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COLOR CENTERS AND LUMINESCENCE IN SINGLE CRYSTALS OF LANTHANUM TRICHLORIDE CONTAINING DIPOSITIVE EUROPIUM

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January 1956

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ABSTRACT

The edge of the fundamental absorption band in pure  $\text{LaCl}_3$  is at about 2,250 Å. There is no change in the absorption spectrum of pure  $\text{LaCl}_3$  in the range 2,250 - 25,000 Å on exposure at room temperature to  $10^7$  r of gamma rays from a  $\text{Co}^{60}$  source. The crystals do not luminesce after such treatment.

In contradistinction,  $\text{LaCl}_3$  containing small amounts of europium exhibits a blue luminescence and thermoluminescence when exposed to ultraviolet or gamma radiation. The luminescent properties are profoundly influenced by long continued gamma irradiation. In addition, color centers are formed which absorb visible radiation.

Chemical as well as paramagnetic resonance experiments show that all of these effects are due to the presence in the  $\text{LaCl}_3$  lattice of dipositive europium. There are at least three different color centers giving rise to three overlapping absorption bands which decay thermally with different rates. The maxima of the absorption bands are at 8000, 6500 and 5500 Å. Studies with polarized light show that the color center transitions are all electric dipole in nature and are highly anisotropic. The most intense band has been tentatively identified with an F-center-like  $s \rightarrow p$  transition.

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\* This work was performed under the auspices of the Atomic Energy Commission at the University of California Radiation Laboratory, Berkeley, California.

Experiments on the thermal decay of the color bands and the glow curve of the crystal indicate that an intimate relationship exists between the color center and the luminescence phenomena.

It is suggested that when these crystals are irradiated dipositive europium loses an electron to become tripositive, the electron being captured by an anion vacancy to form a color center. On thermal freeing of the electron, return to the ground state is accompanied by the emission of visible radiation.

## COLOR CENTERS AND LUMINESCENCE IN SINGLE CRYSTALS OF LANTHANUM TRICHLORIDE CONTAINING DIPOSITIVE EUROPIUM

### INTRODUCTION

In recent years, two broad areas of solid state research, color center and luminescence phenomena, have been growing ever closer together. It has become one of the important aims of modern work on the solid state to achieve a unified point of view for an understanding of the complex nature of the absorption of radiation by crystals possessing color centers and the emission of radiation by luminescent materials.

In the past, most of the work on color centers was confined to pure alkali-halides<sup>1</sup> while that on luminescence was done primarily on powdered phosphors.<sup>2</sup> Interest in recent years in the use of alkali-halide crystals activated with thallium as detectors of nuclear radiation<sup>3</sup> has given impetus to studies on single crystals in which absorption and emission processes can be examined at one and the same time. Indeed, various authors have given attention to the interrelationships between these two processes.<sup>4, 5</sup>

We have recently carried out an investigation on pure  $\text{LaCl}_3$  single crystals and  $\text{LaCl}_3$  single crystals containing varying amounts of  $\text{EuCl}_2$ . These latter materials display optical phenomena, which strikingly illustrate the intimate connection between color centers and luminescence.

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1. F. Seitz, *Revs. Modern Phys.*, 26, 7 (1954).
  2. P. Pringsheim, Fluorescence and Phosphorescence, (Interscience Publishers, Inc., New York, 1949).
  3. R. Hoftadter, *Nucleonics*, 4, No. 4, 2; No. 5, 29 (1949).
  4. A. Halperin, G. F. J. Garlick, *Proc. Phys. Soc.* 68, 758 (1955).
  5. M. Furst, H. Kallman, *Phys. Rev.*, 91, 1356 (1953).

We shall present here primarily an account of the experimental observations. Wherever possible the results have been given theoretical interpretations.

## STUDIES ON PURE LANTHANUM TRICHLORIDE SINGLE CRYSTALS

Effects similar to those observed on exposure of alkali halides to ionizing radiation have been found in alkaline earth dihalides.<sup>6-9</sup> There appear, however, to be no literature reports of studies on color center formation in any halides of valence higher than those mentioned.

Lanthanum trichloride is one of the more than 20 trihalides of the 4f and 5f series of elements which have been shown to possess the hexagonal  $UCl_3$  structure.<sup>10,11,12</sup> Its response to radiation is of interest.

1. Preparation of Single Crystals. Lanthanum trichloride single crystals of optical quality were grown by Sayre, Sancier and Freed.<sup>13</sup> We have modified their procedure in several respects. Pure (<0.1 percent total impurity content)  $La_2O_3$  from the Lindsay Light and Chemical Company was dissolved in concentrated HCl;  $LaCl_3 \cdot 6H_2O$  was prepared

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6. R. Herman and S. Silverman, J. Opt. Soc. Amer. 37, 871 (1947).
  7. A. Smakula, Phys. Rev. 77, 408 (1950).
  8. S. Barile, J. Chem. Phys. 20, 297 (1952).
  9. H. F. Ivey, Phys. Rev. 89, 322 (1953).
  10. W. H. Zachariasen, J. Chem. Phys. 16, 254 (1948); Acta Cryst. 1, 266 (1948).
  11. S. Schubert, A. Seitz, Z. Naturf, 1, 321 (1946); Z. anorg. Chem. 254, 116 (1947).
  12. R. Fricke, A. Seitz, Z. anorg. Chem. 254, 109 (1947).
  13. E. V. Sayre, K. M. Sancier, S. Freed, J. Chem. Phys. 23, 2060 (1955).



by allowing this solution to evaporate over  $P_2O_5$  in a vacuum. The hydrated crystals were placed in a horizontal quartz tube surrounded by a furnace. Dehydration was carried out by raising the temperature to  $350^\circ C$  over a period of several hours while the tube was being swept with tank hydrogen chloride gas. When the dehydration had been completed, the tube was placed in a vertical position, and attached to a vacuum system by means of a standard taper joint. A furnace was then placed around the lower portion of the tube containing the anhydrous chloride. The temperature was raised to  $\approx 1000^\circ C$  and the chloride sublimed into the cooler portion of the tube. In this step impurities were removed which originate in two ways: 1) tank HCl contains 0.2 percent organic material and some of this decomposes on the surface of the chloride, and 2) dehydration, under the conditions described always leaves a small amount of oxychloride which disproportionates to the trichloride and the nonvolatile oxide on sublimation.

After sublimation, the tube was rotated  $120^\circ$  about the standard taper joint. The sublimate was heated to the melting point ( $860^\circ C$  for  $LaCl_3$ ) using a torch and the molten material was allowed to run into an attached sidearm (5 mm i. d. x 4 in.) used for crystal growing. When all of the material ( $\approx 4$  g) had been collected, the crystal growing tube was sealed off under vacuum. A quartz hook was fastened to the top of this tube which was then suspended from a 5-mil platinum wire inside a 3 in. diameter x 18 in. tube furnace, the tip of the vessel being located just below the center of the furnace. The 5-mil platinum wire was in turn attached to a pulley, clutch and gear arrangement driven by a 1/12 rph Cramer synchronous motor. The sample was lowered through the furnace at the rate of 1/16 in. per hr. Temperature readings taken with a chromel-alumel thermocouple continuously displayed on the chart of a Brown recorder with a full scale sensitivity of 1.1 mv. A Solar transformer was used to regulate line voltage. The temperature was controlled to within  $\pm 1^\circ$  by intermittently feeding about 10 percent of the total power to the furnace through a relay activated by a modified Brown amplifier. The amplifier sensed the imbalance in a bridge circuit one arm of which was a platinum resistance thermometer mounted in the furnace.

When crystal growth was completed, the power to the furnace was shut off and the sample allowed to cool to room temperature in the furnace. The cylindrical crystal always broke away cleanly from its quartz container and when the container was opened, the crystal could be extracted intact without difficulty.

It has been our experience as well as that of the Brookhaven workers<sup>13</sup> that the C-axis of the hexagonal  $\text{LaCl}_3$  crystals grow along the axis of the cylindrical vessel. The crystals were transparent and free of macroscopic flaws. Sections of any desired length were cut from the crystal bar with a small coping saw.

Polishing of the crystals was done in an inert atmosphere box using No. 600 emery paper for rough abrasion and finishing off with Linde Saphirin on chamois cloth.

Single crystals of  $\text{LaCl}_3$  are not exceedingly hygroscopic. A highly polished surface can be kept for days without visible deterioration in a nitrogen atmosphere if the relative humidity is kept below 5 percent.

