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Charge Conversion of Irradiated Rare-Earth Ions in Calcium Fluoride. I*

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The mechanism by which the rare-earth ions in CaF_2 can be reduced from the trivalent to the divalent state by exposure to x rays or γ rays has been systematically studied for all the thirteen available ions in the lanthanide series. Each of the ions was irradiated at 77°K and its temperature subsequently raised above room temperature. During the heating process the intensity of the thermoluminescence and the changes in the optical absorption spectrum were measured as a function of temperature. An accompanying paper describes the changes in the emission spectrum with temperature. In general, the temperatures at which significant changes in absorption occur, and for which there is simultaneous thermoluminescent emission, are independent of the particular rare-earth ion, while the emission spectra is characteristic of the rare earth. The absorption spectra have parts characteristic of the individual ions and parts independent of the ion. On the basis of these observations, it is possible to formulate a consistent model of the irradiation-induced charge-reduction process and the subsequent thermal reoxidation process. From 77 to about 330°K the oxidation process is attributed to thermal activation of a variety of hole traps.

I. INTRODUCTION

THE development of the solid-state laser has generated widespread interest in the spectroscopy of ions in crystals. Among the candidates for laser materials, the lanthanide series of rare-earth ions were particularly promising because of the multitude of sharp energy levels lying in the visible and infrared. These ions are easily incorporated into cubic hosts of optical quality such as CaF_2, and laser oscillation has been attained for many of these systems. The spectroscopy of the rare earths has been treated by El'yashevich,[1] Dieke,[2,3] and Wybourne,[4] while Garrett[5] and Sorokin[6] have reviewed some of the laser applications. Although rare earths are most easily stabilized as trivalent ions in these crystals, the divalent state has certain distinct advantages for laser applications. The change of valence, i.e., reduction, has been attained by either exposing the crystals to ionizing radiation,[7–9] baking them in a suitable atmosphere,[10] or electrolytic annealing.[11,12]

This work is concerned with the reduction of rare-earth ions in CaF_2 by exposure to γ or x rays. Thermoluminescence and optical absorption are studied after irradiation at 77°K in order to identify the nature of the holes formed during the irradiation, and the mechanism by which these holes are thermally activated in order to recombine with the electrons trapped at the rare earths. Thermoluminescence has previously been reported in some undoped and rare-earth–doped CaF_2,[13–16] but this work represents the first systematic study of the optical effects resulting from irradiation of all of the thirteen available lanthanide ions. In addition to the glow curves and optical absorption data reported in this paper, high-resolution spectra of the thermoluminescence (described in the following paper,[17] which will henceforth be denoted as II) are used to develop a consistent model for the phenomena observed. Meaningful measurements were made possible by the choice of a slow, linear heating rate with careful tem-

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perature control. In most cases the samples were exposed to 50-kV x-rays in a liquid-nitrogen cold-finger Dewar. After irradiation the sample was maintained at liquid-nitrogen temperature until all transient emission decayed. These effects are associated with unstable trapping levels[18] and were not studied. The sample was then heated at the rate of 2°/min while thermoluminescent glow curves were recorded. This rate was chosen so that peak temperatures could be measured accurately and nearby peaks could be resolved. Furthermore, spectral measurements of the emission, to be described in II, could be made electronically with a scanning monochromator at far greater resolution than if the glow curve was taken at a faster heating rate, and the spectral measurements done photographically. All of the samples used for these experiments were grown by one of the authors (JLM) using the Bridgman-Stockbarger technique.[19] These experimental procedures are reported in detail elsewhere.[20]

In Sec. II of this paper the available data on rare-earth ions in CaF_2 are summarized. It will be argued that since the divalent ions are always found in cubic sites, one can accept the generally held belief that only those ions initially in cubic sites can be reduced by irradiation. The experimental results are presented in Secs. III, IV, and V. The following important points become apparent. The temperatures at which the thermoluminescent glow peaks occur are found to be independent of the rare earth, suggesting that these glow peaks are associated with the activation of hole centers in common with all of the rare earths. On the other hand, the spectral composition of this emission is characteristic of the particular rare earth, and is found to correspond to the fluorescence of trivalent rare-earth ions in cubic sites (for the thermoluminescence below room temperature) and tetragonal sites (above room temperature). Absorption data reveal the presence of a hole center which bleaches along with the divalent ion absorption as the sample is heated. A model is then proposed in Sec. VI to explain this data in terms of the electron-hole pairs which are formed during the irradiation. Recombination occurs after the thermal release of the hole, and the resulting trivalent rare-earth ion is left in an excited state. The decay of this ion to the ground-state results in the observed thermoluminescence.

