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X-ray effects on cation impurity-vacancy pairs in KCl:Eu^{2+}

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X-ray irradiation of KCl:Eu^{2+} at room temperature destroyed impurity-vacancy (I-V) dipoles, converted the doubly valent impurity ion to a singly valent state, and created defect centers, e.g., F centers and a 220-nm optical-absorption band. Eu^+ produced by the irradiation was observed to grow in proportion to the destruction of Eu^{2+}. The 220-mμ band was also observed to grow approximately in proportion to the height of the F band, in agreement with previous workers. The number of dipoles destroyed was equal to or exceeded the sum of the number of converted ions and the number of F centers produced. A possible explanation of these results is that x rays increase the rate of aggregation of dipoles. It is likely that it is the cation vacancies bound in I-V dipoles that are converted to anion vacancies which later form F centers.

I. INTRODUCTION

The presence of divalent cation impurities in alkali halides results in the formation of impurity-vacancy (I-V) dipoles.[1] X irradiation supplies electrons and holes which cause destruction of these dipoles. Three mechanisms may be involved in this destruction; charge transfer to the divalent impurities, conversion of cation vacancies, and aggregation of the dipoles to form dimers.[2]

Charge transfer to the divalent impurities on x irradiation has been observed in rare-earth-doped KCl. Fong and Cape[3] identified the presence of Sm^+ in Sm^{2+}-doped KCl. Luminescence studies suggested the presence of Eu^+ in Eu^{2+}-doped KCl.[4] Chowdari and Itoh[5] postulated the presence of Eu^{3+}, but at optical-absorption wavelengths quite different from those expected for Eu^+.

Enhancement of the F-center production rate in alkali halides containing divalent cation impurities, during the initial stage of x irradiation has long been recognized, and various models have been proposed to explain this. Hayes and Nichols[6] have observed a nearly [100] oriented Cl_2^- or Br_2^- center (the so-called H-N center) in KCl and KBr, respectively, doped with alkaline earths, and x irradiated at liquid-nitrogen temperature. The optical-absorption peak of this center is near 325 nm in KCl, and they attribute it to hole capture at an associated divalent impurity-*bound* cation vacancy complex. Crawford and Nelson[7] then suggested that the 325-nm peak could equally well be due to *isolated* cation vacancies which have been converted to Cl_2^- and an anion vacancy by hole capture. The anion vacancy then captures an electron to become an F center. This explains the increase in the F-center production rate on doping with divalent impurities, if the I-V complex is appreciably dissociated. Hayes[8] believed that it was the impurity-*bound* cation vacancy sites (I-V dipoles) which were the source of the anion vacancies that later formed F centers, and not the isolated cation vacancies. This point of view is equivalent to a dipole capturing a migrating interstitial created by the irradiation to form Cl_2^-.

Ionic conductivity measurements by Ikeya *et al.*[9] in x-irradiated-doped NaCl supported Crawford's view that it was the isolated cation vacancies that were converted. On the other hand, Beltrami *et al.*[10] and Marat-Mendes and Comins[11] have proposed that since most cation vacancies are bound in I-V dipoles at room temperature, the majority of F centers should be created from converted-*bound* cation vacancies. They observed a decrease in I-V dipole density, almost equal to the density of F centers produced. The measurements to be described here partly support the latter view. A review of the subject has been given by Jain.[12]

Another center closely related to the F-center formation mechanism is the so-called V center (220 nm) in KCl and D center in KBr.[13] Crawford and Nelson[7] suggested that the Cl_2^- centers (325 nm) decompose to form Cl_2^0 which absorbs at 220 nm. Christy and Phelps[14] proposed that Cl_3^- was responsible for this absorption peak. Voszka *et al.*[15] suggested that the 220-nm center is created by the association of two 325-nm centers. Chowdari and Itoh,[5] and Hoshi *et al.*,[16] have observed that the 220-nm band is proportional to the F-center band.