2. Spectroscopic Studies. Although no rare earth impurities were detected in the  $\text{La}_2\text{O}_3$  starting material by emission spectroscopic analysis, an examination of the absorption spectrum at liquid nitrogen temperatures of a  $\text{LaCl}_3$  single crystal 1 cm long revealed the presence of some sharp absorption lines which could only be due to a rare earth impurity. The lines could not be detected at room temperature. We were able to show that all of the lines are due to  $\text{Pr}^{+3}$  and a study of their polarization properties has confirmed in detail results of the Brookhaven workers<sup>13</sup> lending support to their analysis of the  $\text{Pr}^{+3}$  spectrum. Aside from the  $\text{Pr}^{+3}$  impurity of approximately 0.01 mole percent, the maximum impurity content due to other rare earths is estimated to be not more than a few parts per million.

The absorption spectrum of a 1cm long  $\text{LaCl}_3$  single crystal taken on a Beckman Model D. U. Spectrophotometer at liquid nitrogen temperature is shown in Fig. 1. The spectral range was extended to 25,000 Å using a Model

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13. E. V. Sayre, K. M. Sancier, S. Freed, J. Chem. Phys. 23, 2060 (1955).

14 Cary Spectrophotometer. The crystal is transparent to light in the region 3,000-25,000 Å. The edge of the fundamental absorption band is at about 2,250 Å with a long wavelength tail extending to roughly 4,000 Å. There is no known  $\text{Pr}^{+3}$  absorption corresponding to the maximum at 2,750 Å. We feel that this band, which is somewhat broader at room temperature, is not due to an impurity but is characteristic of  $\text{LaCl}_3$  itself.

3. Effects of Irradiation. Single crystals of  $\text{LaCl}_3$  were irradiated with the full light of a 125-w Hanovia ultraviolet lamp for several hours. reexamination of the spectrum showed no change from that obtained before irradiation (Fig. 1). The crystals were also irradiated at room temperature with the 1.1 and 1.3 Mev gamma rays of a  $\text{Co}^{60}$  source having a flux of  $2.8 \times 10^5$  r/h. Exposures of the crystals to dosages up to  $10^7$  r produced no measurable changes in the absorption spectrum, showing that  $\text{LaCl}_3$  is resistant to coloration by gamma rays. No irradiation experiments with x-rays were carried out. It is known that crystals of KCl and  $\text{SrCl}_2$  are colored by exposure to x-rays and there is every reason to believe that gamma rays would cause similar effects.

One can think of at least three possibilities to account for the behavior of  $\text{LaCl}_3$  under gamma bombardment. The first is that color centers are formed in large numbers but that their absorption spectrum is in the ultraviolet and therefore masked by the fundamental absorption of  $\text{LaCl}_3$ . The second is that color centers are formed but are unstable at room temperature and so are thermally bleached as quickly as they are formed. Irradiations carried out at low temperatures could settle this point experimentally, but have not been done as yet. The third possibility is that the number of Schottky defects in the crystal is smaller by orders of magnitude than in either the alkali halides or the alkaline earth halides.

To obtain more information bearing on this point,  $\text{LaCl}_3$  was melted in the presence of 0.1 mole percent  $\text{BaCl}_2$ . Irradiation of the microcrystalline material obtained in this way in the gamma source ( $\approx 10^6$  r) did not result in any visible coloration. If all of the  $\text{Ba}^{+2}$  was incorporated into the crystal, an equivalent number of anion vacancies (0.1 percent) would

have been created. On the basis of this one experiment it appears that even when large numbers of anion vacancies are present, color center formation is not observed in  $\text{LaCl}_3$ .

The experiments of Smakula<sup>7</sup> indicate that alkaline earth halides are more resistant to coloration by ionizing radiation than are the alkali halides. The fact that  $\text{LaCl}_3$  is still more resistant makes it tempting to speculate that these differences are connected with the increasing charge on the cations in the series alkali-alkaline earth-lanthanide halides. If such an effect exists, tetravalent halides like  $\text{ThCl}_4$  should be very difficult to color with ionizing radiation.

It is clear that more work both of an experimental and theoretical nature is required to define and understand the differences between halides of different charge type, as revealed in their variable response to ionizing radiation.

#### STUDIES ON LANTHANUM CHLORIDE SINGLE CRYSTALS CONTAINING DIPOSITIVE EUROPIUM

4. Origin and Demonstration of  $\text{Eu}^{+2}$  in  $\text{LaCl}_3$ . One of the original objectives of our work had been an investigation of the sharp line absorption and fluorescence spectrum of  $\text{Eu}^{+3}$  dissolved in  $\text{LaCl}_3$  which is due to highly forbidden electronic transitions from the  $^7\text{F}$  ground state to higher lying excited states. However, an examination of the absorption spectrum on a high resolution spectrograph of  $\text{LaCl}_3$  single crystals containing 10 percent europium revealed only the absorption due to the 0.01 percent  $\text{Pr}^{+3}$  impurity referred to in Section 2. No lines due to  $\text{Eu}^{+3}$  were seen. This crystal was slightly yellow and it completely absorbed radiation below 4,200 Å.

When the crystal was exposed, to the full light of a 125-w ultraviolet lamp, a very bright blue luminescence was observed which persisted for several minutes after shutting off the light. The spectrum of this luminescence was photographed. It consisted of a broad band centered at about 4,100 Å. After the luminescence had completely subsided, it

was noticed that the crystal had acquired a deep blue color. By heating the crystal, the blue color could be made to disappear. Also, when the crystal was heated, more of the blue luminescence was observed. The whole cycle could be repeated any number of times.

A clue to an understanding of these results came from the work of Przibram<sup>14</sup> who found that alkali halides which have crystallized with traces of a europium halide from an aqueous solution emit the red line fluorescence characteristic of the  $\text{Eu}^{+3}$  ion. If these crystals are heated to a temperature above  $200^{\circ}\text{C}$ , however, the lines are replaced in the fluorescence spectrum by a continuous band in the blue between 4,230 and 4,450 Å. Przibram thought that the new fluorescence was caused by the transformation on heating of  $\text{Eu}^{+3}$  to  $\text{Eu}^{+2}$ . In support of this idea he drew on observations of Jantsch and Klemm<sup>15</sup> who found evidence for the reaction  $\text{EuCl}_3 \rightarrow \text{EuCl}_2 + 1/2 \text{Cl}_2$  at a high temperature in vacuum. Similar observations have since been made by other workers.<sup>16</sup> It seems that this reaction has never been studied in detail.

Preparation of the mixed lanthanum-europium crystals<sup>17</sup> differs from the preparation of pure  $\text{LaCl}_3$  only in that one starts with the mixed lanthanum-europium chloride hydrates in which of course all of the europium is present in the tripositive state. Presumably during the sublimation of the anhydrous chlorides which is carried out at  $1,000^{\circ}\text{C}$  in vacuum,

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14. K. Przibram, *Nature* 135, 100 (1935); *Verhandl. deut. physik Ges.* 16 22 (1935).
  15. G. Jantsch, Klemm, *anorg. Chem.* 216, 80 (1933).
  16. G. P. Baxter, F. D. Tuemmler, *J. Am. Chem. Soc.* 59, 113 (1937).
  17. The europium used in this work was 99.8 percent  $\text{Eu}_2\text{O}_3$  from Research Chemicals, Inc., Burbank, Calif. Absorption spectra of single crystals of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  grown from this material were identical with similar spectra reported in the literature (K. H. Hellwege, H. G. Kahle, *Z. Physik.* 129, 62 (1951). No absorption lines due to other rare earths were found.

dipositive europium is formed which is incorporated as such into the crystal.

By preparing the mixed crystals in a  $\text{Cl}_2$  atmosphere, the reduction of europium was prevented for neither luminescence nor blue color formation was observed. Remelting in a vacuum or in a  $\text{H}_2$  atmosphere of crystals produced in the presence of  $\text{Cl}_2$  resulted once again in their displaying luminescence and coloration phenomena.

It was possible to demonstrate the existence of  $\text{Eu}^{+2}$  in the crystals directly by means of a paramagnetic resonance experiment.

The electronic configuration of  $\text{Eu}^{+3}$  is  $4f^6$  aside from closed shells giving rise by application of Hund's rules to the ground state  ${}^7F_0$ . Since this state has  $J=0$ , it is non-degenerate and therefore non-magnetic. Europium in the tripositive oxidation state cannot therefore give rise to paramagnetic resonance absorption.