II. RARE-EARTH IONS IN CaF_2

The CaF_2 lattice can be visualized as a cubic array of F^- ions with a Ca^{2+} at every other body-center position. When rare-earth ions are added, they enter the lattice substitutionally for Ca^{2+} ions, but they are more stable in the trivalent state. This additional positive charge requires some form of charge compensation, and several different kinds of compensators have been identified by optical and magnetic resonance experiments. The type and symmetry of compensation is strongly dependent on the starting materials used to grow the crystals, the method of growing, and thermal treatments given the crystals. A survey of the extensive magnetic resonance and optical data on the various compensators has been given by Weber and Bierig.[21] The two most common types of charge compensators are interstitial fluoride ions in the adjacent body-center position leading to tetragonal (C_{4v}) symmetry at the rare-earth site, and substitutional O^{2-} ions at one of the eight surrounding octohedral F^- ions producing trigonal (C_{3v}) symmetry. In oxygen-free crystals, cubic symmetry can also be found, resulting from nonlocalized compensation by interstitial F^- ions. Thermal treatment of the crystals can cause diffusion of these compensators and a corresponding change in the symmetry at the impurity has been observed.[22–24] Quantitative calculations of the thermodynamic equilibrium of optical centers predict the thermal effects observed.[25] Although the cases mentioned above are the dominant ones, many other sites are seen in rare-earth–doped CaF_2; for example, ten different sites have been observed in $CaF_2:Yb^{3+}$.[26] A summary of the large amount of work done on this subject has also been given by one of the authors.[20]

In the case of the divalent rare earths, cubic symmetry is observed at the site of the divalent ion with only a few exceptions. McClure and Kiss[7] have produced all of the divalent rare-earth ions in CaF_2 by γ-irradiation and measured their optical-absorption spectra. However, these are measurements of broad absorption bands, and therefore give little information about the symmetry site of the rare earth. The paramagnetic resonance studies of Hayes and Twidell[8] do yield this information. After x-raying samples containing Tm^{3+} or Ho^{3+} at 77°K, they found divalent thulium or holmium only at cubic sites. Evidence is also observed of the hole center produced at the same time. They suggest that only those Tm^{3+} ions initially at cubic sites were reduced, since it is unlikely that charge-compensating ions would be mobile at 77°K. Sabisky[27] has studied the effect of γ rays on the concentration of Ho^{2+} in CaF_2. For trivalent ion concentrations of about 0.1%, he has achieved reduction of almost 20% of the ions, but found that this reduction process saturates; very little additional reduction takes place for γ-ray

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doses greater than 10 Mrad. The conversion efficiency was much lower for relatively large or small total trivalent ion concentrations. For low concentrations (e.g., 0.002%), divalent holmium was not observed. This is attributed to minute quantities of impurities present.[16] For high concentrations (0.4%) only 3% of the ions can be converted to the divalent state. This also strengthens the model that only those ions in cubic sites can be reduced, since large concentrations decrease the fraction of rare-earth ions in cubic sites.

The reduction of several other rare-earth ions in cubic sites to the divalent state has been reported, including lanthanum and erbium,[28] dysprosium,[16,29,30] and gadolinium.[24] The symmetry of the stable Eu^{2+} ion has been confirmed by EPR measurements to be cubic.[31,32] O'Connor and Bostick[9] have used 2.5-MeV electrons to reduce samarium. They were able to reduce up to 50% of the ions, and suggest that the high-energy electrons displace interstitial fluorine compensators to create additional cubic rare-earth sites capable of electron capture. Merritt and co-workers[33] found Pr^{2+} in cubic sites after electrolysis, and believe that their work confirms the suggestion that the electrolytic technique involves the diffusion of interstitial fluoride compensators away from the rare earths.

The only exceptional cases of divalent ions in noncubic sites which have been reported involve ions already stable in the divalent state, such as ytterbium,[34] or crystals doped with the rare-earth oxide instead of fluoride,[35] introducing trigonal oxygen compensators into the crystal. In crystals reduced chemically, with near 100% reduction efficiency, a small fraction (approximately 1%) of the divalent ions has been observed in sites having departures from cubic symmetry[36]; however, this has not been observed in irradiated crystals where the efficiency of conversion is low. The extensive literature cited above therefore offers convincing evidence that in the case of interest in this work (irradiation of oxygen-free crystals) only those rare-earth ions in cubic sites are reduced to the divalent state. In the cases of electrolytic and chemical reduction, the causes of the departure from cubic symmetry are probably removed by diffusion of charge compensators, and these techniques are therefore more efficient and stable means of producing divalent rare earths.

