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# Influence of concentration and aggregation-precipitation state of divalent europium in the room-temperature coloring of KCl

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The first stage of the room-temperature $F$-center coloring in europium-doped KCl has been investigated as a function of the impurity concentration as well as of the aggregation-precipitation state of the europium ions in the crystal with the use of optical-absorption, photoluminescence, electron-paramagnetic-resonance (EPR), and ionic-thermocurrent (ITC) techniques. For the range of europium concentration employed in this work (50—600 ppm), the initial $F$ coloring increases with concentration monotonically. The effects of x irradiation are (a) to reduce the number of isolated $Eu^{2+}$-cation vacancy dipoles, (b) to increase the number of trapped electrons, and (c) to convert the doubly valent impurity ions to the monovalent state. It is reported that the amount of the first-stage coloration is proportional to the square root of the total europium concentration. Evidence has been gathered to show for the first time, that the x irradiation greatly increases the rate of aggregation of dipoles as previously suggested by Muccillo and Rolfe. The results presented in this paper suggest that the $Eu^{2+}$-cation vacancy dipoles act as the dominant traps for the radiation-induced halogen interstitials. The influence of the aggregation-precipitation state of the $Eu^{2+}$ ions on the initial $F$-coloring efficiency has also been studied in considerable detail. It was found that the metastable precipitated phase which has been tentatively associated with the Suzuki phase shows a slightly higher coloring rate than the isolated dipoles or the first products of aggregation. However, the $F$-coloring efficiency decreases as a function of the Eu precipitation into the metastable and stable phases possessing the $EuCl_2$ structure.

## I. INTRODUCTION

It is well known that the introduction of divalent cation impurities ($M^{2+}$) into alkali-halide crystals produces an enhancement of the first-stage $F$-center production rate. In order to understand this situation, several models have been proposed in the literature. Among them, Crawford and Nelson[1] suggested that a positive-ion vacancy can be converted to an $F$ center during the irradiation processes. Later, Ikeya *et al.*[2] proposed that the cation vacancies act as saturable traps for the mobile interstitial halogen defects. According to these models the transition from the first to the second stage of the $F$-center coloration curve would result from the exhaustion of these vacancies and the amount of the first-stage coloration should be proportional to the square root of the impurity concentration. Crawford,[3] Sibley and Russell,[4] and Ikeya and co-workers[2,5] have found evidences supporting these models. In the last few years, however, evidence has been gathered to show that it is the $M^{2+}$-cation vacancy dipoles and dipole aggregates which play the major role during the first-stage coloration and that the transition from the first to the second stage in the $F$-center production does not involve the exhaustion of the dipole traps.[6–13] Recently, Comins and Carragher[14] and Aguilar *et al.*[15] have developed similar models for the $F$-center production in alkali halides doped with divalent cation impurities in which it was considered that the $M^{2+}$-cation vacancy dipoles or dipole aggregates act as the dominant traps for the halogen interstitial defects created during irradiation. According to these models, the amount of the first-stage coloration is proportional to the square root of the impurity concentration providing a new explanation for the origin of this relationship.

The effects of the x irradiation in europium-doped KCl have been studied previously by Chowdari and Itoh[16] and more recently by Kao and Perlman.[17] However, these authors have reached opposite conclusions about the mechanism responsible for the first-stage coloration. While Chowdari and Itoh proposed that the isolated cation vacancies are converted to *F* centers during irradiation, Kao and Perlman considered that the cation vacancies bound in the impurity dipoles are those which are converted to *F* centers. This last conclusion amounts to considering that the $Eu^{2+}$-cation vacancy dipoles act as traps for the radiation-induced interstitial defects. It should be pointed out that in neither of the two investigations mentioned above, the influence of the europium concentration in the *F*-coloring kinetics has been analyzed. This determination appears to be a relevant one in order to test the various models for *F*-center growth. Also, the effect of the aggregation-precipitation state of the divalent europium ions in the *F*-coloring efficiency has not been investigated. This last point appears to be important since one would expect that the state of aggregation precipitation of the impurity ions should determine the ability of trapping of interstitial defects and hence the *F*-coloring rate. Unfortunately, in almost all previous work dealing with the influence of divalent cation impurities in the *F*-coloring growth of alkali-halide crystals, the state of the impurity has not been characterized and only in some of them the influence of the first products of aggregation has been analyzed.[13,18,19] To our knowledge, an investigation of the influence of the precipitated phases of divalent cation impurities in the coloring rate of alkali halides has not been performed up to now.