The electronic configuration of  $\text{Eu}^{+2}$  is  $4f^7$  giving rise to the ground state  ${}^8S_{7/2}$ . In  $\text{LaCl}_3$  each cation is surrounded by nine chloride ion nearest neighbors, which make the local symmetry of the electric field  $C_{3h}$ . If  $\text{Eu}^{+2}$  takes the place of  $\text{La}^{+3}$  in the lattice, it would find itself in a field of predominantly  $C_{3h}$  symmetry. Using the matrix elements of Penney and Schlapp<sup>18</sup> for a field of this symmetry, one finds that the  $J=7/2$  state is split by the electric field into four doubly degenerate levels with spacings  $-5D$ ,  $-3D$ ,  $D$ ,  $+7D$ , where  $D$  is the crystal field splitting parameter. Since the  $\text{Eu}^{+2}$  ion is in a spectroscopic S state, the crystal field splitting might be small enough to be in the microwave region. If this is the case, it can be shown from a first order perturbation calculation that in a paramagnetic resonance experiment one should observe seven equally spaced lines arising from transitions between the split magnetic levels of different Stark components of the ground state.

Using conventional 3 cm paramagnetic resonance equipment and with the c-axis of a crystal containing one percent europium, parallel to the static magnetic field, paramagnetic resonance absorption was observed at room temperature. The absorption consists of seven main groups of lines approximately equally spaced and centered about  $g = 2.0$ . The overall splitting due to the crystalline field is about 5,220 gauss ( $0.50 \text{ cm}^{-1}$ ). Each of the seven

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18. W. G. Penney, R. Schlapp, Phys. Rev. 41, 194; 42, 662 (1932)

main groups of lines is composed of 12 hyperfine lines arising from the interaction of the electronic spin with the nuclear spins  $5/2$  of the isotopes  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$  present in almost equal abundance. The separations between the hyperfine lines of  $\text{Eu}^{151}$  and  $\text{Eu}^{153}$  in this crystal are 41 and 18 gauss respectively giving 2.2 for the ratio of the two nuclear moments. This is to be compared with the ratio 2.23 observed by Bleaney and Low<sup>19</sup> in SrS phosphors activated with europium. No attempt has been made to estimate the concentration of  $\text{Eu}^{+2}$  in the crystal by this method although it could be done in principle.

In connection with some other studies,  $\text{EuCl}_3$  was added to molten KCl or  $\text{SrCl}_2$ . In agreement with earlier work<sup>14, 20</sup> these materials exhibited a blue fluorescence under ultraviolet light. Neither long lived luminescence nor color center formation was observed. Paramagnetic resonance experiments showed that once again reduction of europium had occurred for the spectrum characteristic of  $\text{Eu}^{+2}$  was observed in both KCl and  $\text{SrCl}_2$ . In the case of  $\text{Eu}^{+2}$  in  $\text{SrCl}_2$  there is no field splitting whatsoever showing that the crystalline electric field is strictly cubic. In the case of KCl there appears to be a Stark splitting of the ground state but it is smaller than in  $\text{LaCl}_3$ . The application of this method to studies of "impurity" ion complexes is obvious.

5. Production and Thermal Decay of Color Centers. Having established that  $\text{Eu}^{+2}$  plays a necessary part in the luminescence and color center phenomena of  $\text{LaCl}_3$  it is now of interest to investigate the effects themselves in greater detail.

Fig. 2 shows some absorption spectra of a crystal containing 10 percent europium (presumably all or most of it in the dipositive state) taken after the crystal had been exposed at room temperature for varying lengths of time to the full light of a 125-w ultraviolet lamp. The spectra were taken

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19. B. Bleaney, W. Low, Proc. Phys. Soc., 68, 55 (1955)

20. F. D. S. Butement, Trans. Faraday Soc. 44, 1617 (1948).

on a Beckman Model D. U. Spectrophotometer. The bottom curve represents the absorption spectrum of an unirradiated crystal. The edge of the fundamental absorption band is at about 4,000 Å, while in pure  $\text{LaCl}_3$  (Fig. 1) the fundamental absorption edge is at 2,250 Å. The  $\text{Eu}^{+2}$  ion is responsible for the shift of the absorption toward the visible. One is here dealing with a transition probably involving the excitation of one of the f electrons to an outer d shell. Exposure for five seconds to the ultraviolet source results in a measurable change in the absorption spectrum. A pronounced, broad absorption band arises on continued exposure and is responsible for the blue color of the crystal. Inspection shows that the broad band is composed of at least three overlapping bands with maxima at 8000, 6500 and 5500 Å. Some sharpening of the band occurs when the crystal is cooled to liquid nitrogen temperatures, but no additional structure is revealed.

If one allows the crystal to stand at room temperature in the dark for three days, the dotted curve is obtained. This curve has only two maxima, the long wavelength component having bleached out more rapidly than the others.

More detailed studies of the decay of the color centers at room temperature show (Fig. 3) that the three bands decay with different rates. This means that to each band there must correspond a different color center. The fact that the 5500 Å band has increased after a four-day decay period indicates that some electrons leaving thermally less stable traps are captured before returning to the ground state by the more stable traps responsible for the 5500 Å band.

Because of the strong ultraviolet absorption of the crystal, color center formation is heaviest in the layer facing the ultraviolet lamp. In most of the work, therefore, crystals were colored by exposure to the  $\text{Co}^{60}$  source to produce a uniform distribution of color centers. The color center bands in the gamma irradiated crystals differ only in minor ways from those produced by ultraviolet irradiation.

It was of interest to investigate the rate of bleaching of the color centers as a function of temperature to establish, if possible, a correlation between the thermoluminescence and the decay of the color centers.



The glow curve of a crystal containing .01 percent europium (Fig. 8) showed that there are two broad temperature regions centering around  $100^{\circ}\text{C}$  and  $200^{\circ}\text{C}$  in which the thermoluminescence reaches maxima. This was confirmed visually on a crystal containing one percent europium which had been given a 10 min. gamma-irradiation. Before heating, the top curve in Fig. 4 was obtained. The crystal was then heated in an oil bath at  $115^{\circ}\text{C}$  for 10 min. During the first few minutes of this heating period, a strong luminescence was observed visually. After the crystal had been allowed to cool to room temperature, the second absorption curve shown in Fig. 4 was obtained. The crystal was then heated for another 10 min. at  $115^{\circ}\text{C}$  but there was no further change in the absorption spectrum and no luminescence was observed. This was followed by a 10 min. heating period at  $200^{\circ}\text{C}$ . Another burst of luminescence occurred which persisted for about 5 min. The absorption spectrum after this treatment showed that substantial bleaching of the remaining absorption band had taken place. (Curve marked  $200^{\circ}\text{C}$  in Fig. 4) No further bleaching occurred on continued heating at this temperature. The remainder of the color band was bleached by heating to  $300^{\circ}\text{C}$  but the luminescence was too faint to be seen visually.

These experiments taken together with the glow curve indicate that an intimate connection exists between the absorption and emission phenomena.

6. Anisotropy of the Color Centers. A crystal containing 10 percent europium which had been irradiated in the  $\text{Co}^{60}$  source for 10 min. was examined with light polarized by introducing a sheet of polaroid between the monochromatic light beam and the crystal. The results obtained using a Beckman Spectrophotometer are shown in Fig. 5.

Light was sent through one cm thickness of crystal in a direction parallel to the crystallographic c-axis ( $S \parallel C$ ) to observe the isotropic "axial" spectrum and through 0.5 cm thickness in a direction perpendicular to the crystallographic axis ( $S \perp C$ ) to observe the birefringent "transverse" spectrum. The transverse spectrum was separated into its two components by polarizing the entering light so that its electric vector was oriented parallel with ( $E \parallel C$ ,  $\pi$  spectrum) or perpendicular to ( $E \perp C$ ,  $\sigma$  spectrum) the crystallographic c-axis.

A comparison of the axial and transverse spectra of a uniaxial crystal differentiates between transitions of an electric dipole or magnetic dipole nature occurring within it. During the observation of the axial spectrum both the electric and magnetic vectors of the incident light are oriented perpendicular to the crystallographic axis. In the observation of the  $\sigma$  polarized transverse spectrum only the electric vector of the incident light is perpendicular to the c-axis and conversely during the observation of the  $\pi$  spectrum only the magnetic vector of the incident light is perpendicular to the axis. Therefore, if the axial and  $\sigma$  spectra coincide the transition must be of an electric dipole nature. A magnetic dipole transition is indicated by coincidence of the  $\pi$  spectrum with the isotropic axial spectrum.

From Fig. 5 it can be seen that the isotropic axial spectrum ( $S \parallel C$ ) and the  $\sigma$  transverse spectrum ( $S \perp C, E \perp C$ ) coincide to within the experimental error of the measurements, demonstrating directly that all of the color center transitions are of an electric dipole nature.

The 8000 A band is almost entirely missing from the  $\pi$  transverse spectrum showing that it is due to an electric dipole aligned perpendicular to the c-axis.

