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Addendum to "Optical absorption and luminescence investigations of the precipitated phases of Eu^{2+} in NaCl and KCl single crystals"

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Optical absorption and luminescence investigations performed on the system KCl-$EuCl_2$ revealed that, in addition to the precipitated phase which nucleates at temperatures below 100 °C and which has been ascribed to the Suzuki phase, three other Eu-precipitated phases can be nucleated in the potassium chloride lattice under a suitable thermal treatment of the samples. The structures of the precipitated phases appear to be similar to those which nucleate in europium-doped NaCl. The absorption, excitation, and emission spectra associated with each of them are presented.

In a recent paper we reported the investigation of the optical absorption and luminescence spectra associated with the precipitated phases of Eu^{2+} in monocrystalline sodium and potassium chlorides.[1,2] It was found that for the system NaCl-$EuCl_2$, the fluorescence spectrum of the well-aged samples consists of three different emission bands peaking at 410, 439, and 485 nm. The band at 410 nm was associated with the stable dihalide phase $EuCl_2$, while those peaking at 439 and 485 nm were ascribed to the metastable precipitated $EuCl_2$-platelike zones parallel to $\{111\}$ and $\{310\}$ planes of the matrix lattice, respectively. The optical absorption spectrum (II_b) of these crystals consists of two broad bands whose centers of gravity peak at 260 and 349 nm with a crystal field splitting $10Dq = 9890$ cm^{-1}. On the other hand, for the system KCl-$EuCl_2$ only one emission band at 427 nm was observed in crystals stored at room temperature for five years without any previous heat treatment or by aging the quenched samples at temperatures below 100 °C. The corresponding optical spectrum (II) consists of two bands peaking at 244 and 349 nm with a $10Dq$ value of 12 331 cm^{-1}. In this case, the precipitated phase responsible for the optical and fluorescence spectra described above was tentatively associated with the Suzuki phase of Eu^{2+} in the potassium-chloride lattice.

In this paper, we are reporting that for europium-doped KCl, in addition to the precipitated phase which nucleates at temperatures below 100 °C, three other Eu-precipitated phases can be nucleated in the lattice under a suitable thermal treatment of the doped samples. The absorption, excitation, and emission spectra associated with each of them are presented. The experimental details and data analysis are similar to those described in our previous paper.[2]

Figure 1(a) shows the optical absorption spectra of a potassium-chloride sample doped with 270 ppm of divalent europium, after a fast quenching from 600 °C (I), and after aging the same sample for 820 h at 200 °C (II_b). The main difference between spectra I and II_b is the position of the high-energy band. In II_b this band peaks at 262 nm and has a well-resolved structure. In I it peaks at 243 nm and presents much less structure. The structure of the broad bands composing spectrum II_b can be more easily observed in the second derivative of the absorption curve which is shown in Fig. 1(b). Spectrum II_b can be tranformed into I by heating the samples at 600 °C for ~2 h.

In Table I we summarize the peak position and width for each of the observed bands in the optical spectrum II_b of Eu^{2+} in KCl. Values for the peak position and width of the absorption bands in the

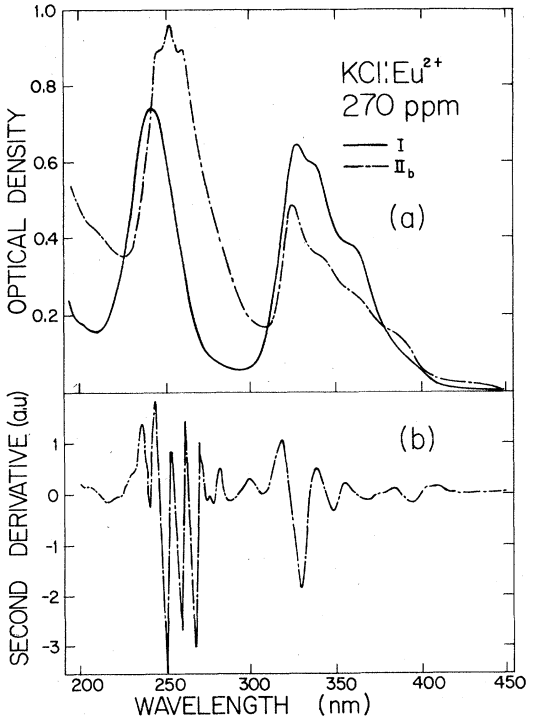

FIG. 1. (a) room-temperature optical absorption spectra of Eu^{2+} in KCl with an impurity concentration of 270 ppm for a freshly quenched crystal (I) and after aging the same sample for 820 h at 200 °C (II$_b$). (b) Second derivative of the optical absorption spectrum II$_b$.