In the present paper we report a detailed investigation of the room-temperature (first-stage) *F*-coloring kinetics of europium-doped potassium chloride as a function of the impurity concentration. Emphasis has been paid to determine the effect of x irradiation on the $Eu^{2+}$-cation vacancy dipole concentration in order to get a deeper insight into the nature of the interstitial halogen traps responsible for the first-stage coloration processes. Also, the influence of the precipitated phases of $Eu^{2+}$ in this host crystal on the initial rate of *F*-center growth has been analyzed, taking advantage of our previous investigations dealing with the optical-absorption and luminescence spectra associated with these phases.[20,21] In these studies it has been shown that the optical spectrum of the $Eu^{2+}$ ion is quite sensitive to its aggregation-precipitation state in the alkali-halide matrix. In particular, Table I summarizes the peak positions of the different emission bands observed in the system KCl-$EuCl_2$, as well as the complexes responsible for them. It should be pointed out that divalent europium was selected to make this study in view of the fact that several techniques such as optical absorption, photoluminescence, electron paramagnetic resonance (EPR), and ionic thermocurrents (ITC) can be employed simultaneously to obtain information about the changes which can occur during the irradiation processes.

## II. EXPERIMENTAL

Single crystals of europium-doped KCl were grown in our laboratory using the Czochralski technique under a controlled atmosphere of dry argon. Doping was achieved by adding to the melt different initial concentrations of $EuCl_2$, which was previously reduced from $EuCl_3 \cdot 6H_2O$ using standard techniques.[22] Thermal quenching was performed by heating the samples at 500 °C for ~2 h and then dropping them onto a copper block at room temperature.

TABLE I. Emission bands observed for $Eu^{2+}$ in KCl depending on the thermal treatment given to the crystals, as well as their assignation. All peak positions are given in nm.

| Peak position of the emission band | Thermal treatment | Assignation | Ref. |
|---|---|---|---|
| 410 | Annealed at 200 °C | Stable dihalide phase $EuCl_2$ | 21 |
| 419 | Quenched from 500 °C | Isolated $Eu^{2+}$-cation vacancy dipoles | 20 |
| 427 | Annealed at temperatures $\leq$ 100 °C | Metastable Suzuki phase | 20 |
| 439 | Annealed at 200 °C | Metastable {111} $EuCl_2$-like plate zones | 21 |
| 478 | Annealed at 200 °C | Metastable {310} $EuCl_2$-like plate zones | 21 |

Irradiation of the crystals was performed at room temperature with a Phillips stabilized dc generator with a tungsten target tube operated at 30 kV and 20 mA. The x rays were always filtered through a 1-mm aluminum filter. Care was taken to avoid heating of the crystals during irradiation.

Optical-absorption and luminescence measurements were made at room temperature using a Perkin Elmer model 330 double-beam recording spectrophotometer and a Perkin Elmer model 650-10S fluorescence spectrophotometer, respectively.

The concentration of divalent europium in the crystals employed was determined directly from the optical-absorption spectrum of the doped samples using the same procedure as the one described elsewhere.[23] Also, the number of $Eu^{2+}$ ions which changed their valence state during irradiation was determined from the difference between the intensities of the $Eu^{2+}$ low-energy absorption band before and after irradiation. In order to determine the dipole concentration in the quenched samples, ITC measurements were performed with the experimental setup that has been described in a previous paper.[24] On the other hand, EPR measurements were made with a Varian V-4502-12 spectrometer to follow the number of $Eu^{2+}$-cation vacancy dipoles which were destroyed during irradiation. To do that, the total concentration of $Eu^{2+}$-cation vacancy dipoles, which was previously determined from the ITC spectrum, was associated with the intensity of the fine-structure groups in the EPR spectrum for the case in which the magnetic field was applied along the $\langle 001 \rangle$ direction. Then, the observed intensities of the fine-structure groups after irradiation were compared to those originally observed before irradiation. During all this process, care was taken to use the same operating conditions of the EPR spectrometer. It should be pointed out, that in some cases, the data obtained by EPR following this procedure were compared with those obtained by ITC and the results showed that they did not differ by more than $\sim 10\%$, which is within our experimental error.