In this paper, the effect of x-rays on Eu^{2+}-doped KCl is studied using both the ionic-thermal-current[1] (ITC) and optical-absorption methods. Dipole destruction is determined using ITC. Charge transfer to the Eu^{2+} impurity ion is observed, as well as a correlation between the F center and 220-nm optical-absorption bands. The number of dipoles destroyed is shown to be equal to or to exceed the sum of the number of converted ions, and the number of F centers produced. A possible explanation of these results is that x-rays increase the rate of aggregation of dipoles. It is likely that it is the cation vacancies bound in I-V dipoles that are converted to anion vacancies which later form F centers.

II. EXPERIMENT

The samples used in this work are grown in our laboratory from the melt using the Kyropoulos method. The boule of Eu^{2+}-doped KCl is cleaved into 0.8-cm × 0.8-cm × 0.6-mm-thick pieces. This crystal is then further cleaved into two 0.3-mm-thick pieces. The difference in thickness of the two samples is no more than 0.02 mm. Both samples are annealed at 500 °C for 2 h in a vacuum furnace to dissociate any dipole complexes, quenched to room temperature within a few minutes, and electrodes painted on one of them with Aquadag.

A. Dipole destruction

ITC measurements are carried out on this latter piece, before and after x irradiation, to determine dipole destruction. Optical-absorption measurements are carried out on the other sample, for the same x-ray dose, to determine defect production. Attempts are then made to correlate the two measurements.

In the ITC method, the samples are first polarized by application of an external field of 15 kV/cm for 8 min at 240 °K. The temperature is lowered to that of liquid nitrogen with the field still applied. The field is then removed, the samples are short-circuited and heated at a uniform rate of 6 °K/min. One records a short-circuit current peak as a function of temperature as the dipoles disorient. The samples are contained in a cold-finger cryostat equipped with a heating system, temperature controller, vacuum system, and inert gas supply. Currents are measured with a Victoreen electrometer and recorder.

X-rays destroy dipoles resulting in smaller ITC peaks. The x irradiations are carried out at room temperature using the unfiltered output of a Phillips x-ray diffraction tube at 40 kV and 25 mA, with the sample placed 12 cm from the x-ray target.

Defect centers produced by the x irradiation are identified and studied optically using a Beckman DK-2A double beam uv-visible-ir spectrophotometer. The optical spectra are taken at −180 °C in the range 185–1550 nm. Samples are placed in an Andonian Associates liquid-helium cryostat that has been adapted to fit the spectrophotometer. This cryostat is provided with an exchange gas chamber and a heater, allowing the sample to be maintained at any one of a broad range of temperatures. There are four windows in the tail of the cryostat, one of beryllium, one of brass, and two of quartz. The sample is x irradiated through the Be window, rotated, and studied optically through the quartz windows.

ITC and optical-absorption measurements were taken on four pairs of samples with Eu^{2+} impurity concentrations in the melt of 0.02, 0.05, 0.1, and 0.3 mole %, in addition to the pure crystal. X-ray irradiation times ranged from 5 min to 1 h. Some samples were x-irradiated up to 32 h to see larger changes in the optical-absorption spectrum.

B. Aggregation

Dipole aggregation in unirradiated samples at room temperature was measured for the 0.1- and 0.3 mole % samples. For lower concentrations aggregation was neglected.

III. THEORY

The dipole densities (N) were calculated by measuring the areas under the ITC peaks with a planimeter to get the total charge (Q) released by reorienting I-V dipoles.[1]

$$N = kT_p Q / A\alpha p^2 E_p \,, \tag{1}$$

where E_p and T_p are the polarizing field and temperature, respectively. A is the sample area, k is Boltzmann's constant, p is the dipole moment, and α is a geometrical factor equal to $\frac{1}{3}$ in these experiments.

Defect-center densities ρ (cm^{-3}) were calculated from the optical densities μ (cm^{-1}) using Smakula's equation[17] for a Gaussian optical band

$$\rho f = 0.87 \times 10^{17} n/(n^2+2)^2 \, \mu W/cm^3 \,, \tag{2}$$

where f is the oscillator strength, n is the index of refraction ($n = 1.469$ for KCl), and W is the full width of the band at half-maximum (eV).