optical spectrum of quenched (I) and annealed samples at temperatures below 100 °C (II) were reported in our previous paper.[2] In Table II values are given for the crystal field splitting 10*Dq* of spectra I, II, and II$_b$, along with those measured from the optical spectra of Eu^{2+} in NaCl. The value for the 10*Dq* splitting measured from spectrum II$_b$ is smaller than the one measured from spectrum II which has been tentatively associated with the Suzuki phase. This result may indicate that the structure of the precipitated phase which nucleates at 200 °C is different to that responsible for spectrum II. It is interesting to note that spectrum II$_b$ for Eu^{2+} in KCl is quite similar to that observed[2] in the well-aged samples of NaCl: Eu^{2+}. Also, the values for 10*Dq* measured from both spectra are very similar.

Figures 2 and 3 show the evolution of the optical absorption and emission spectra, respectively, as a function of the annealing time at 200 °C for a quenched sample containing 270 ppm of divalent europium. In order to obtain these spectra, the crystal was heated at 200 °C for the periods of time shown in the figures and then quenched to room temperature to record the spectra. In all cases, the fluorescence spectra were obtained exciting with light (350 nm) lying in the low-energy band of the optical spectrum. Figure 2 shows that the high-energy band in the optical spectrum of the quenched samples moves to longer wavelengths (i.e., from 243 to 262 nm) as a function of the aging time at this particular temperature while the peak position of the center of gravity of the low-energy band does not change. This results in a decrease of the value for the 10*Dq* splitting. On the other hand, it is clearly apparent from Fig. 3 that the fluorescence spectrum is strongly dependent on the aggregation state of the Eu^{2+} ions. In particular, the aging at 200 °C produces the growth of the emission bands peaking at 439 and 478 nm for times up to ~400 h. As the annealing treatment proceeds, a saturation of the growth of the these bands takes place. The emission at 410 nm begins

TABLE I. Peak position and width of the bands composing the broad high- and low-energy bands of spectrum II$_b$ of Eu^{2+} in KCl at room temperature.

High-energy band			Low-energy band		
Peak positions (nm)	Bandwidth (10^3 cm^{-1})	Center of gravity (nm)	Peak positions (nm)	Bandwidth (10^3 cm^{-1})	Center of gravity (nm)
289	2.07	262	395	1.10	349
279	1.25		382	1.07	
273	1.17		371	1.08	
267	1.14		361	1.14	
259	1.37		350	1.24	
251	1.29		342	1.20	
244	1.86		330	1.39	

TABLE II. Values for the 10*Dq* splitting of Eu^{2+} in NaCl and KCl.

Host	Spectrum	Center of gravity of the high-energy band (nm)	Center of gravity of the low-energy band (nm)	10*Dq* (cm^{-1})	Ref.
NaCl	I	240	347	12 849	2
	II_a	262	345	9182	2
	II_b	260	349	9809	2
KCl	I	243	343	11 997	2
	II	244	349	12 331	2
	II_b	262	349	9515	this work

to grow at ~200 h and its intensity also saturates in about 400 h. During this process the intensity of the emission band peaking at 419 nm which has been assigned[2] to Eu^{2+}-cation vacancy dipoles, as well as to the first products of aggregation decreases. In Fig. 4, the quantitative evolution of the intensities of these bands as a function of the annealing time is presented.

The excitation spectra obtained by monitoring the fluorescence bands peaking at 419, 410, 439, and 478 nm are shown in Fig. 5. They were corrected for intensity of the excitation source as a function of wavelength. The value for the 10*Dq* splitting measured from the excitation spectra of the emissions at 410 (9824 cm^{-1}), 439 (9185 cm^{-1}), and 487 nm (9389 cm^{-1}) is very similar. This fact may indicate that the crystal field at the Eu^{2+} site in each of the precipitated phases responsible for these emissions is nearly identical, and therefore their structure might be similar. The excitation spectrum of the 419-nm band in the quenched samples shows that in this case the value of the 10*Dq* splitting is larger than those measured from the spectra corresponding to the emission bands in the aged samples. This result suggests that the crystal field at the Eu^{2+} site is larger