To follow Eu precipitation into the metastable and stable phases, the evolution of the intensities of the emission bands given in Table I was determined as a function of the annealing time at different temperatures, following the same procedure as the one described previously.[20]

## III. RESULTS

### A. Preirradiation

Before x irradiation the observed optical-absorption spectrum of the quenched samples consisted of two broad bands whose centers of gravity peaked at 243 and 343 nm which were due, respectively, to transitions from the $4f^7$ $(^8S_{7/2})$ ground state of the $Eu^{2+}$ ion to the $e_g$ and $t_{2g}$ states of the $4f^6 5d$ configuration.[25,26] The separation between them is a measure of the 10-Dq splitting of the $5d$ orbitals by the cubic crystal field. On the other hand the emission spectrum consisted of only one band peaking at 419 nm.

ITC measurements performed in the quenched samples prior to irradiation show a single-current peak with an activation energy of $0.65 \pm 0.02$ eV and a relaxation time $\zeta = 7.4 \times 10^{-14 \pm 0.5} s^{-1}$ in good agreement with previous work.[24] From the area under the observed ITC peak, the dipole concentration ($N_d$) was calculated in the quenched samples and the result was compared with the total concentration of $Eu^{2+}$ ions ($N_T$) as determined from the absorption spectrum. It was ascertained that $N_d$ approaches $N_T$ closely and that they do not differ by more than 10%.

The EPR spectrum characteristic of a vacancy impurity dipole made up of $Eu^{2+}$ with a cation vacancy in a $\langle 110 \rangle$ nearest-neighbor position was observed before x irradiation. This spectrum has been described in considerable detail by Nair *et al.*[27] For brevity, neither the EPR nor the ITC spectra are presented here since they can be found in the literature.[24,27] It should be pointed out that in order to follow the changes in dipole concentration produced by the x irradiation, the EPR technique was preferred over the ITC in view of the fact that measurements can be performed in shorter times.

### B. Irradiation

#### *1. Spectrum of irradiated crystals*

Figure 1 shows the absorption spectrum of a KCl crystal doped with 580 ppm of divalent europium after quenching from 500 °C (dashed line) and after 130 h of room-temperature x irradiation (continuous line). In addition to the well-known $F$, $K$, $R_1$, $R_2$, and $M$ bands, three absorption bands peaking at 876, 975, and 1132 nm were observed after irradiation. The latter three bands have been ascribed by Kao and Perlman[17] to the presence of $Eu^+$ in the irradiated samples. The observations of these bands is quite difficult in the first-stage of the $F$-coloring growth curve, even under high-resolution conditions of the optical spectrophotometer. The conversion of the divalent impurity ions produces a decrease in the absorption coefficient of

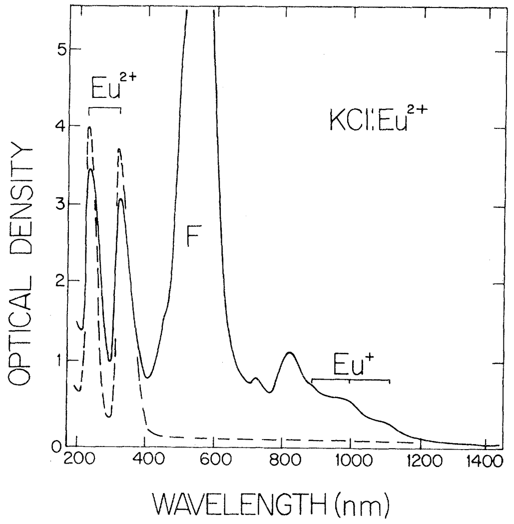

FIG. 1. Optical-absorption spectrum of a KCl crystal doped with 580 ppm of $Eu^{2+}$ after quenching from 600 °C (dashed line) and after 130 h of room-temperature x irradiation (continuous line).

both the high- and low-energy bands in the absorption spectrum characteristic of the $Eu^{2+}$ ions. Also, the $V_2^M$ band peaking at ~220 nm was observed superimposed on the high-energy band of the $Eu^{2+}$ spectrum after irradiation.

