption lines composing set II are quite similar to those of set I, we are tempted to suggest that the former is also due to the transitions $^7F_0 \rightarrow {}^5D_2$. The presence of these two sets in our irradiated samples may indicate that there are two kinds of Eu^{3+} centers, each one with a different crystal field. This fact can be explained by considering that the doubly valent europium ions in the stable dihalide-phase $EuCl_2$ may change to the tripositive state with an efficiency similar to that of the Eu^{2+} ions, which form the metastable precipitated phases parallel to {111} and {310} planes of the matrix lattice. According to this explanation three sets of absorption bands, corresponding to the transition $^7F_0 \rightarrow {}^5D_2$, should be expected in the absorption spectrum of our irradiated samples, since three different types of precipitates are present before irradiation (Fig. 1). However, since the crystal field at the site occupied by the Eu^{2+} impurity in the two metastable precipitated phases mentioned above has been found[18] to be nearly identical but different to that at the site occupied by the Eu^{2+} ion in the second-phase precipitate $EuCl_2$, only two significant sets of transitions should be expected, as was found in this work.

Figure 4 shows the emission spectrum in the wavelength range 600–800 nm, when the excitation is performed at 465 nm, of the same irradiated sample whose absorption spectrum is given in Fig. 1. The fluorescence spectrum consists of a great number of bands that are due to transitions originating in the excited levels $^5D_1$ and $^5D_0$ of the Eu^{3+} ion and terminating on the Stark levels of the various ^7F manifolds. It is important to point out that all emission bands have a halfwidth of ~5 nm. The reason for the latter is that in order to record the weak emission spectrum of the Eu^{3+} ions, we were required to use at least a band-pass selection of 5 nm for the grating-emission monochromator. Table I summarizes the peak positions of the observed emission bands, as well as their assignment. The peak position of the emission bands given in this table for the transitions $^5D_1 \rightarrow {}^7F_J$ and $^5D_0 \rightarrow {}^7F_J$ are in good agreement with those previously reported for Eu^{3+} in other host lattices.[19–23] Unfortunately, the emission spectrum of the Eu^{3+} ion in the irradiated samples could not be analyzed for wavelengths smaller than 600 nm, where emissions from the $^5D_2$ state to the ^7F manifolds are expected. The reason for the latter is that the Eu^{2+} ions produce a strong continuous fluorescence in the spectral range 380–550 nm (Fig. 1) that obscures the weak Eu^{3+} emissions. However, the dip observed in the absorption spectrum at ~470 nm (marked with a vertical arrow in Fig. 2) may be due to the transition $^5D_0 \rightarrow {}^7D_0$, the excitation being produced by the light used for the absorption measurements.

The excitation spectra for the two prominent emission bands peaking at ~658 and 740 nm were obtained in the range 440–700 nm. Figure 5 shows, as an example, the excitation spectrum for the 740-nm emission band. It consists of four main bands peaking at 463, 467, 525, and 526 nm, in addition to a very weak band peaking at ~580 nm. This excitation spectrum correlates quite well with

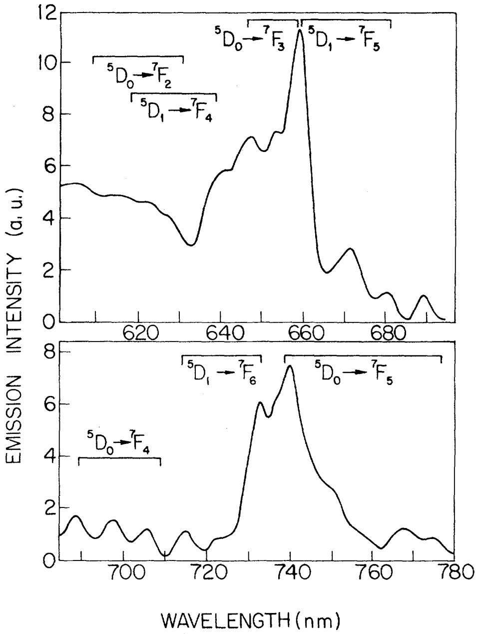

FIG. 4. Room-temperature emission spectrum of Eu^{3+} in x-irradiated NaCl:Eu^{2+} when the excitation is performed at 465 nm.

TABLE I. Observed transitions in nanometers in the fluorescence spectrum of Eu^{3+} in x-irradiated europium-doped NaCl at room temperature.