The optical density of the 6500 A band is almost exactly twice as great in the  $\pi$  spectrum ( $S \perp C, E \parallel C$ ) as in the  $\sigma$  spectrum showing that the direction of the electric dipole giving rise to this transition is preferentially along the c-axis.

The 5500 A band seems to be essentially unpolarized, the apparent higher optical density of this band in  $\pi$  as compared with  $\sigma$  polarization being due to the overlapping of the band with the 6500 A band which has a much stronger absorption in  $\pi$  polarization.

The independent nature of the three color bands demonstrated in their thermal decay characteristics receives additional support from these polarization studies.

It is tempting to speculate that the intense 6500 A absorption band is analogous to the F-band in alkali halides and represents a  $1s \rightarrow 2p$  transition. The  $2p$  state would undergo Stark splitting in the non-cubic crystal field

and the observed band therefore would correspond to a transition from the 1s ground state to one of the Stark components of the 2p state.

7. Study of Luminescence Induced by Ultraviolet Light. The buildup and decay of the luminescence of a crystal containing one percent europium was measured in the following way: the crystal and a photo-multiplier tube (931 A) were in a light-tight box fitted with two shutters -- one between the photo-multiplier and the crystal, the other between the crystal and a 125-w ultraviolet lamp.

The crystal was irradiated with ultraviolet light for the desired period of time. It was then rotated so that the irradiated face of the crystal was facing the phototube. If the crystal was not rotated, luminescent intensities 10 times lower were observed. Apparently the luminescence is induced in the outer layers of the crystal. A similar effect was pointed out before (Section 2) in the formation of color centers by ultraviolet irradiation. Both effects are undoubtedly due to the strong absorption of light below 4,000 Å by the crystal which prevents penetration into the interior.

For a study of the decay of the luminescence the phototube was operated at 1,000 v dc and the output of the tube fed to an RCA ultra-sensitive dc microammeter. Decay curves obtained after 5, 15, 60 and 600 sec. of ultraviolet irradiation are shown in Fig. 6 on a plot which is logarithmic in photo-multiplier current. The 60 and 600 sec. curves coincide. Apparently, the luminescent centers in the outer layers of the crystal become saturated in times of the order of one min. under the conditions of this experiment. If one assumes that the photo-multiplier current is a linear function of light intensity in the range covered by the graphs, the non-linearity of the curves means that the luminescent decay is not a first order process. An expression of the form  $I_t = \frac{I_0}{(\alpha t + 1)^n}$  with  $n = 1.1$  will fit the data. Similar expressions are often applied to luminescent decay curves of phosphors but their physical interpretation is not clear cut. We shall come back to this point in the discussion section.

As with the color centers, gamma-irradiation produces a uniform distribution of luminescence throughout the body of the crystal. The intensity of luminescence induced by our gamma source is not as great as that from

exposure to the ultraviolet lamp. Internal absorption is undoubtedly responsible for part of the observed difference. Although less intense, the gamma-induced luminescence is much longer lived than the ultraviolet-induced luminescence. The half-life of the former is about one hour as compared with a few minutes for the latter.

8. Effects of Intense Gamma-Irradiation on the Color Center and Luminescence Phenomena. Irradiation of crystals containing 10 percent or one percent europium for 30 min. in the  $\text{Co}^{60}$  source renders them opaque to visible radiation. In order to study saturation effects, a crystal containing 0.01 percent europium was used. The results are given in Fig. 7. In this crystal gamma-irradiation at first evokes a small increase in absorption throughout the visible and near-ultraviolet region of the spectrum. The absorption maxima though much less intense, correspond very roughly to those found in crystals containing 10 percent or one percent europium. After an irradiation of 82 min. the color center band has reached maximum intensity. Continued gamma-irradiation reduces the intensity of the band until after approximately 24 hr. (1477 min.) the intensity is comparable with the band originally produced after 27 min. of irradiation. Visually, the crystal after a 24 hr irradiation is indistinguishable from the unirradiated crystal. The luminescent intensity of the crystal decreases linearly by a factor of 50 in going from a 27 min. to a 24 hr irradiation period. The luminescence was measured within 10 min. after removal of the crystal from the gamma source.

Although the crystal containing 0.01 percent europium shows neither appreciable color center formation nor luminescence at room temperature after heavy gamma-bombardment, profound changes have nevertheless taken place within it. Evidence for this comes from the glow curves reproduced in Fig. 8. These curves were obtained by heating the crystal at a uniform rate of 10 Centigrade degrees per minute and measuring the light output with the blue phototube of a Beckman Spectrophotometer. The light intensity is given in arbitrary units of phototube current.

The glow curve after a 10 min. gamma-irradiation shows that the crystal is luminescing strongly at room temperature. The light emission increases

as the temperature is raised and reaches a peak at 85° C. There is a second, partially resolved peak at 200° C. At 300° C no more luminescence can be detected.

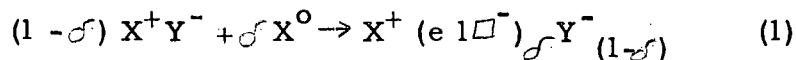
The glow curve after 22 hr of gamma-irradiation is quite different. The luminescence at room temperature is barely detectable. In addition, the shape of the curve has been altered. The 85° C peak is no longer present and there is now only a single broad peak with maximum at 225° C.

Although the total energy stored by the crystal is apparently not much increased by intense gamma-irradiation, it seems to become more difficult to release the stored energy thermally the longer the crystal is subjected to radiation. The change in the luminescent behavior is apparently due to the capture of an increasing proportion of available electrons by the traps of greatest thermal stability as gamma-irradiation continues.

## DISCUSSION

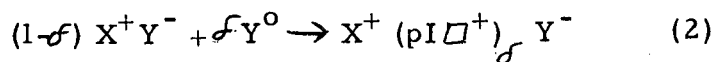
It is now generally accepted that in alkali halide crystals F-centers, ( $e \square^-$ ), are due to electrons bound to anion vacancies,  $\square^-$ , while V-centers, ( $p \square^+$ ), are positive holes (neutral halogen atoms) bound to cation vacancies,  $\square^+$ . By the addition of a stoichiometric excess of alkali metal or halogen it is possible to produce crystals in which one can study separately either F-centers or V-centers. These additively colored crystals have played an important role in the study of color centers.<sup>21</sup>

Additive coloration of an alkali halide by excess alkali metal can be formulated as follows:



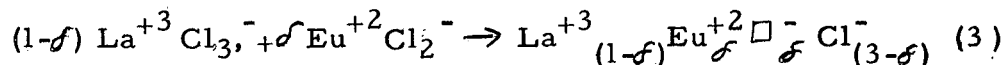
21. The symbolism used here is that suggested, for example, by A. L. G. Rees in Chemistry of the Defect Solid State, Methuen Co., Ltd., London (1954), p. 18.

Additive coloration by excess halogen is represented by the equation:

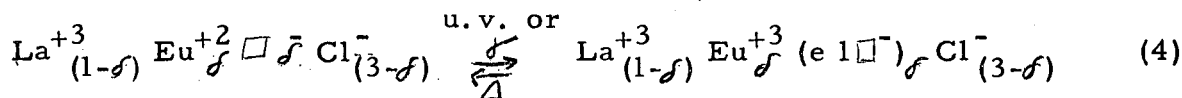


In the past, the process of additive coloration has been thought of primarily in the specific sense indicated above. Studies in recent years on crystals containing variable valency cation impurities make desirable a somewhat extended concept of additive coloration which can include these systems as well. The nature of this extended concept will be made clear by the following examples.

Incorporation of  $Eu^{+2}$  in  $LaCl_3$  with the creation of anion vacancies can be described by the equation:



The stable state of this crystal involves a large concentration of anion vacancies without associated electrons. We would like to propose that the blue color produced on exposure of the crystal to radiation (Section 4) is due to the formation of color centers in the reaction:

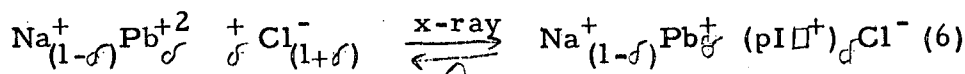
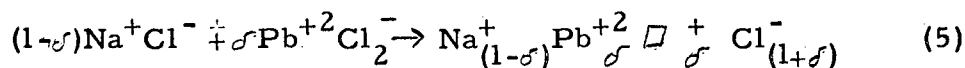


The reverse reaction occurs when the crystal is heated and results in the emission of visible radiation.

The analogy of additive coloration in the alkali halide-excess alkali metal system and the  $LaCl_3$ - $EuCl_2$  system should be clear from a comparison of equation (1) with equations (3) and (4).