### 2. *Dependence of coloring on Eu concentration*

Figure 2 shows the *F*-center growth curves as a function of europium concentration for quenched samples. They have a similar shape corresponding to the well-known two stages of irradiation, an early fast first stage and a late slow second stage. They also show the usual behavior on increasing impurity concentration, i.e., the coloring increases in a monotonic way as the Eu concentration increases up to ~600 ppm which is the highest concentration employed in this work. The amount of the first-stage coloration has been obtained by extrapolating the linear part of each *F*-center growth curve to meet the ordinate. Once this was done the concentration of *F* centers was determined by using the Smakula equation for a Gaussian-shaped band with an oscillator strength of 0.55. The results are plotted in Fig. 3 as a function of the square root of the total europium concentration as determined from the optical-absorption spectra. The curve exhibits a quite good linear dependence and the correlation coefficient for this plot obtained by a least-squares adjustment is 0.991.

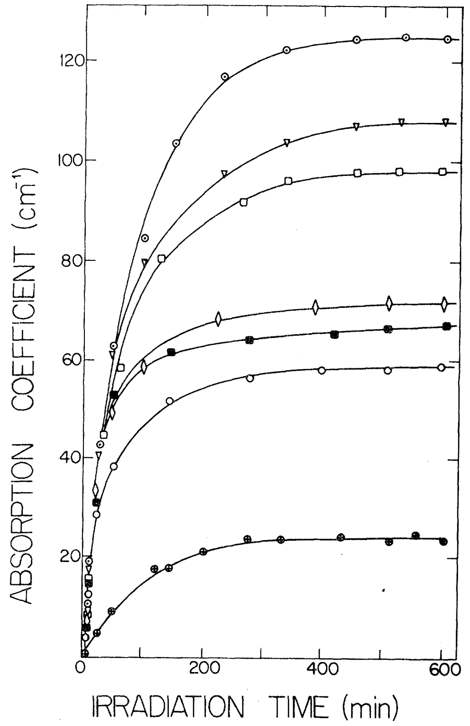

FIG. 2. *F*-center growth curves as a function of europium concentration; ⊕, pure; ○, 50 ppm; ■, 100 ppm; ◇, 150 ppm; □, 290 ppm; ∇, 320 ppm; ⊙, 540 ppm.

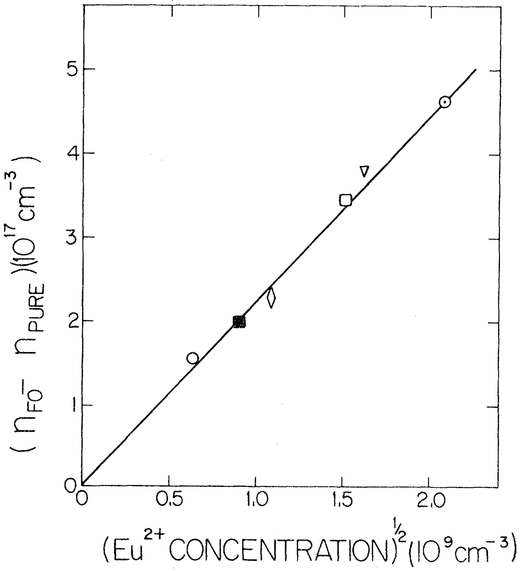

FIG. 3. Relationship between the first-stage coloration and the impurity concentration. To do this plot the amount of the first-stage coloration ($n_{F\text{pure}}$) corresponding to the pure crystal was subtracted to that ($n_{F0}$) obtained from the curves shown in Fig. 2 for the doped samples. Symbols represent the Eu concentration given in Fig. 2.