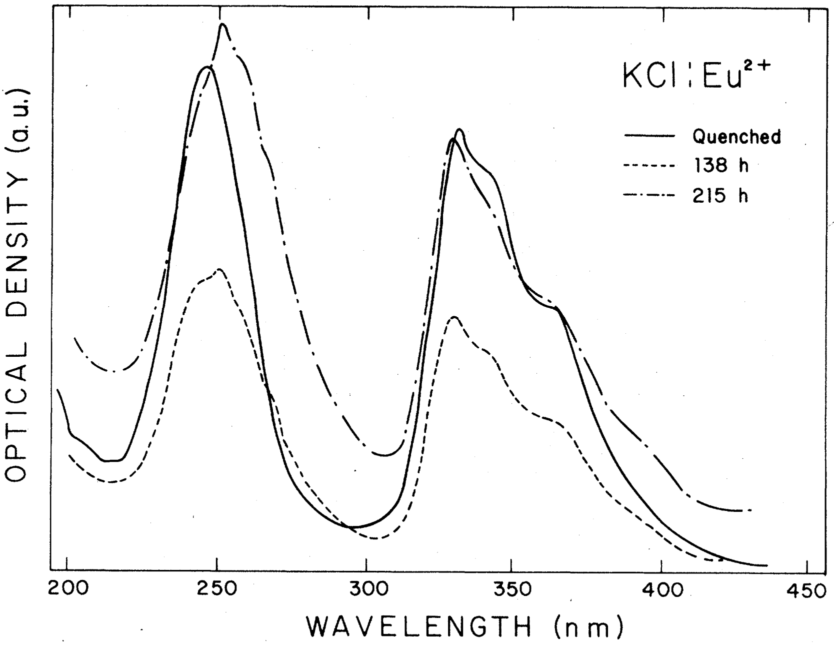

FIG. 2. Evolution of the optical absorption spectrum of Eu^{2+} in KCl as a function of the annealing time at 200 °C.

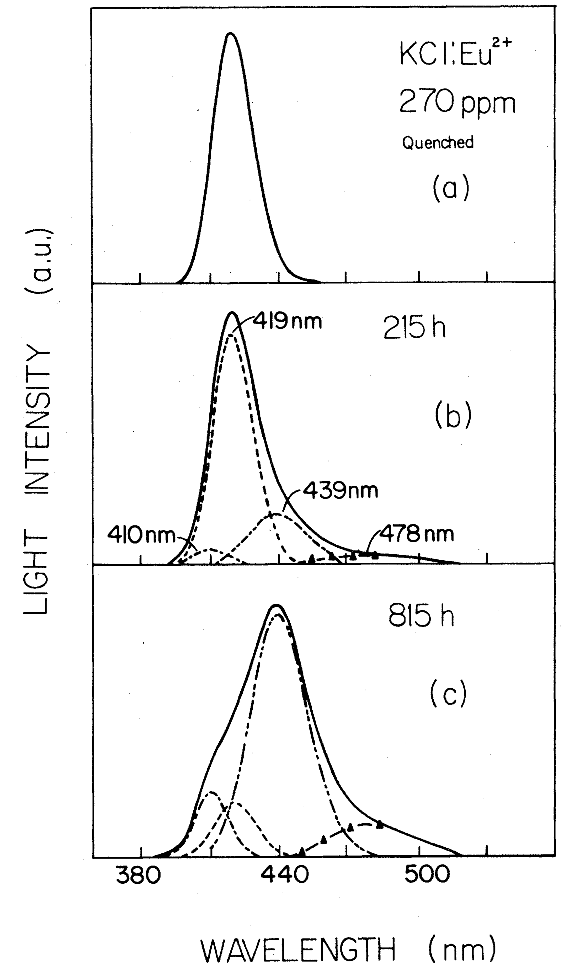

FIG. 3. Evolution of the emission spectrum for europium-doped KCl as a function of the annealing time at 200 °C. The decomposition of the spectra into the bands at 419, 410, 439, and 478 nm is shown by the dashed lines.

when the impurity is dispersed into the lattice forming (I-V) dipoles than at the site occupied by the impurity in the precipitated phases which nucleate at 200 °C. However, it is smaller than at the site occupied by the impurity in the precipitated phase which can be produced by aging the crystals at temperatures below 100 °C and responsible for spectrum II and the emission band at 427 nm.