In terms of an energy level scheme, the action of radiation may be thought of as resulting in the removal of electrons from the full valence band of the crystal to the conduction band with consequent trapping by anion vacancies. The positive holes left in the lattice migrate until they encounter  $Eu^{+2}$  ions from which they remove electrons to form  $Eu^{+3}$ . Trapped electrons may be thermally freed to re-enter the conduction band. They may either be recaptured by other vacancies or may return to the ground state by reaction with  $Eu^{+3}$  ions. The fluorescence levels of  $Eu^{+2}$  are presumably involved in the emission of visible radiation in the reaction  $Eu^{+3} + e \rightarrow Eu^{+2}$ .

Schulman, Ginther and Klick<sup>22</sup> in a study of NaCl crystals containing small amounts of Pb<sup>+2</sup>, concluded that darkening of these crystals on x-ray irradiation was due to reduction of the lead either to the monovalent or metallic state. They ascribe the bleaching of the discoloration by heating to 200° C and the reappearance of the characteristic Pb<sup>+2</sup> absorption band in the clear crystal to the re-oxidation of the lead by the positive holes (neutral halogen atoms) stored in the crystal. If one assumes that the reduction of Pb<sup>+2</sup> proceeds in the first instance to the monovalent state, then the reaction can be formulated as follows:



The reactions (5) and (6) are analogous to reaction (2) which describes the alkali halide-excess neutral halogen system.

The systems LaCl<sub>3</sub>-EuCl<sub>2</sub> and NaCl-PbCl<sub>2</sub> are examples of hetero-type solid solutions. Reactions of the type 3-6 make it clear that in heterotype solid solutions in which one of the cations has a variable valency (e. g. Eu<sup>+2</sup>, Eu<sup>+3</sup>, Pb<sup>+</sup>, Pb<sup>+2</sup>) while the other has a fixed valency (e. g. La<sup>+3</sup>, Na<sup>+</sup>) it may often be possible to produce larger and more stable concentrations of F and V centers than can be produced in the pure crystals themselves. Investigations of systems of this sort undoubtedly will bring to light other radiation-induced "solid state" oxidation-reduction reactions involving ions of the transition metals.

It is of interest to consider the ionic arrangement of LaCl<sub>3</sub> in detail in order to get a better understanding of the physical situation which underlies the ideas discussed above.

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22. J. H. Schulman, R. J. Ginther, C. C. Klick, J. Opt. Soc. Amer. 40, 854 (1950)

A diagram of two planes of the  $\text{LaCl}_3$  lattice perpendicular to the  $c$ -axis of the crystal is given in Fig. 9. In the diagram the anion and cation radii are in the correct ratio but the interionic distances are twice the actual distances. One need consider only two lattice planes since alternate planes are equivalent. Ions in one plane are denoted by full circles, ions in the other plane by dashed circles. The large circles around minus signs represent the chloride ions. The small circles around plus three and plus two signs represent lanthanum ions and dipositive europium ions respectively. The squares and rectangles stand for electron-anion vacancy complexes. The assumption implicit in this diagram is that the  $\text{Eu}^{+2}$  ions enter lattice positions normally occupied by  $\text{La}^{+3}$  ions. Indeed, our entire discussion presupposes that  $\text{EuCl}_2$  and  $\text{LaCl}_3$  can form heterotype solid solutions in the concentration range 0-10 percent  $\text{EuCl}_2$ . Although the upper limit of the concentration range has not been experimentally determined, the similarity in ionic radii<sup>23</sup> ( $\text{La}^{+3} = 1.04 \text{ \AA}$ ,  $\text{Eu}^{+2} = 1.09 \text{ \AA}$ ,  $\text{Eu}^{+3} = 0.96 \text{ \AA}$ ) is a factor in favor of a fairly extensive solid solution range.

A number of the more plausible models for color centers in these crystals are included in the diagram. They are meant to be analogous to various models of color centers which have been postulated for alkali halide crystals.<sup>1</sup> The analogy should not be carried too far, however, for several reasons. One is that convincing evidence exists especially for the models of F and F' centers in alkali halides. Such evidence is still completely lacking for the  $\text{LaCl}_3 - \text{EuCl}_2$  system. For another, in alkali halides there are no centers strictly analogous to the H and M centers given in Fig. 9 which involve anion vacancies associated with dipositive europium ions. Still a third reason is the difference in the crystal structures of the alkali halides and  $\text{LaCl}_3$ . A theoretical investigation, for example, of an F center in  $\text{LaCl}_3$  would have to take into account the cation distribution about an anion vacancy which is vastly

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23. G. T. Seaborg and J. J. Katz, The Actinide Elements, National Nuclear Energy Series IV - 14A, McGraw-Hill Book Company, Inc., New York (1954) Chapter 18, p. 769.



different both structurally and with respect to charge distribution compared with the situation found in the alkali halides. Undoubtedly future studies will eventually result in more explicit models for color centers which will be able to account for, among other things, the polarization properties of the absorption bands in the  $\text{LaCl}_3\text{-EuCl}_2$  system.

The primary purpose of Fig. 9 is to illustrate the large number of different centers which can be postulated in principle. Presumably electrons associated with different centers would have different energies of activation for thermal release. The color centers then can be thought of as representing electron traps having various trap energies. Electrons leaving these traps and combining with  $\text{Eu}^{+3}$  ions determine the luminescent properties of the crystal.

Randall and Wilkins,<sup>24</sup> by making specific assumptions about the trap energies, have derived a luminescence decay law which is similar to the one used in Section 7 to reproduce the decay curves obtained with  $\text{LaCl}_3\text{-EuCl}_2$  crystals. These workers came to the conclusion that the release of electrons from traps and not the probability of recombination with excited centers is the factor governing the rate of luminescence decay of all crystal phosphors in which the luminescence processes last longer than a small fraction of a second.

One of the main experimental methods for investigating trap depths in the past has been a study of glow curves of phosphors. The method has several limitations, two of which will be mentioned here. First, it has been generally recognized that the resolving power of the method is quite poor. At a very low rate of heating, even deep traps will be depopulated at relatively low temperatures so that the low temperature branch of the curve is blurred; whereas, at a very high rate of heating, many of the shallow traps will retain their electrons up to relatively high temperatures.

Second, while a glow curve may represent, with a certain approximation, the distribution of trap energies in a phosphor, the relative numbers of traps of various depths can be derived from the areas under the corresponding peaks only if it can be assumed that the luminescence yield is

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24. J. T. Randall, H. H. Wilkins, Proc. Roy. Soc. A 184, 365, 390 (1945).

independent of temperature. However, in many instances the yield decreases very strongly with increasing temperature, and since this is probably due to internal conversion occurring while the electrons are in the conduction band, the numbers of deep traps which would be indicated by the height of the high-temperature peaks would be relatively too low.

Clearly, any attempt at understanding the luminescence decay process presupposes a knowledge both of the energy distribution of the traps and of the relative numbers of electrons in different traps.

The absorption spectra of color centers in luminescent materials afford the means to observe trapped electrons directly and their investigation may add importantly in the future to our understanding of luminescence phenomena.

In principle, trapped electrons possess unique absorption spectra characteristic of particular color centers. Studies of the thermal decay of the color center bands could give detailed information on the distribution of trap energies irrespective of the actual form of the distribution. This is due to the fact that there is no simple correlation between the energy required to remove an electron from a trap thermally and the energy of the optical transition of the electron in the trap. The limitation in the resolving power of this method then is in the number of different traps (color centers) that can be observed. Under the most favorable circumstances, every color center present gives rise to a completely resolved band.

The relative numbers of traps of various depths can be calculated directly from the areas under each absorption band if one makes an assumption concerning the oscillator strengths of the various optical transitions. Such assumptions are certainly less drastic than the assumption of a temperature independent luminescence yield which must be made in order to get similar information from glow curve data.

In the  $\text{LaCl}_3\text{-EuCl}_2$  system three color centers were found which decay thermally with different rates. The glow curve shows only two peaks, however. This demonstrates the increased resolving power of the spectral method. In the present study we have gone so far as to show qualitatively the intimate connection between the thermal decay of the color center bands and the thermoluminescent properties of the crystal.

No attempt has been made as yet to obtain in detail trap energies or numbers of traps of various depths from absorption spectra. We have indicated above how this may be done, and hope to study this aspect in the future.

#### ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the continuing interest and friendly cooperation of Dr. B. B. Cunningham in all phases of this problem.

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One of us (D. M. G.) wishes to express his personal appreciation to Dr. G. T. Seaborg of the University of California Radiation Laboratory and to Dr. W. M. Manning of the Argonne National Laboratory for their thoughtfulness in making possible for him a year's stay at the Radiation Laboratory.