In order to get a deeper insight into the nature of the interstitial halogen traps, the influence of the x irradiation on the dipole concentration was analyzed. It was ascertained that during the *F*-center growth the concentration of $Eu^{2+}$-cation vacancy dipoles decreases considerably. Figure 4 shows the data for two different europium concentrations. In this figure, the dipole destruction ($\Delta N_d$), the *F*-center production, and the number of divalent europium ions which have changed their valence state ($\Delta Eu^{2+}$) during irradiation are presented. The dipole destruction increases rapidly in the early stage of irradiation and the transition from the first to the second stage of *F*-center formation is not the result of the exhaustion of the dipole concentration.

Figure 5 shows the evolution of the intensities of the absorption and EPR spectra of a quenched sample ( ~180 ppm) as a function of the x-irradiation time. Reference to this figure shows that the intensity of the EPR spectrum corresponding to the $Eu^{2+}$-cation vacancy dipoles decreases much faster than the intensity of the absorption spectrum. Similar results were obtained in the more heavily doped samples.

### C. Effect of the aggregation-precipitation state of the Eu impurity in the *F*-coloring

To investigate the effect of the initial concentration of $Eu^{2+}$-cation vacancy dipoles on the *F*-coloring efficiency, the number of *F* centers produced by a fixed dose (30 min) of x irradiation after a variable time following quenching was measured in a heavily doped sample ( ~500 ppm). The irradiation time employed brings the coloring to an intermediate point on stage I of the *F*-center growth curve. The results of these measurements are given in Fig. 6. In the same figure it is included the concentration of isolated dipoles measured by ITC as a function of the time elapsed at room temperature after quenching. The initial rate of *F*-center growth is essentially constant even when the dipole concentration is decreasing as a function of time. Also, the amount of divalent impurity ions which are converted to the monovalent state is independent of the aggregation processes occurring at room temperature up to ~400 h.

Figure 7 shows the efficiency of coloring as a function of the precipitation of the Eu impurity into the metastable Suzuki phase responsible for the emission band peaking at 427 nm (Ref. 20) (see Table I). Each point in the figure corresponds to a different sample of the same crystal block. To obtain these data, all samples ( ~500 ppm) were initially heated at 500 °C for 2 h and then quenched to room temperature. Then, they were annealed at 100 °C for different periods of time and irradiated under the same condition (30 min). The dipole concentration as a function of time at this temperature, measured by EPR, as well as the evolution of the intensity of the emission band at

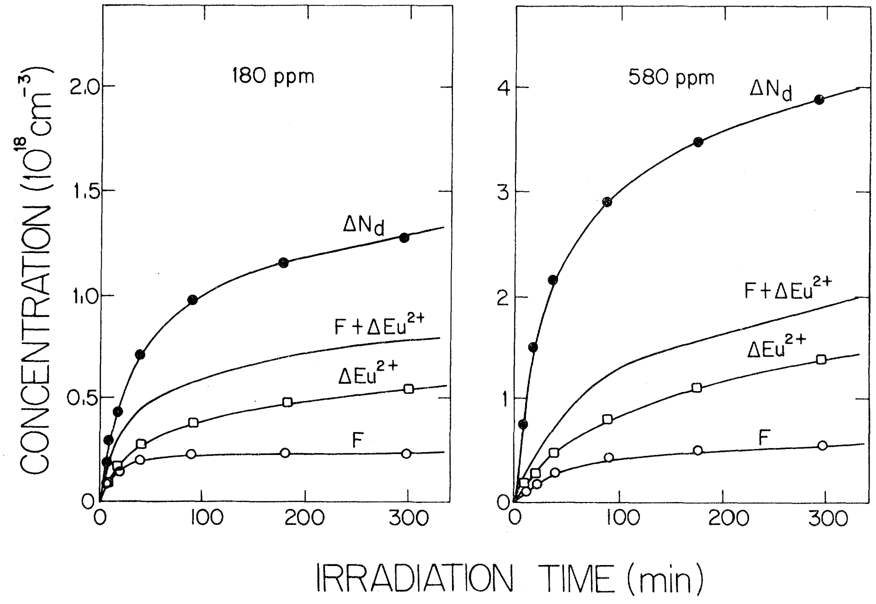

FIG. 4. Dipole destruction ($\Delta N_d$), *F*-center production (*F*), and number of divalent europium ions which have changed their valence state ($\Delta Eu^{2+}$) during irradiation.