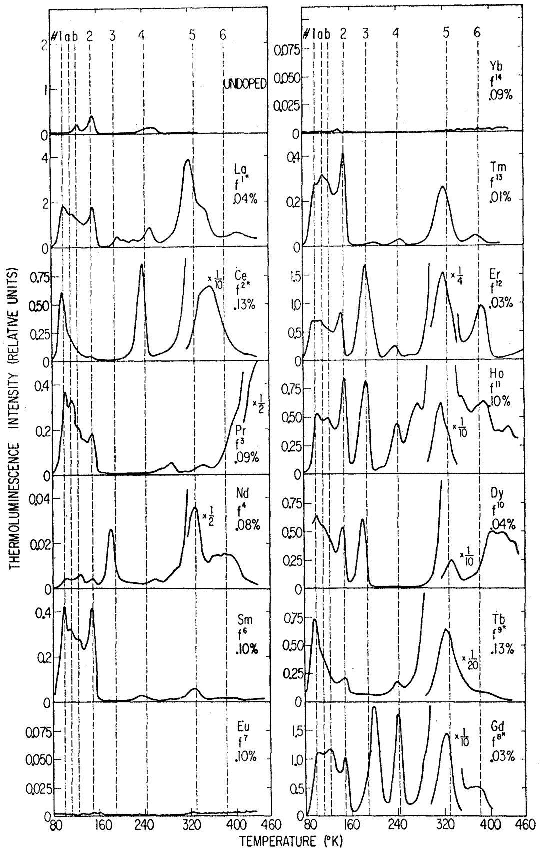

FIG. 1. Thermoluminescence of rare-earth-doped CaF_2. All crystals grown from G&S CaF_2 except Ho and Tm. Dotted lines indicate average glow peak temperatures (listed in Table I). An additional weak peak is seen at 285°K for some ions. For Eu and Yb, cf. text and Fig. 2. *These ions are believed to have $4f^{n-1}5d$ configuration in their ground state. (Ref. 7).

III. THERMOLUMINESCENCE

A. Glow Curves for Rare-Earth Ions in CaF_2

The glow curves for dilute concentrations of the thirteen rare-earth ions in CaF_2 are shown in Fig. 1; an undoped sample is also included. The glow intensity integrated over wavelength according to the S-5 spectral response of the photomultiplier used (RCA 1P28), is plotted in microamps of anode current.[37] The sample temperature, plotted along the abscissa, is measured with a copper-Constantan thermocouple cemented directly to the crystal. The left column of Fig. 1 shows the first half of the lanthanide series, with the number of $4f$ electrons for the divalent state of the ion indicated. Some of the ions, denoted by asterisks, are believed to have the $4f^{n-1}5d$ configuration mixed into their ground state,[3,7] and this notation is simply intended to describe the number of excess electrons outside the La^{3+} core. Opposite each of these ions is the corresponding ion in the second half of the series; that is, the ion with an equal number of holes (where possible).

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TABLE I. Peak temperatures of glow curves.

Rare Earth	No. 1 (°K)	1a (°K)	1b (°K)	2 (°K)	3 (°K)	4 (°K)	5 (°K)	6 (°K)
La	102	116		152	196	252	322	∼350
Ce	99	113		150		239	356	
Pr	103	113	125	149			345	
Nd	106		128	150	182	260	330	370
Sm	100	110	125	148		235	326	400
Eu								
Gd	103		122	149	200	241	325	376
Tb	98	115		150		241	325	391
Dy	102	114		148	183	244	335	406
Ho	104		122	152	190	242	318	391
Er	96, 102	110		146	188	240	323	387
Tm	102	114		151	192	246	322	378
Yb								
Av	101	113	125	150	190	244	330	383
Mean dev.	±2	±2	±2	±1	±5	±5	±9	±13

The most important fact about the thermoluminescent emission of the rare earths in CaF_2 is evident from this figure: The temperatures at which the thermoluminenscence reaches a peak are essentially independent of the rare-earth ion studied. Most of the glow curves have the same form: a series of low-intensity glow peaks below room temperature, and a large peak at approximately 330°K. This similarity is especially evident in the second half of the series, where the ionic radii of the trivalent rare earths are closer to that of Ca^{2+}. It has been suggested that these ions are consequently somewhat easier to reduce.[21] The relative intensities differ from one rare earth to another, and in some cases peaks are weak or missing, but whenever there is emission, the peaks occur at nearly the same temperatures and the glow curves are very similar. Vertical lines have been drawn in the figure to indicate the average temperature for each of the glow peaks, labeled No. 1 through No. 6. All of the peak temperatures for these glow curves are recorded in Table I. The mean deviations from the average varies from ±1° and ±2° for the low-temperature peaks, to ±9° for peak No. 5.