The excitation spectra corresponding to the emission bands peaking at 410, 439, and 478 nm in KCl are nearly identical to those reported for the emission bands at 410, 439, and 485 nm in the well-aged samples of europium-doped NaCl. In particular, the values for the 10*Dq* splitting mea-

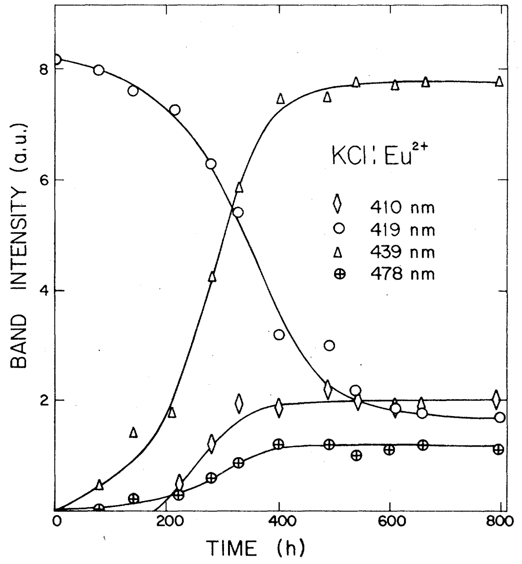

FIG. 4. Intensity (area under the curve) of the emission bands of Eu^{2+} in KCl (270 ppm) vs the aging time at 200 °C.

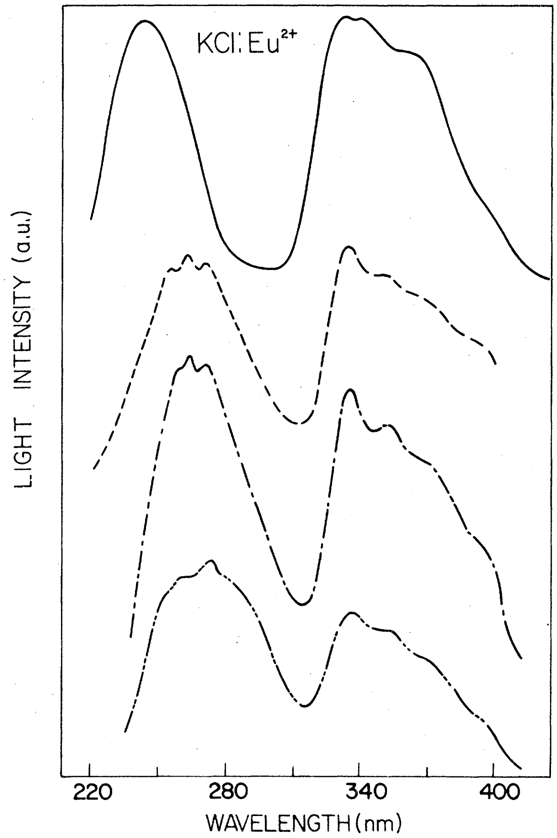

FIG. 5. Excitation spectra for the emission bands peaking at 419 (solid curve), 410 (dashed curve), 439 (dot-dashed curve), and 478 nm (double-dot-dashed curve).

sured from all of them are similar. Unfortunately, the system KCl-$EuCl_2$ has not been studied, as far as we known, by means of the x-ray and electron microscopy techniques. Nevertheless, in view of the similarities with the system NaCl-$EuCl_2$ we are tempted to suggest that the structure of the precipitated phases responsible for the emission bands at 439 and 478 nm are similar to those responsible for the emissions at 439 and 485 nm in NaCl. The latter two have the structure of $EuCl_2$ in two dimensions and are coherent with the matrix. On the other hand, the correlation between the emission band peaking at 410 nm and the emission spectrum of $EuCl_2$ reported in our previous paper is quite satisfactory. This agreement might indicate that the precipitated phase responsible for the 410-nm band is the stable dihalide phase $EuCl_2$. Evidence obtainable mainly through x-ray studies is, however, required to confirm the assignment of the emission bands observed in the aged samples.

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[1] J. García M., J. Hernández A., E. Carrillo H., and J. Rubio O., Phys. Rev. B 21, 5012 (1980).

[2] F. J. López, H. Murrieta S., J. Hernández A., and J. Rubio O., Phys. Rev. B 22, 6428 (1980).