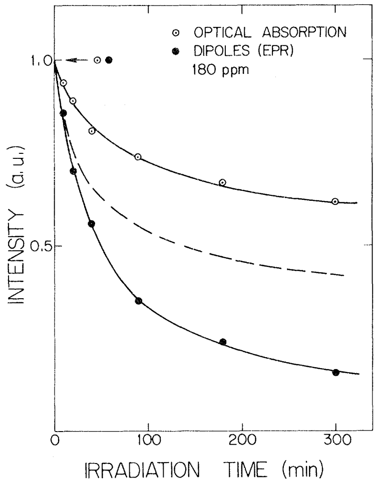

FIG. 5. Decay in intensities of the EPR and optical-absorption spectra as a function of the irradiation time. Dashed line represents the decay in intensity of the optical-absorption spectrum after subtracting the number of dipoles which have trapped the interstitial defects.

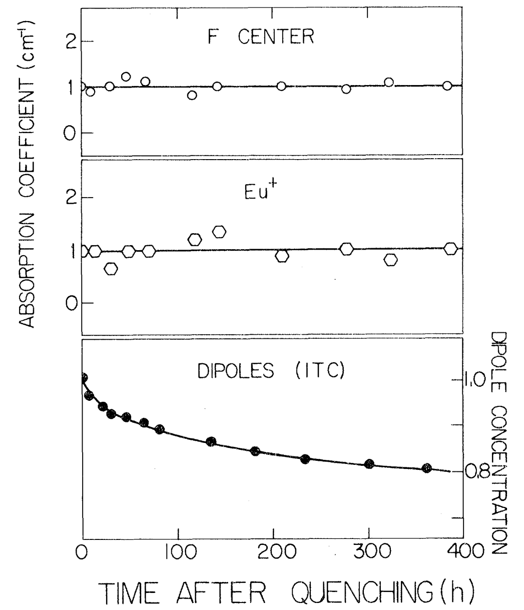

FIG. 6. *F*-center production and $Eu^+$ concentration (normalized to unit) induced by a 30-min irradiation as a function of the time elapsed between quenching and irradiation.

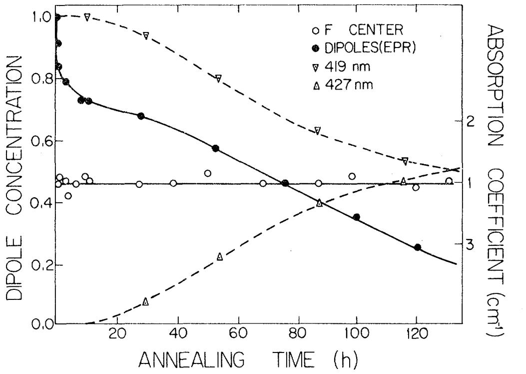

FIG. 7. Efficiency of coloring (normalized to unit) as a function of the aging time at 100 °C. Dipole decay, as well as the intensities of the emission bands peaking at 419 and 427 nm (Table I) are also included for comparison.

427 nm which gives information of the Eu precipitation into the Suzuki phase, are also included in Fig. 7 for the sake of comparison. The results indicate that the initial rate of coloring is independent of the aggregation-precipitation state of the impurity up to ~120 h, even when a considerable amount of europium ions have been precipitated to form the metastable phase. However, the coloring curve for a sample in which almost all the impurity is precipitated into the Suzuki phase, as revealed by the emission spectrum, shows a slightly higher coloring rate than that corresponding to a sample in which only isolated impurity vacancy dipoles are present.

Figure 8 shows the *F*-coloring efficiency as a function of the formation of the precipitated phases possessing the $EuCl_2$ structure in the KCl matrix responsible for the emission bands peaking at 410, 439, and 478 nm (Table I). To do this, samples (~300 ppm) were cleaved from the same crystal block, heated for 2 h at 500 °C, and quenched to room temperature. Then, they were annealed at 200 °C for different periods of time. Each point in the figure corresponds to a different sample irradiated 38 min after the annealing treatment. The dipole concentration as a function of time at this particular temperature, measured by EPR, as well as the evolution of the intensities of the emission bands mentioned above, which gives information about the precipitation of Eu into the second-phase precipitates with $EuCl_2$ structure, are also included in Fig. 8. As a difference with the annealing treatment at 25 and 100 °C, the aging at 200 °C produces a considerable influence in the initial efficiency for coloring and it decreases as a function of the annealing time. After 1200 h the efficiency is quite similar to that measured in a nominally pure sample.