IV. RESULTS AND CONCLUSIONS

Figures 1 and 2 show the optical spectra of $KCl{:}Eu^{2+}$ before and after 32 h of x-ray irradiation, respectively, for an impurity concentration

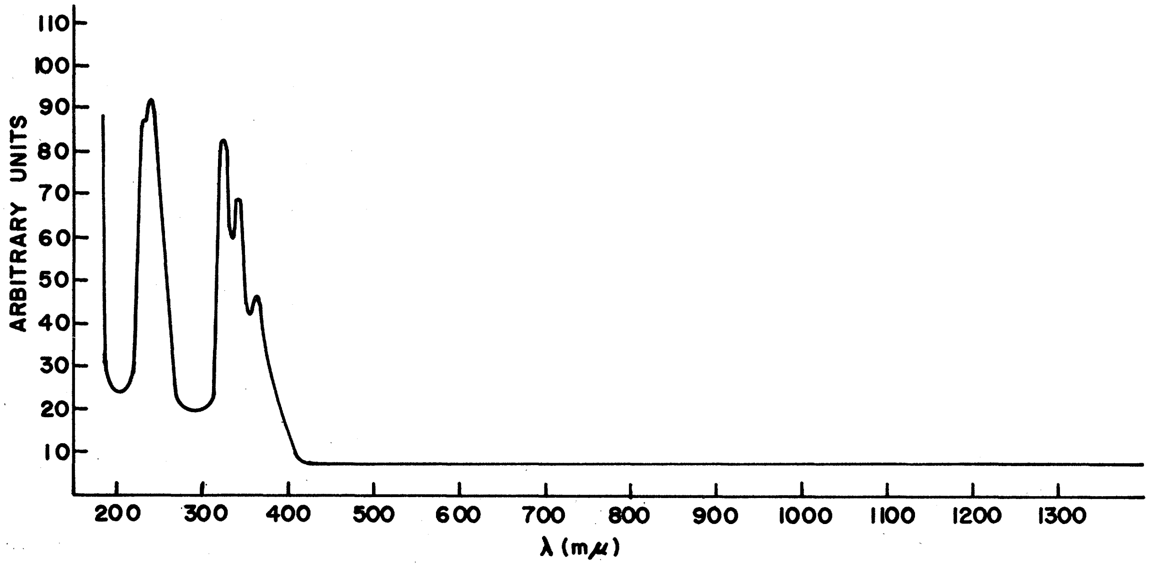

FIG. 1. Optical Spectrum of KCl:Eu^{2+} before x-ray irradiation for impurity concentration in the melt of 0.3 mole%.

in the melt of 0.3 mole %. Absorption peaks of Eu^{2+} occured at 234, 239, 327, 342, and 362 nm. After irradiation, there are, in addition, *K*- and *F*-center bands at 450 and 545 nm, and R_1, R_2, and *M* bands at 662, 730, and 810 nm, respectively. For long irradiation time, there are three peaks observed at 875, 975, and 1135 nm which we attribute to Eu^+ (Sec. V). Both the 327- and 362-nm peaks were used to determine the relative concentration of Eu^{2+}. The difference in the results from these two peaks were within experimental error. This meant that, in these room temperature experiments, there was no hidden peak near 325 nm (the *H*-*N* center) sometimes reported in the literature.[6] The 975 nm peak was used to determine the relative concentration of Eu^+.