The near coincidence of the glow peaks for all of the rare earths indicates that the emission cannot be associated with direct thermal ionization of the divalent rare-earth ion. Otherwise, the thermal activation would be a function of the ionization potential of each rare earth, modified by the lattice environment, and the glow peaks would differ considerably. Results similar to this have been obtained by Arkhangelskaya[15] for Er, Ho, Tm, and Dy. However, because of a faster heating rate, he was unable to resolve the peaks labeled Nos. 1, 1a, and 1b. Note that even in the case of the undoped CaF_2 a few weak peaks are seen. This emission may come from residual impurities in the crystal or from recombination of the holes formed in the pure materials by irradiation. However, the fact that the glow peaks resemble those for the rare earths further supports the above arguments.

The case is not so clear for the high-temperature glow peaks (those occurring above 360°K) where the coincidence of peak temperatures is no longer apparent, and direct thermal ionization of the rare earths may occur. Fong[16] has studied the high-temperature glow curves of dysprosium and thulium exposed to γ rays at room temperature. He concluded that the thermally activated emission process above room temperature involved the transfer of electrons rather than the excitation of holes into the valence band.

Although the thermoluminescent glow curves do not depend strongly on the rare-earth ion considered, the spectra of this emission is a property of the particular ion, corresponding to the fluorescence of the trivalent rare earth. (This will be shown in II.) This explains the lack of any glow peaks for ytterbium in Fig. 1, since the only fluorescent levels for Yb lie in the infrared. The infrared glow curve for Yb was measured with an RCA7102 photomultiplier, and is shown in Fig. 2. A fast, nonlinear heating rate was used in this case (cf. inset), so direct comparison cannot be made with the curves in Fig. 1. However, the result for Yb is compared with the glow curve for Ho measured under the same conditions. Again the curves are seen to be very similar. The glow emission for Eu was very weak and could only be observed by using the fast heating rate; this is also shown in Fig. 2. In fact, the presence of Eu in CaF_2 reduces the thermoluminescent intensity from that of the undoped crystal. The reason for this is believed to be the relative ease in reducing Eu to the divalent state. Most of the reducible europium is already in the divalent state, so that irradiation and subsequent heating produce little change.

The reproducibility of the curves in Fig. 1 has been tested by comparing the glow curves for five different runs on the same sample under identical conditions. The results showed that the intensity of the observed emission was reproducible to within 10%. The temperatures corresponding to maxima and minima were also reproducible; for peaks Nos. 2, 3, 4, and 5 the

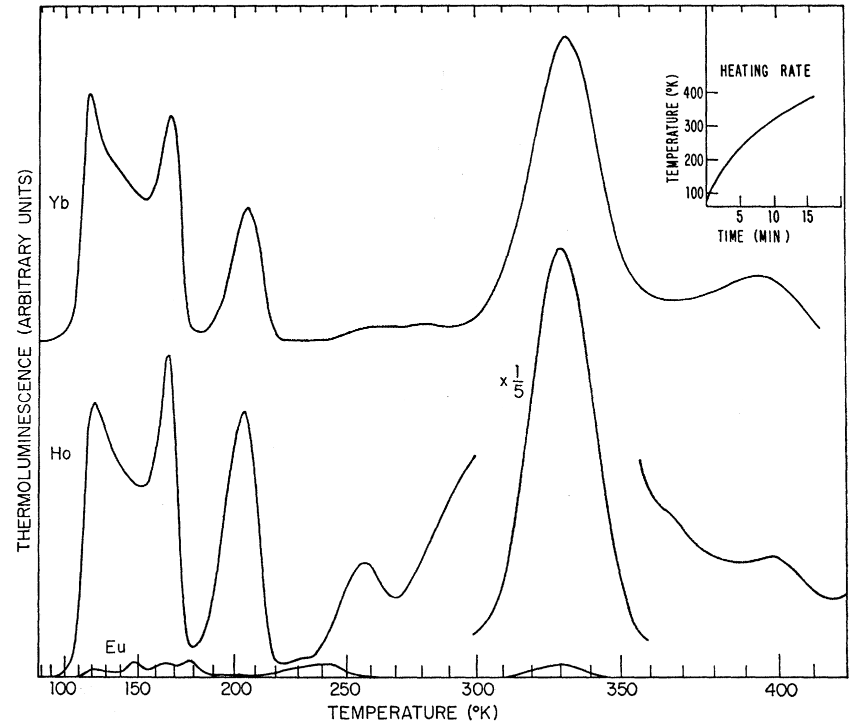

FIG. 2. Thermoluminescence of Yb, Ho, and Eu, using the fast, nonlinear heating rate shown in inset. Ho and Eu are measured with S-5 photomultiplier; Yb measured with S-1.

mean deviations of these extrema from the average values was ±1°K, which corresponds to the error associated with the temperature measurements. Peaks Nos. 1, 1a, and 1b seem to be more sensitive to heating rate, impurities, crystal growth, and other factors, since the deviations observed for these peaks are generally ±2°K. With regard to reproducibility, it is also important to consider the effect of the past history of the sample on the glow curve. One glow curve measurement may affect the succeeding curve on the same sample, if the traps were not completely emptied or their distribution was changed by the first run. These effects were not found at the low dosages and slow heating rates used for these studies.