Terminating level	Emitting level $^5D_0$	Emitting level $^5D_1$
$^7F_1$	585–600	
$^7F_2$	620–630	
$^7F_3$	646	
	652	585–600
	658	
$^7F_4$	688	617–630
	698	638
	706	
	715	
$^7F_5$	740–760	658
	766	672
	770	680
	774	
$^7F_6$	805	722
	810	733
	818	
	820	

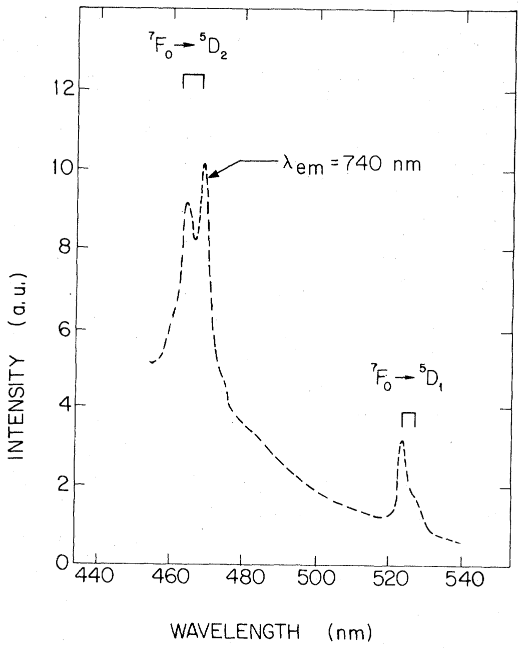

FIG. 5. Excitation spectrum of the band peaking at ~740 nm in the emission spectrum.

the second-derivative presentation of the 465-nm absorption band given in Fig. 3. In particular, the bands at 467 and 463 nm correspond to sets I and II, respectively. However, the triplet structure of these sets is not clearly resolved in the excitation spectrum. The reason for the latter is that a band-pass selection of ~1.5 nm for the grating excitation monochromator was necessary to be used in order to analyze the weak Eu^{3+} emissions. The presence of both sets I and II in the excitation spectrum indicates that the two Eu^{3+} centers mentioned above are contributing to the emission bands. According to the energy-level scheme of the Eu^{3+} ion, the band peaking at 525 nm in the excitation spectrum is the one expected for the transition between the ground state $^7F_0$ and the excitated state $^5D_1$. The band at ~ 527 nm may be associated with the same transition occuring in the other Eu^{3+} center. Also, the very weak band peaking at ~580 nm is the one that should be expected for the transition $^7F_0\rightarrow{}^5D_0$. It should be noted that the excitation spectrum allowed us to determine the presence of the absorption at 525 and 580 nm, which was not possible in the absorption spectrum of the irradiated samples because they are hidden under the F and the F-aggregate bands.

When the previously irradiated crystal is illuminated with F or M light, the intensity of the absorption bands due to Eu^{3+} decreases. Simultaneously, the characteristic emission of Eu^{2+} is observed, and the intensity of the Eu^{2+} absorption bands increases. Since illumination with light of these wavelengths produces ionization of the F and M centers, it is very likely that the electron produced by this process recombines with Eu^{3+}, leaving the divalent impurity ion in an excited state. Then, the decay of this excited divalent ion to its ground state results in the observed emission. This process could be written as follows:

$$F\ (\text{or } M)+h\nu\rightarrow e^- ,$$

$$\mathrm{Eu}^{3+}+e^-\rightarrow(\mathrm{Eu}^{2+})^*\rightarrow\mathrm{Eu}^{2+}+h\nu\ (\mathrm{Eu}^{2+}) ,$$

where the symbol $*$ represents an excited state. This process explains the recovering intensity of the Eu^{2+} absorptions, the bleaching of the absorption bands due to Eu^{3+}, and the appearence of the Eu^{2+} fluorescence when the crystal is illuminated with light in the region of the F and M absorption bands.

On the other hand, when a well-aged crystal is heated for ~2 h at 500 °C and then fast quenched to room temperature, both the metastable and stable precipitated phases of Eu^{2+} in the host NaCl are destroyed. Then, the optical-absorption, emission, and electron paramagnetic resonance spectra due to Eu^{2+}-cation vacancy dipoles in solution are observed. In particular, the former consists of two broad bands whose centers of gravity peak at 240 and 347 nm. The emission spectrum consists of only one band peaking at 427 nm as a difference with the emission spectrum of the well-aged samples presented in Fig. 1. The x irradiation at room temperature of one of these crystals also produces the conversion of the doubly valent impurity ions to the tripositive state as stated by the observation of the band peaking at 465 nm in the optical-absorption spectrum of the irradiated samples. This spectrum is shown in Fig. 2 by a dashed line. A comparison between this spectrum and that obtained in the well-aged crystals, under the same irradiation dose and europium concentration, shows that the number of Eu^{2+} ions that have changed to the tripositive state are much greater in the well-aged samples than in the fast-quenched ones. This result indicates that the efficiency for the conversion of the Eu^{2+} to Eu^{3+} is much greater in the well-aged crystals in which precipitates with the EuCl_2 structure are present before irradiation, than in the quenched ones in which the Eu^{2+} ions are principally in the form of I-V dipoles in the NaCl matrix. The reason for this fact may be that the charge-compensation can be achieved more easily in the europium-precipitated phases than in the host NaCl.