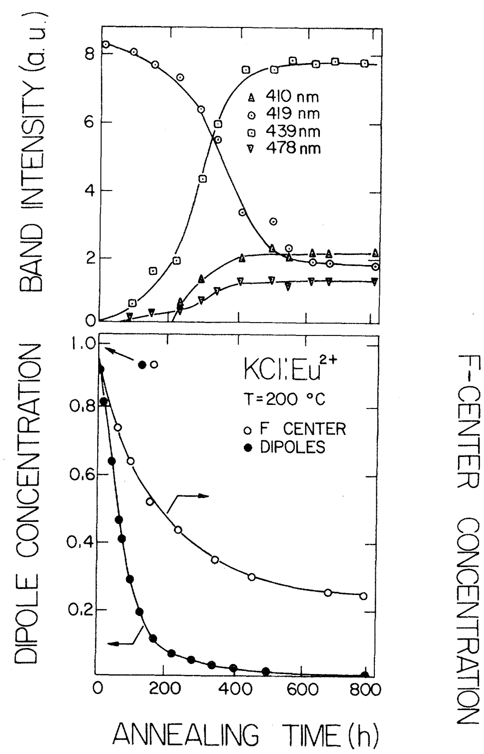

FIG. 8. Efficiency of coloring (normalized to unit) as a function of the aging time at 200 °C. Dipole decay as well as the evolution of the intensities of the emission bands peaking at 410, 419, 439, and 478 nm (Table I) are included for the sake of comparison.

## IV. DISCUSSION

According to the models of Comins and Carragher[14] and Aguilar *et al.*,[15] it is expected that the number of dipoles destroyed ($\Delta N_d$) should be equal or less than the sum of the number of $F$ centers produced ($F$) and the number of divalent ions which have changed their valence state ($\Delta \mathrm{Eu}^{2+}$) during irradiation. In contrast with this expectation, the data given in Fig. 4 show that $\Delta N_d \gg (F + \Delta \mathrm{Eu}^{2+})$. However, these results are in good agreement with those previously reported by Kao and Perlman.[17] These authors also found that in slightly doped samples $\Delta N_d = (F + \Delta \mathrm{Eu}^{2+})$. From this fact, they suggested that the $\mathrm{Eu}^{2+}$-cation vacancy dipoles act as the dominant traps for the interstitial defects. On the other hand, in order to explain that in the heavily doped samples $\Delta N_d \gg (F + \Delta \mathrm{Eu}^{2+})$, Kao and Perlman considered that the x irradiation may increase the rate of aggregation of dipoles as previously suggested by Muccillo and Rolfe.[28] In order to obtain evidence of this effect, the measurements reported in Fig. 5 were performed. The difference in the decrease of the intensities of the EPR and absorption spectra may be explained considering that there exist $\mathrm{Eu}^{2+}$ complexes in the irradiated samples which are contributing to the absorption spectrum but not to the EPR spectrum corresponding to the isolated dipoles. These complexes may be (a) the dipoles which have trapped the radiation-induced interstitial defects. This is a reasonable assumption since it appears that point defects near the $\mathrm{Eu}^{2+}$ ion produce only a small perturbation to the cubic crystal field acting on the Eu site.[25,26] Therefore, it is expected that the trapping of the interstitial defect by the $\mathrm{Eu}^{2+}$-cation vacancy dipole does not alter significantly the optical transitions of the impurity ion in the dominant cubic crystal field, and that the absorption and emission spectra of these complexes should be quite similar to those of the isolated dipoles and must be superimposed on them; and (b) dimers, trimers, etc., which could be formed during the irradiation processes, and for which it is known that their absorption and emission spectra are superimposed on those corresponding to the $\mathrm{Eu}^{2+}$-cation vacancy dipoles.[20] In order to determine if both types of complexes (a) and (b) were present in the irradiated samples, we first assumed as a working hypothesis that the different decrease of the intensities of the EPR and absorption spectra was only due to the presence of complexes (a). On the other hand, since $N_d$ is closely equal to $N_T$ in the samples before irradiation, it is expected that if the number of complexes (a) is subtracted from the total $\mathrm{Eu}^{2+}$ concentration still remaining in the samples after irradiation, the resulting value should be quite close to the dipole concentration determined from the EPR spectrum. To do this, we assumed that only one halogen interstitial defect is trapped at the $\mathrm{Eu}^{2+}$-cation vacancy dipoles. With this hypothesis the number of dipoles which have trapped the interstitials is equal to the number of $F$ centers produced. It was ascertained that the number of $\mathrm{Eu}^{2+}$ ions determined from the absorption spectrum after making the subtraction mentioned above, is still much larger than the dipole concentration as shown in Fig. 5. It should be noticed that if more than one interstitial defect is trapped at the dipoles then, the difference mentioned above will be much larger. This result may indicate that complexes (b) (dimers, trimers, etc.) are present in the irradiated samples. At this point, it could be thought that the concentration of these dipole aggregates could be the result of the room-temperature aging of the samples during the times involved in the measurements.