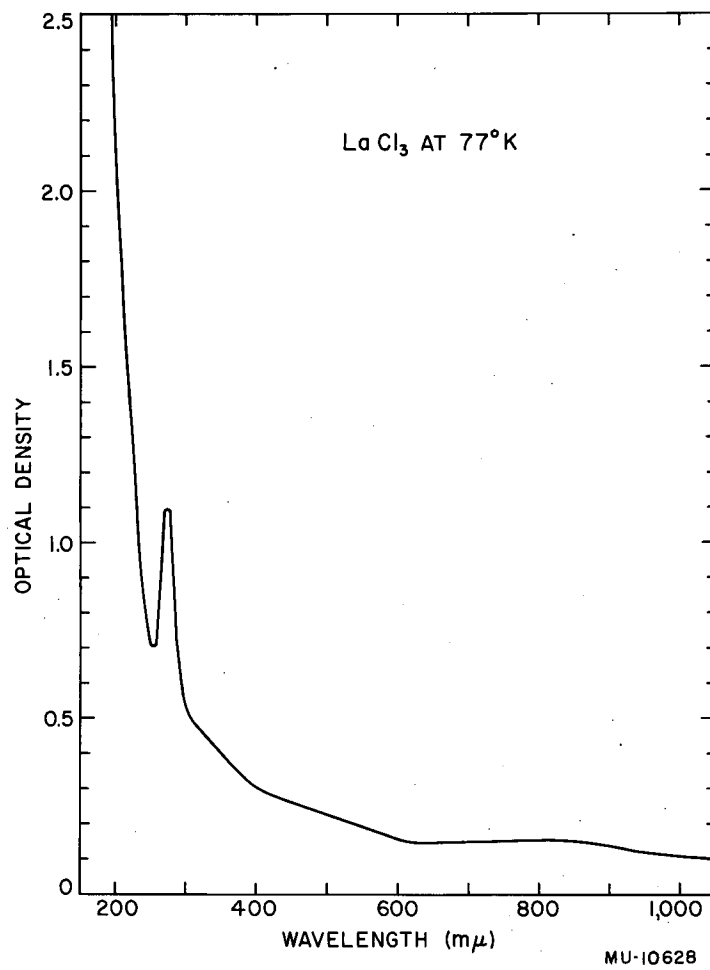


Fig. 1. The absorption spectrum of LaCl<sub>3</sub> at liquid nitrogen temperatur

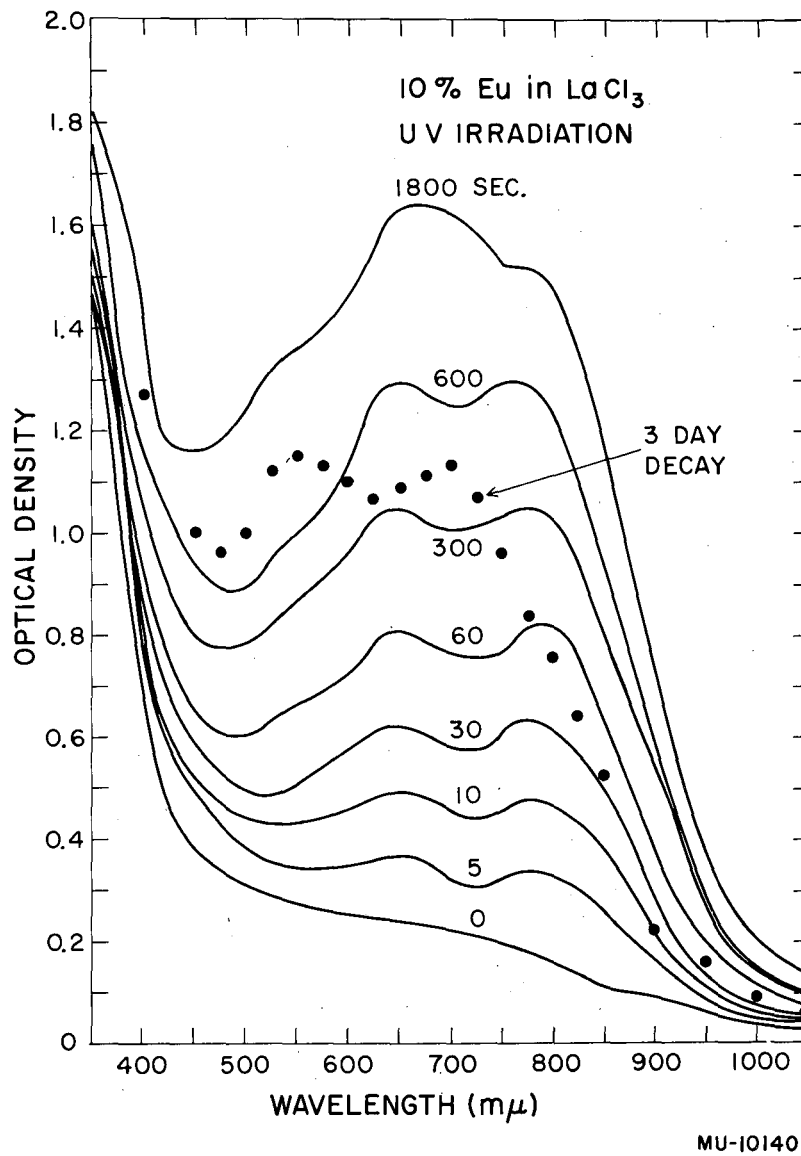


Fig. 2. The growth of color center bands as a function of the time of exposure to ultraviolet light.

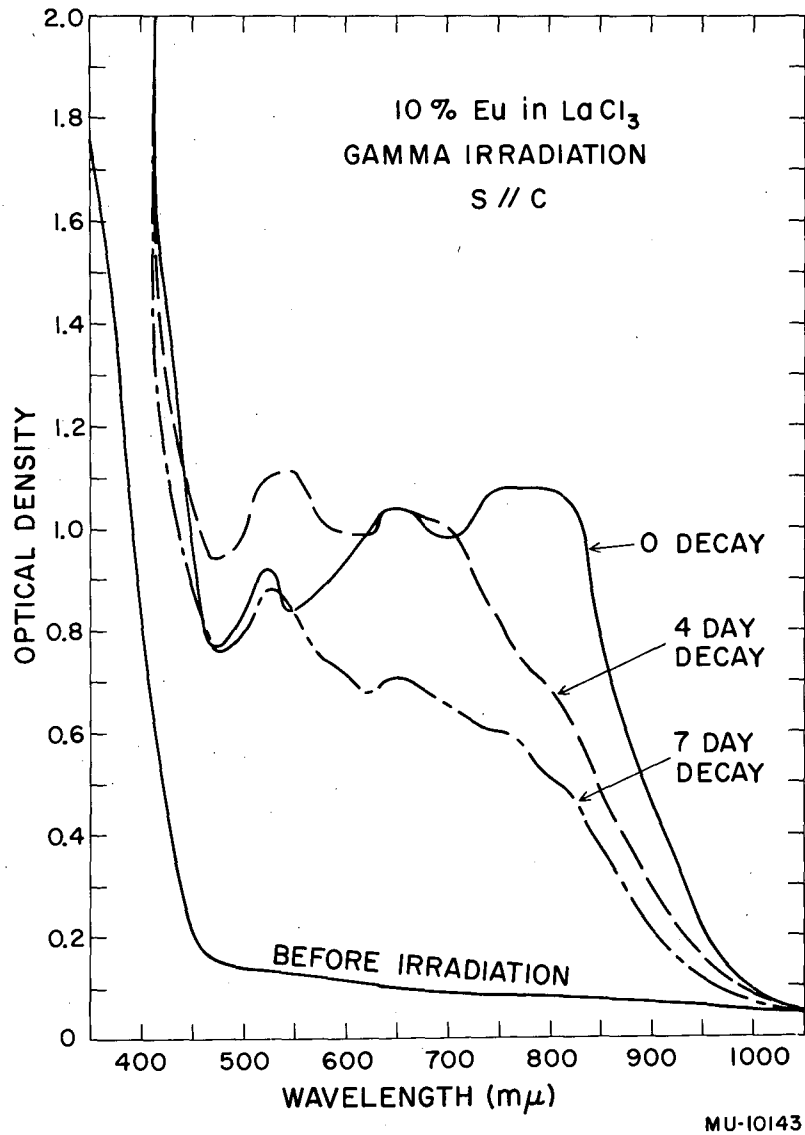


Fig. 3. Thermal decay of color centers at room temperature.