To aid in choosing the best source material for the CaF_2 samples, glow curves were measured on undoped crystals grown from CaF_2 powder obtained from Fisher Scientific, A.D. Mackay (optical grade), Gallard and Schlesinger (referred to as G & S), and Optovac. The results are compared in Fig. 3. Except for peak No. 2 at 135°K, very little thermoluminescence was seen from the G & S sample. Analysis of this powder also indicated a high degree of purity, so this was used as a source powder for most of the experiments discussed in this work. The effect of the source of CaF_2 on a rare-earth–doped sample is shown in Fig. 4 which gives glow curves for 0.03% Er in CaF_2 grown from G & S, Fisher, and Optovac powder. When the rare-earth ion is present, the source of CaF_2 is no longer as important in determining the shape of the glow curve. Glow peak No. 3, at approximately 188°K, is obviously most sensitive to the choice of calcium fluoride powder used. A strong concentration dependence for this glow peak was also found.

An important difference between the doped and undoped cases concerns glow peak No. 5 at approximately 330°K. In the erbium-doped case, as indeed happens for most of the rare earths, this peak is much larger than the glow peaks occurring below room temperature. However, for the undoped crystals, little evidence is seen of this peak.

To find the optimum conditions for irradiation, the effect of the x-ray dosage on the glow curves was considered. All irradiations were made at full power (50 kV and 20 mA), but the irradiation time was varied from 1 sec to 50 h. The peak intensities of the five major thermoluminescent glow peaks are plotted in Fig. 5 as a function of the irradiation time. For some points, two or three runs have been made at the same dosage to compare results. The initial growth of the glow peaks is linear for the first 2 or 3 h; after 20 to 30 h the curves begin to saturate in a manner similar to the saturation of the production of divalent rare earths by irradiation.[20,27] Although each of the glow peaks saturates at roughly the same total dosage, the five curves shown in Fig. 5 are not all of the same form and normalization would not result in one "universal curve." This is further evidence that the different glow peaks result from different types of "hole traps."

The glow curves presented here were obtained with

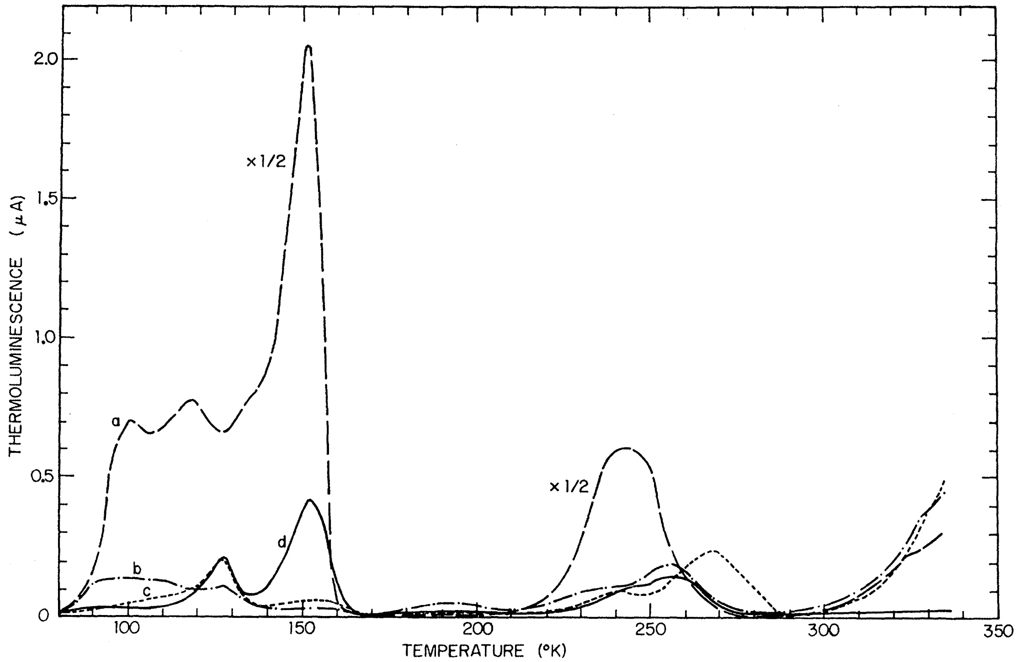

FIG. 3 Glow curves of undoped CaF_2 grown from different sources. (a) Optovac crystal (scale reduced by $\frac{1}{2}$), (b) Mackay (Optical Grade) powder, (c) Fisher powder, and (d) G&S powder.