Figure 3 shows dipole density, determined from

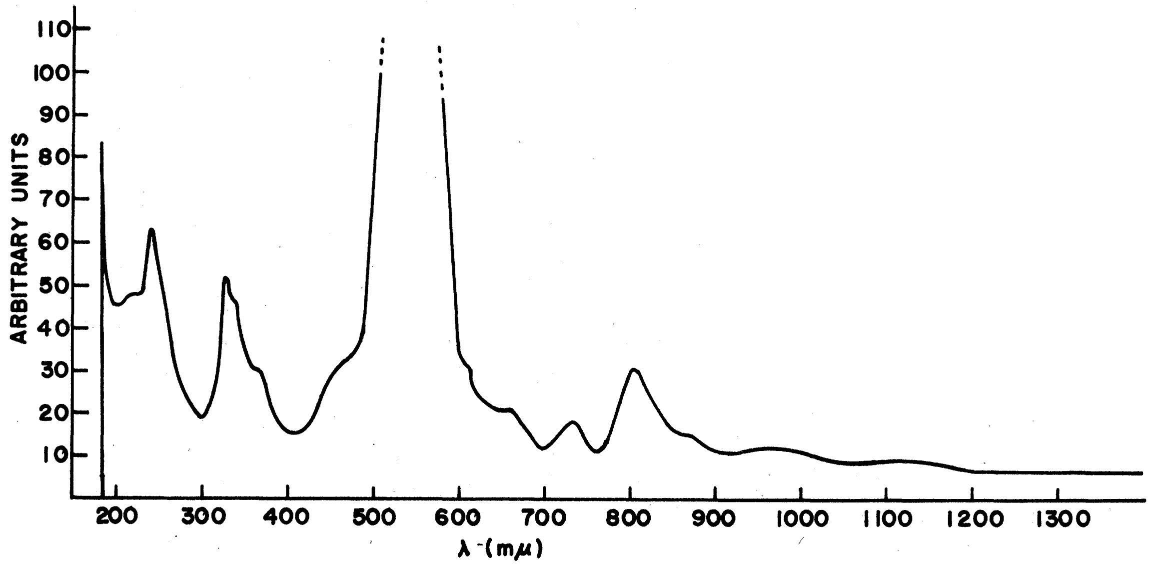

FIG. 2. Optical Spectrum of KCl:Eu^{2+} after 32 h of x irradiation (0.3 mole%).

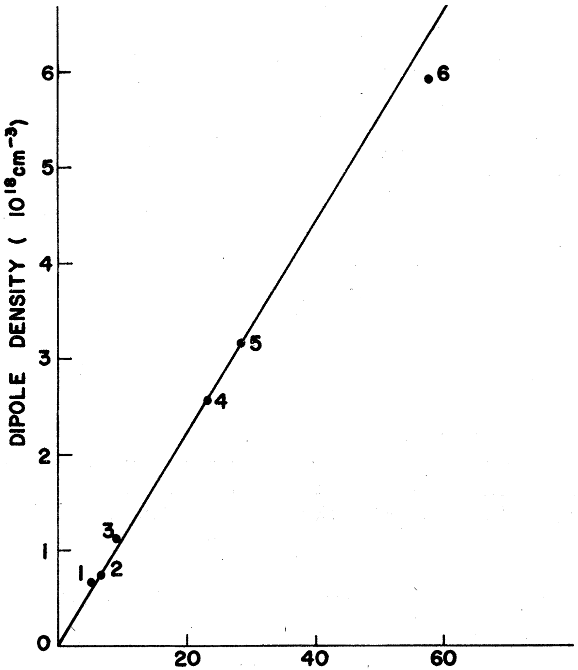

FIG. 3. *I-V* dipole density vs optical density (O.D.) of Eu^{2+} at 327 nm, before x irradiation. Points 1, 2—0.02 mole%, 3—0.05 mole%, 4, 5—0.1 mole%, 6—0.3 mole%.

ITC using Eq. (1) versus optical density (μ) of the 327-nm peak of Eu^{2+}, determined from optical absorption, for impurity concentrations in the melt of 0.02, 0.05, 0.1, and 0.3 mole % before x-irradiation. (All dipole densities were measured 1 h after quenching from 500 °C to room temperature.) Points 1–6 are for 0.02, 0.05, 0.1, and 0.3 mole %, respectively. One sees that the concentrations may differ even in the same crystal. All points except 6 lie on a straight line through the origin showing that the dipole density is proportional to the Eu^{2+} density. This is the expected result since there should be one Eu^{2+} center for each dipole due to charge compensation. For high concentrations (point 6) the dipole density is lower than expected because the dipole-aggregation rate is very fast at room temperature (see ahead).

Figure 4 shows the optical density of the 975-nm peak versus the reduction in optical density of the 327-nm peak (Eu^{2+}). A straight line is roughly obtained within experimental error. The amplitudes of the 875-, 975-, and 1135-nm peaks are proportional and all grow in proportion to the destruction of the Eu^{2+} peak. We attribute them to Eu^+.