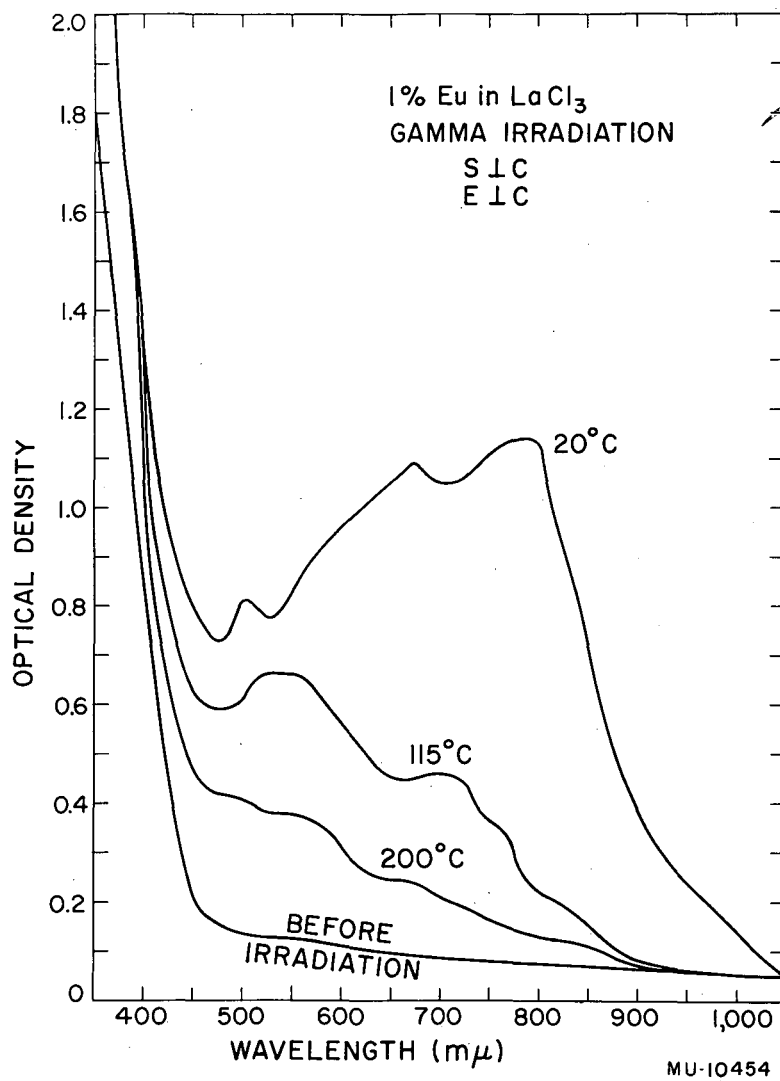


Fig. 4. The effect of thermal bleaching on color center bands.

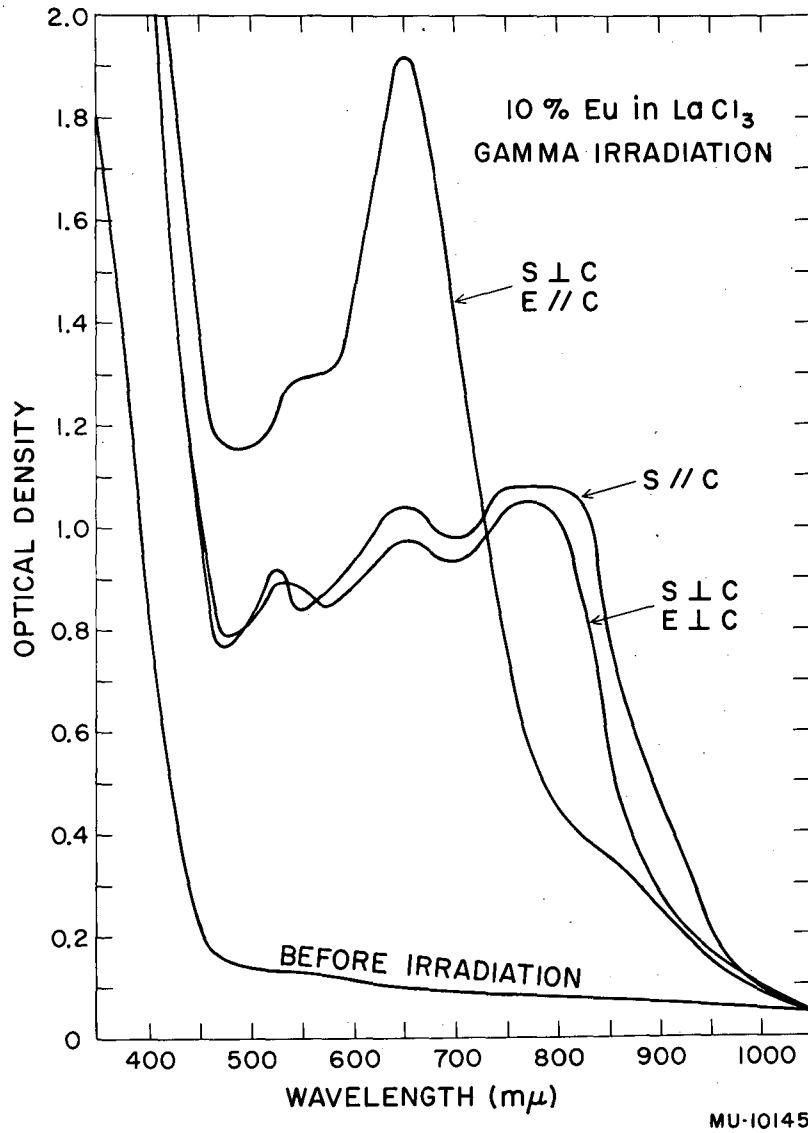


Fig. 5. Anisotropy of the color center of europium in  $\text{LaCl}_3$ . The  $S \perp C$  curves have been adjusted to 1 cm thickness.

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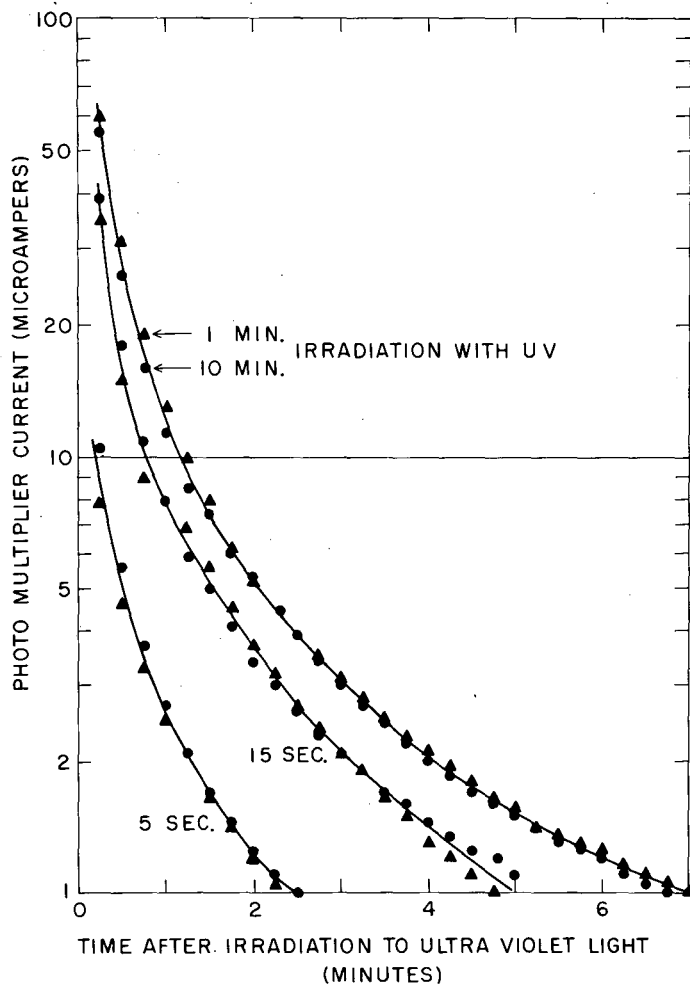


Fig. 6. Phosphorescence decay curve of a one percent europium crystal.