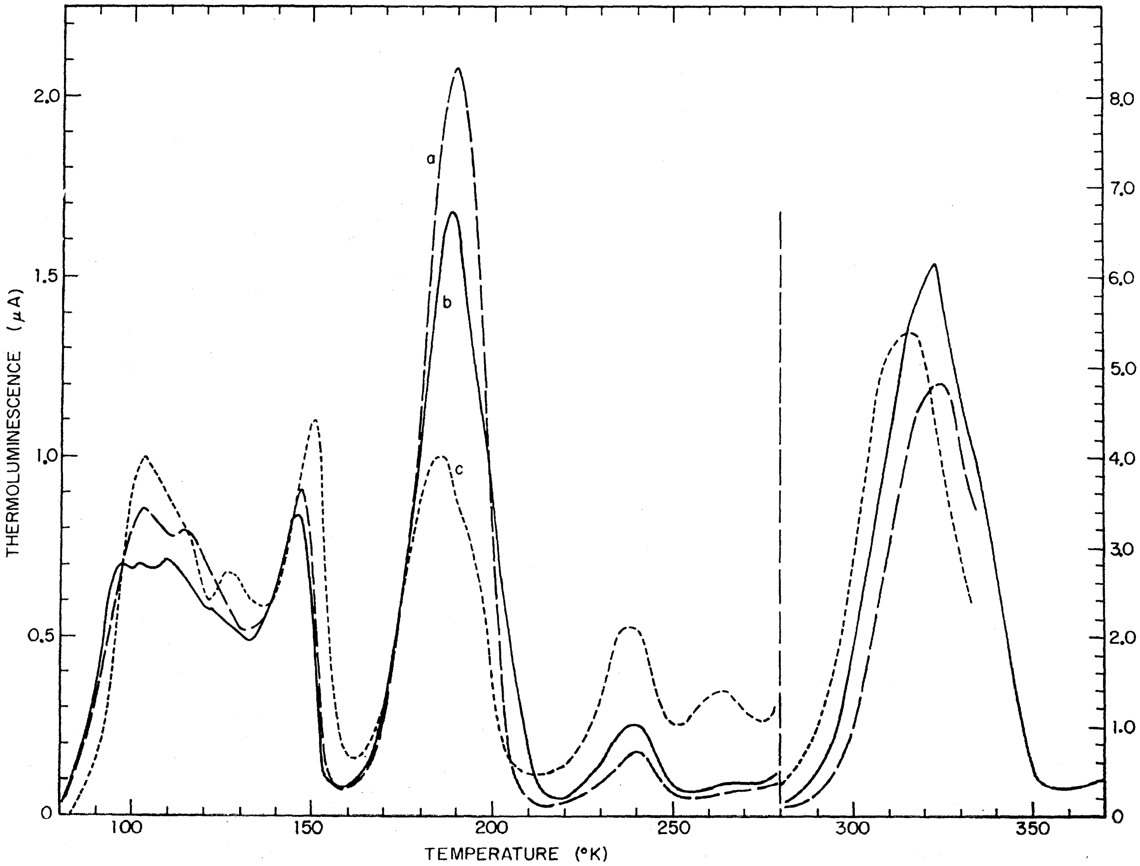

FIG. 4. Glow curves of erbium-doped CaF_2 grown from different sources. (a) Optovac, (b) G&S, (c) Fisher.

irradiation times within the linear range of Fig. 5. These dosages were chosen to produce the minimum amount of damage to the crystal, thereby keeping the problem of rare-earth charge conversion as simple as possible.

The effect of oxygen on the thermoluminescence was investigated to determine whether or not oxygen was present in appreciable quantities in the crystals studied.[20] For a crystal doped with Er_2O_3 instead of ErF_3, glow peak No. 1 was reduced by a factor of 70/3, and the rest of the glow curve was even more strongly quenched. Similar results were obtained for a crystal doped with ErF_3 and annealed at 1000°C for 14 h in 10 μ pressure of air. The presence of oxygen therefore quenches the luminescence, presumably because the trigonal O^{2-} compensation of the rare earths inhibits their reduction to the divalent state. Spectral measurements of the emission from these samples, to be reported in II, substantiate the fact that very little oxygen is present in the samples doped with rare-earth trifluorides.