Figure 5 shows that the optical density of the 220-nm centers is approximately proportional to that of the *F* centers in agreement with the results of others.[5,16]

Figure 6 shows the aggregation of dipoles in the unirradiated samples at room temperature for 0.1- and 0.3-mole % concentration. For lower concentrations room temperature aggregation can be neglected.

Figures 7–10 show the relationships amongst dipole destruction, Eu^{2+} reduction, and *F*-center production for concentrations of 0.3, 0.1, 0.05, and 0.02 mole %, respectively. Dipole destruction exceeds the sum of Eu^{2+} reduction and *F*-center

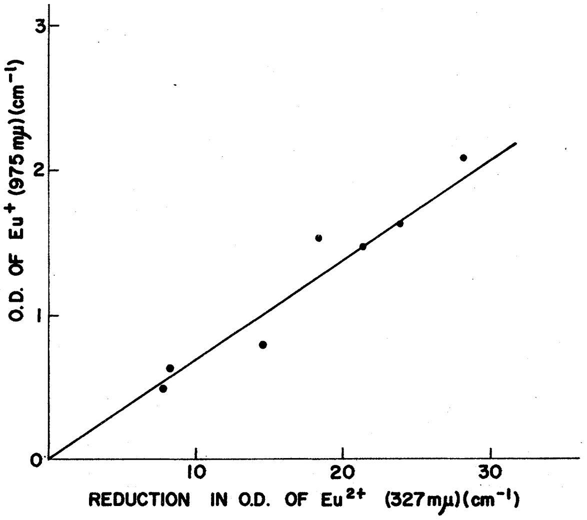

FIG. 4. O. D. of Eu^+ at 975 nm vs reduction in O. D. of Eu^{2+} at 327 nm (0.3 mole%).

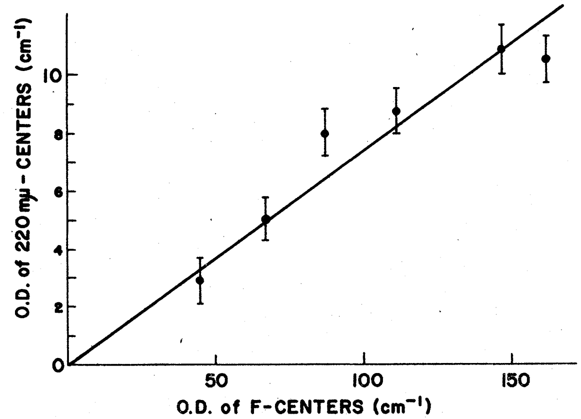

FIG. 5. O. D. of 220-nm centers vs O. D. of *F* centers for x-ray irradiation times of 5, 10, 20, 30, 45, and 60 min (0.1 mole%).

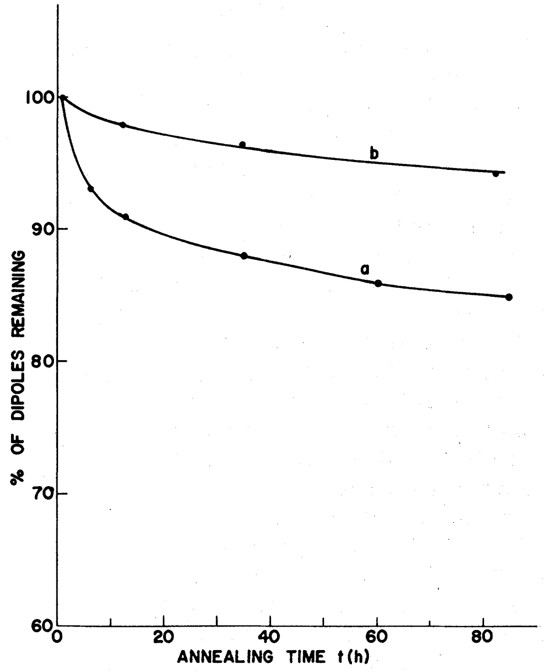

FIG. 6. Aggregation of KCl:Eu^{2+} I-V dipoles at room temperature. Percent of dipoles remaining vs time t. a—0.3 mole%, b—0.1 mole%.