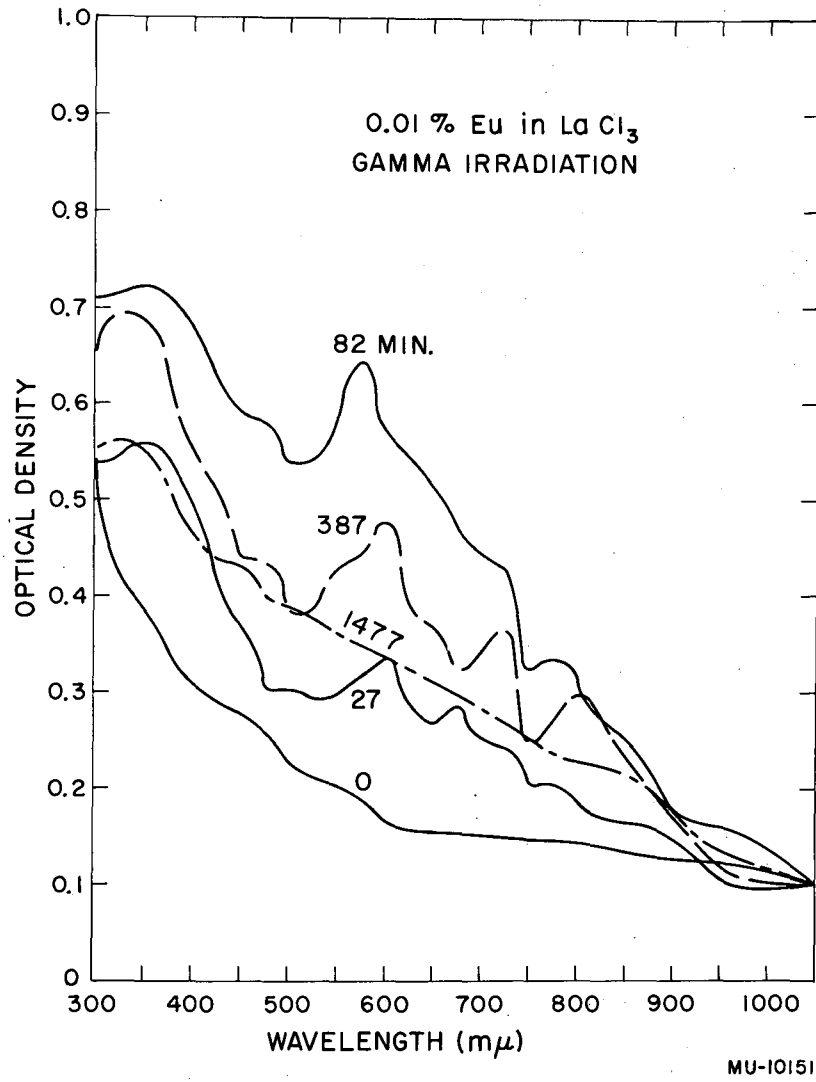
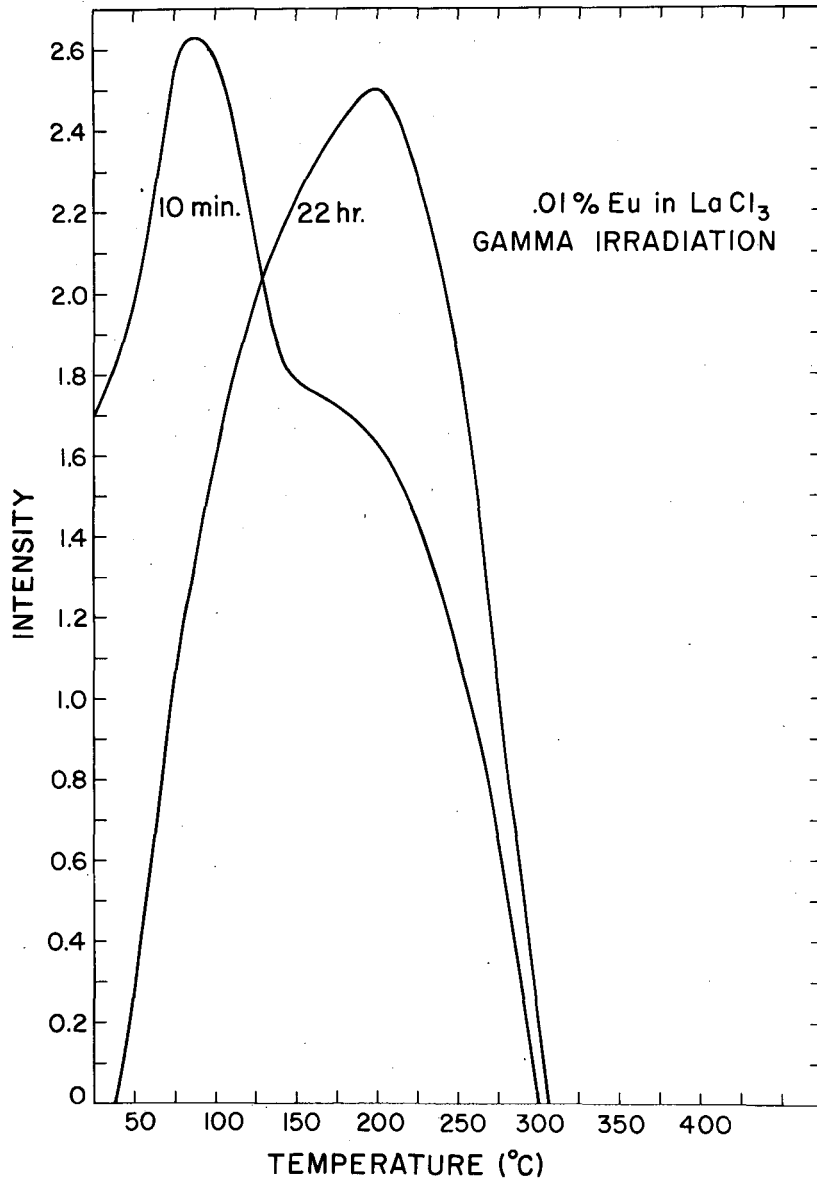
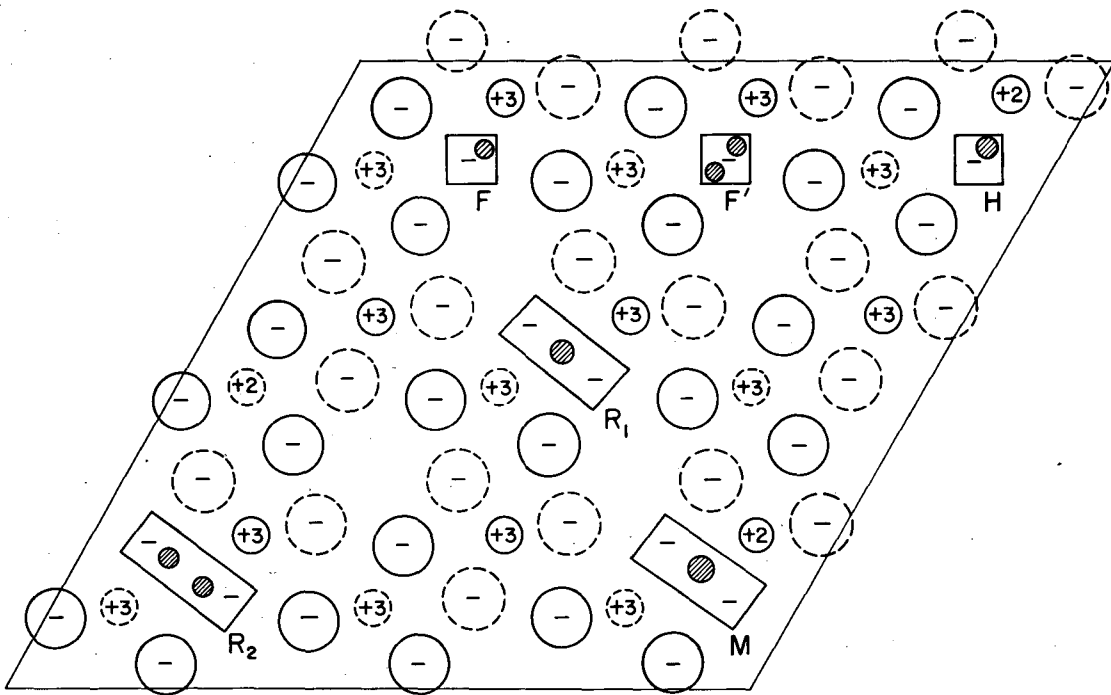


Fig. 7. The effect of gamma irradiation on the formation and bleaching of color centers in the 0.01 percent europium crystal.



MU-10457

Fig. 8. Glow curves for the 0.01 percent  $\text{Eu}^{+2}$  crystal after 10 min and 22 hr of gamma irradiation.



MU-10458

Fig. 9. Diagram of two planes of the  $\text{LaCl}_3$  crystal showing various possible vacancies. The atomic diameters are to scale, but the inter-atomic distances are expanded to twice their relative value.