To check this point, ITC measurements were performed on a twin unirradiated sample to follow dipole aggregation at 25 °C. It was ascertained that this process is very slow at this temperature resulting in a $\sim 2\%$ decrease of the ITC peak in $\sim 300$ min which is the largest time involved in the measurements shown in Fig. 4. This result establishes, therefore, that the major number of dipole aggregates present in the irradiated samples are not the result of the room-temperature aging. It rather appears that it is a consequence of the x irradiation which increases considerably the rate of dipole aggregation. Due to this fact and also because the $Eu^{2+}$ ions change their valence state during irradiation, a linear relationship between the number of $F$ centers produced and the number of $Eu^{2+}$-cation vacancy dipoles which are destroyed by irradiation, similar to that previously reported in strontium-doped KCl (Ref. 8) and KBr (Ref. 9), was not obtained in this case.

The data given above indicate that in europium-doped KCl, dipole destruction as a result of x irradiation is mainly due to three mechanisms which operate simultaneously: (1) interstitial trapping, (2) change of valence of the divalent europium ions forming the dipoles, and (3) radiation-induced dipole aggregation. The latter effect has been previously suggested by Muccillo and Rolfe[28] in their experiments dealing with the effects of $\gamma$ irradiation in strontium-doped KBr. Although this suggestion has been invoked in several papers dealing with the irradiation processes of alkali-halide crystals doped with divalent cation impurities, this is the first time, as far as we know, that experimental evidence has been gathered to show that the rate of dipole aggregation is increased by irradiation. This was possible in view of the optical and paramagnetic properties of the $Eu^{2+}$ ion which allowed us to employ several techniques simultaneously.

The correlation between the amount of the first-stage coloration and the square root of impurity concentration reported in our Fig. 3 may give support to the models of Comins and Carragher and Aguilar *et al.* for $F$-center formation in which this type of dependence is predicted. It should be noticed, however, that in neither of these models has the possibility that the divalent impurity ions may aggregate and/or change their valence state during irradiation been taken into consideration. Therefore, it will be very interesting to include these effects in the models to determine if the amount of first-stage coloration is still predicted to be proportional to the square root of the impurity concentration as it was experimentally determined in this work.

The lack of correlation between the production rate of $F$ centers and the concentration of nonaggregated dipoles is in accordance with previous data[13,18,19] on several alkali-halide crystals doped with divalent cation impurities and suggests that the isolated dipoles are as equally efficient as the first products of aggregation (dimers, trimers, etc.) for the trapping of the mobile interstitial defects. Also, the independence of the first-stage coloring rate on the precipitation process of the impurity into the metastable Suzuki phase may suggest that this precipitate is contributing to the coloring in a quite similar manner as the isolated dipoles. On the other hand, the lowering coloring rate for samples in which precipitates with the $EuCl_2$ structure have indicated that these precipitates are not good traps for the radiation-induced interstitials.

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