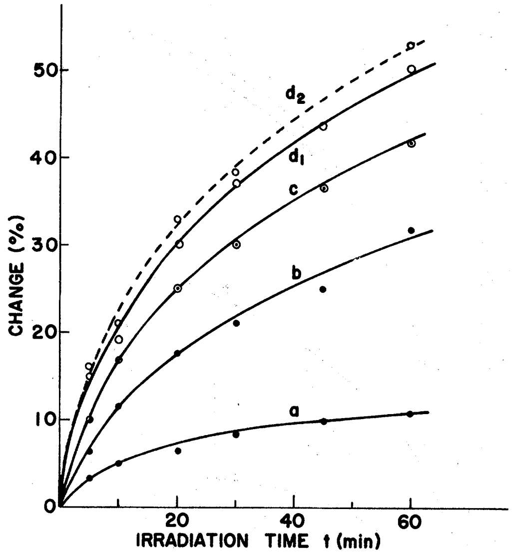

FIG. 8. a–percent increase in F centers. b–percent reduction in Eu^{2+}. c–sum of Eu^{2+} destruction and F center production. d_1, d_2—percent reduction in dipoles; d_1—corrected for aggregation, d_2—uncorrected. a, b, c d_1,d_2 all normalized to the original dipole density. Abscissa is irradiation time t (0.1 mole%).

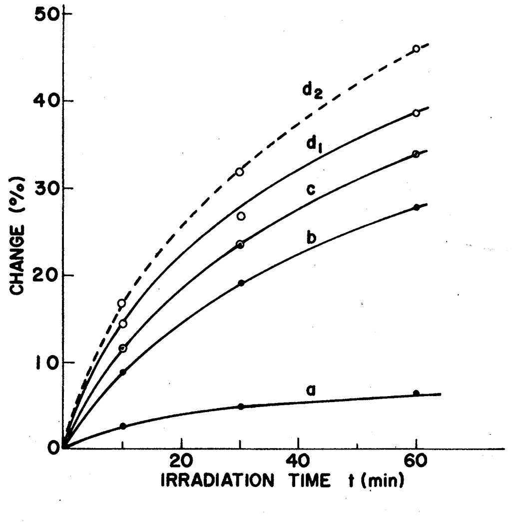

FIG. 7. a–percent increase in F centers. b–percent reduction in Eu^{2+}. c–sum of Eu^{2+} destruction and F center production. d_1, d_2—percent reduction in dipoles; d_1—corrected for aggregation, d_2—uncorrected. a,b,c, d_1,d_2 all normalized to the original dipole density. Abscissa is irradiation time t (0.3 mole%).

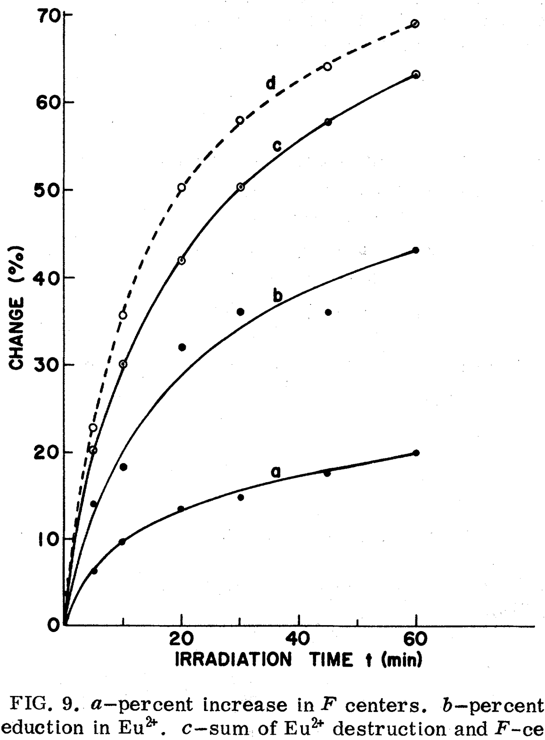

FIG. 9. a–percent increase in F centers. b–percent reduction in Eu^{2+}. c–sum of Eu^{2+} destruction and F-center production, d—percent reduction in dipoles. a,b,c,d, all normalized to the original dipole density. Abscissa is irradiation time t (0.05 mole%).