In order to obtain a deeper insight into this point, crystals of KCl, KBr, and KI doped with Eu^{2+} were also exposed to room-temperature x irradiation. It was found that the Eu^{2+} ions do not change to the tripositive state in samples that had been aged for six years at room temperature without any previous heat treatment, since any absorption due to Eu^{3+} was observed in the optical spectrum of the irradiated samples. It is known that the annealing of all these crystals at room temperature does not produce the formation of the stable precipitated dihalide phase EuX_2 $(X = \mathrm{Cl,Br,I})$ in the alkali-halide matrix.[24] In particular, for the system KCl-$EuCl_2$, it has been reported that the aging of the doped samples at temperature below 100 °C produces the precipitation of the Eu^{2+} ions into the Suzuki phase.[18] The above-mentioned result was also obtained in the fast-quenched samples. However, the x irradiation of an europium-doped KCl crystal that was aged for ~1000 h at 200 °C produces the conversion of Eu^{2+} to Eu^{3+}, as evidenced by the observation of a weak absorption band at 465 nm superimposed on the tail of the F band (560 nm) in the optical spectrum of the irradiated samples. This annealing treatment has been reported to be adequate for production of metastable precipitated $EuCl_2$-like plate zones, as well as of the stable dihalide-phase $EuCl_2$ in the host KCl.[25] The number of Eu^{3+} ions produced by the x irradiation, however, is smaller than that in the well-aged samples of NaCl. This result may corroborate the fact that the conversion $Eu^{2+} \rightarrow Eu^{3+}$ occurs more favorably in those crystals where precipitates with the $EuCl_2$ structure are present before irradiation than in the quenched ones. It also appears that this conversion does not occur in those crystals where Suzuki precipitates are present before irradiation. Annealing experiments are in progress in an attempt to produce precipitates with the $EuBr_2$ and EuI_2 structure in KBr and KI, respectively, in order to determine if the conversion of the doubly valent europium ions to the tripositive state is also enhanced when these precipitates are present in the samples before irradiation.

The experimental observations reported above appear to be in disagreement with the suggestion of Chowdari and Itoh[10] in the sense that, in quenched samples of europium-doped KCl, the Eu^{2+} ions convert to the tripositive state after x irradiation at room temperature. However, it should be pointed out that the samples employed by these authors to perform their experiments were only heated for 5 min at 500 °C after they were grown. It is possible that this annealing treatment is not adequate to dissolve the europium precipitates present in the "as-grown" samples, and therefore some conversion of the Eu^{2+} to Eu^{3+} may have occurred in their irradiated samples. On the other hand, our data also indicate that the conclusion of Parfianovich *et al.*,[12] in the sense that Eu^{3+} is not produced in an alkali-halide crystal under x irradiation, is not correct.

The higher efficiency for the conversion of the Eu^{2+} to Eu^{3+} when the divalent impurity ions are precipitated in the NaCl crystal-forming phases with the structure of $EuCl_2$ compared with that in the fast-quenched samples may suggest that the trivalent valence state of the rare-earth europium ion is more stable in the $EuCl_2$ structure than in the NaCl matrix. This result can be compared with those previously reported by Merz and Pershan,[26] who found that the trivalent rare-earth impurity ions in CaF_2 can change to the divalent valence state by exposing the doped crystals to ionizing radiation. However, this conversion occurs only in the case where the trivalent ions are not locally compensated and, therefore, they are occupying an approximately cubic site in the calcium fluoride lattice.

Finally, we may conclude that the x irradiation of an europium-doped alkali-halide crystal may produce the conversion of the doubly valent europium ions to the tripositive state. However, the efficiency of this process appears to be quite dependent on the state of the Eu^{2+} ions in the crystal. We have established that for the case of NaCl and KCl, this conversion can be enhanced considerably when Eu precipitates possessing the $EuCl_2$ structure are present in the samples before irradiation. It would be very interesting to determine if the same situation appears in other alkali-halide crystals when Eu precipitates are present in the samples before irradiation.

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