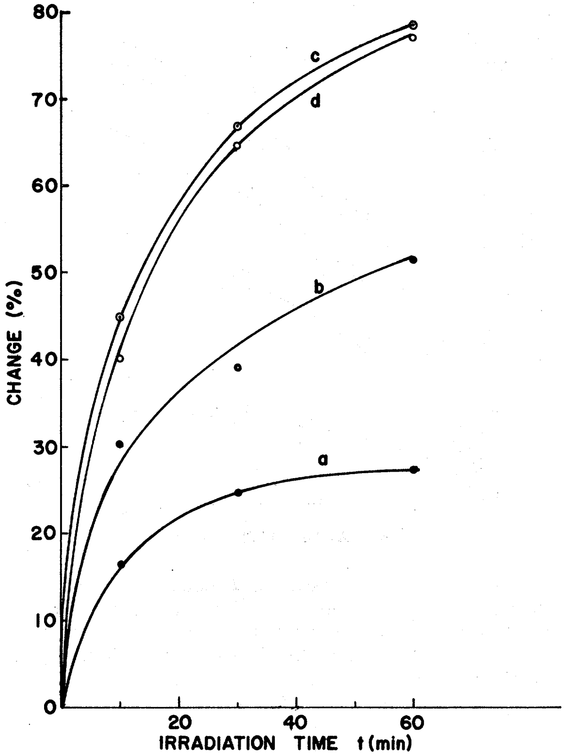

FIG. 10. *a*—percent increase in *F* centers. *b*—percent reduction in Eu^{2+}. *c*—sum of Eu^{2+} destruction and *F*-center production, *d*—percent reduction in dipoles. *a*, *b*, *c*, *d* all normalized to the original dipole density. Abscissa is irradiation time *t* (0.02 mole%).

production for the higher concentrations but is equal to this sum for the lowest concentration. This is so even when corrections are applied for the considerable aggregation of dipoles determined with unirradiated samples for the higher concentrations. A possible explanation is that x irradiation increases the rate of aggregation as previously suggested by Mucillo and Rolfe[18] in their γ-ray experiments.

V. DISCUSSION

Optical-absorption wavelengths determined for Eu^{2+} agreed with those previously reported.[5] The three peaks at 875, 975, and 1135 μm, which we attribute to Eu^{+}, are similar to those for Sm^{+} (at 860, 960, and 1120 μm) found by Fong[3] in γ-irradiated KCl:Sm^{2+}. Hole capture by Eu^{2+} to form Eu^{3+} is possible. However, absorptions attributed to Eu^{3+} by Chowdari[5] and McClure[19] occur at 465, 526, and 578 μm and are hidden by large *F*-center peak here.

The low (0.02 mole%) concentration measurements, where the rate of aggregation is negligible, show that dipole destruction is a result of the sum of impurity-ion conversion and *F*-center production within experimental error. Thus, we believe that *F* centers result from dipole destruction, i.e., the conversion of the cation vacancy *bound* in the *I*-*V* dipole into an anion vacancy (see Hayes[8]), which later captures an electron to become an *F* center. In addition, the fact that the 220-nm centers grow approximately in proportion to the *F* centers suggests agreement with part of Crawford and Nelson's[7] model. In this model a Cl_2^- ion (325 nm) is produced along with the anion vacancy when a hole is captured and is ionized to a Cl_2^0 (220 nm), which we observe in our room-temperature experiments. However, we believe that anion vacancies originate from the cation vacancies in *I*-*V* dipoles and not from isolated cation vacancies as Crawford believes. The above *H*-*N* center (325 nm) was not seen here but has previously been observed after x irradiation at dry-ice and liquid-nitrogen temperatures. While the foregoing is plausible, our measurements cannot decide among the various models proposed for the 220-nm center.

ACKNOWLEDGMENT

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