B. Concentration Dependence

The rare-earth concentration dependence of the glow curves was studied for several different ions. Figure 6 shows the glow curves obtained for crystals grown from G & S CaF_2 and doped with erbium in concentrations ranging from 0.03% to zero. There seem to be three distinct behaviors exhibited by these peaks. The low-perature glow peaks Nos. 1, 1a, 2, and 4 are not strongly concentration-dependent and show up even in the "undoped" crystal, which probably contains a small amount of erbium or other rare earths. The glow peaks above room temperature are more strongly concentration-dependent. Glow peak No. 3 is quite unusual; not only the intensity but also the temperature and shape of this glow peak are functions of the concentration. If this experiment is repeated on a set of crystals grown from CaF_2 believed to be less pure, all three effects described above are enhanced. It should be pointed out that the "undoped" crystal in Fig. 6 probably contains more erbium than those in Fig. 3 since the former was grown in the furnace simultaneously with doped crystals.

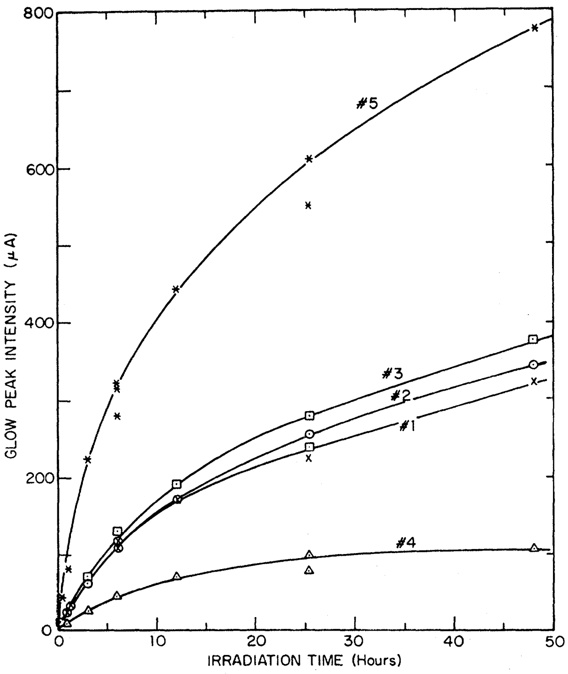

FIG. 5. Dosage dependence of the glow peaks. Sample doped with 0.1% erbium. Curves are identified by glow peak numbers given in Fig. 1.

Concentration studies of Dy and Gd display additional interesting features. For a concentration of 0.3% or higher, the glow curve is quenched. In the case of Dy, increasing the concentration produces additional glow peaks in the high-temperature range, above 350°K: The 0.01% sample has only a single peak at 409°K, at 0.04% an additional peak appears at 425°K, and 0.1 and 0.3% samples show multiple peaks in this region. In all cases examined, glow peak No. 3 shows a decrease in peak temperature with increasing concentration. This effect is partially responsible for the average deviation of ±5°K listed for this peak in Table I.

C. Activation Energies

Theoretical treatments of thermoluminescence have been given by several authors,[38–42] enabling the determination of activation energies E_g associated with individual glow peaks. These energies have been estimated from the data in Fig. 1 using two different methods. First, the activation energies are measured from Arrhenius diagrams, where the logarithm of the emission intensity is plotted as a function of $1/T$. Taking any reasonable model for the type of kinetics involved in the recombination luminescence, the initial rise of the glow intensity can be shown to grow exponentially with time. Hence an Arrhenius plot is linear in this initial portion of the curve, and the slope is a measure of E_g. Values of E_g measured in this way are listed in Table II for glow peaks for which the leading edge was measurable.

Activation energies have also been estimated using the equations of Halperin and co-workers.[41,42] For the case of interest in this work they obtained the working equations:

$$(E_g)_1=(1.72/\tau)kT_g^2(1-2.58\Delta)$$

for first-order processes, and

$$(E_g)_2=(2/\tau)kT_g^2(1-3\Delta)$$

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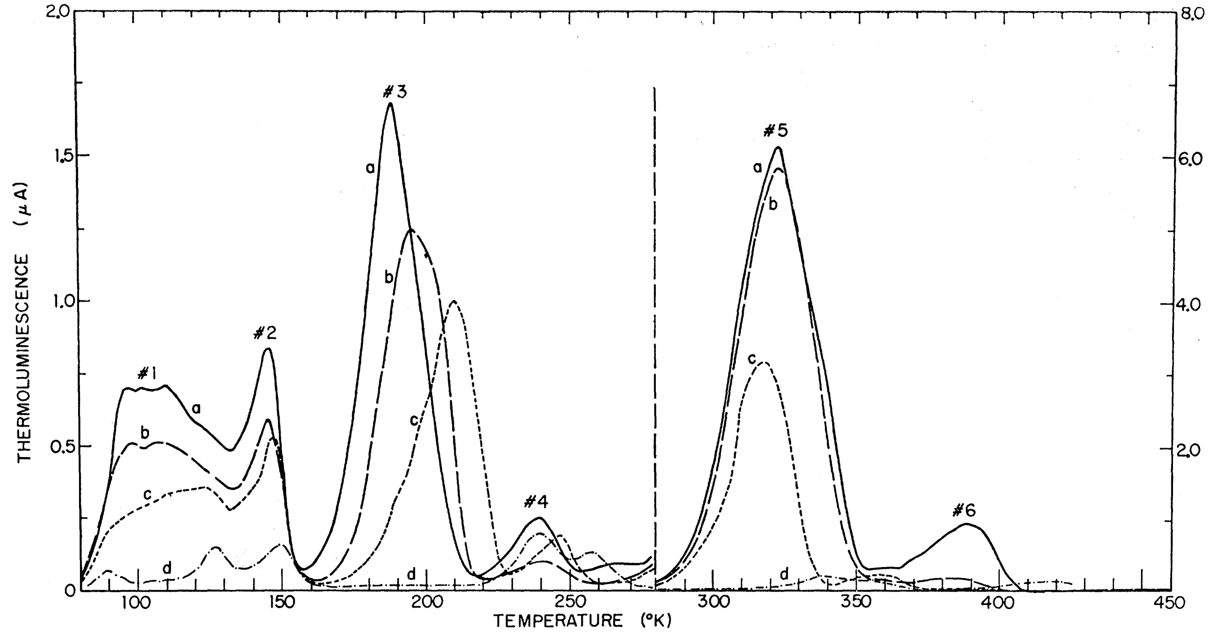

FIG. 6. Concentration dependence of CaF_2:Er glow curves. (a) 0.03%, (b) 0.01%, (c) 0.004%, (d) undoped. All crystals grown from G&S CaF_2. Concentrations are atomic percent added to the melt.

TABLE II. Activation energies of rare-earth glow peaks. Values using Arrhenius diagrams are without parentheses; values using method of Halperin and Braner are in parentheses. The order of the kinetics is given to the right of the energy value; assignments in square brackets are very uncertain.

	Glow Peaks					
Rare Earth	No. 1 E_g (eV)	No. 2 E_g (eV)	No. 3 E_g (eV)	No. 4 E_g (eV)	No. 5 E_g (eV)	No. 6 E_g (eV)
La	0.13 (0.17±0.03) [2]	··· (0.50±0.18) [2]	0.57 (0.71±0.15) [1]	··· ··· ···	0.85 (1.08±0.16) 2	··· ···
Ce	0.12 (0.17±0.03) 2	··· ··· ···	··· ··· ···	0.63 (0.84±0.15) 2	0.85^a (0.61±0.08) 2	··· ···
Pr	0.16 (0.18±0.03) [2]	··· (0.55±0.16) [2]	··· ··· ···	··· ··· ···	··· (1.08±0.24) [2]	··· ···
Nd	··· ··· ···	··· (0.46±0.13) [2]	0.53 (0.71±0.15) 2	··· ··· ···	1.01 (1.05±0.11) 2	··· ···
Sm	0.10 $(0.12\pm0.03)^b$[2]	··· (0.23±0.08) [1]	··· ··· ···	··· (0.47±0.13) 2	0.59^c (1.11±0.11) 2	··· ···
Gd	0.17 ··· ···	··· (0.28±0.10) [1]	0.49 (0.56±0.10) 2	0.92 (0.89±0.17) 2	0.98 (0.74±0.08) 1	··· ···
Tb	0.10 (0.15±0.03) 2	··· ··· ···	··· ··· ···	··· ··· ···	0.75^a (1.01±0.11) 2	··· ···
Dy	0.16 ··· ···	··· (0.23±0.06) [1]	0.44 (0.45±0.08) 1	··· ··· ···	1.02 (1.18±0.12) 2	··· ···
Ho	0.20 ··· ···	··· (0.25±0.06) [1]	0.38 (0.29±0.06) 1	0.62 (0.77±0.18) 2	0.87^a (1.05±0.11) 2	··· ···
Er	0.10 ··· ···	··· (0.23±0.10) [1]	0.45 (0.49±0.11) 2	··· (0.55±0.11) 1	0.95^a (0.81±0.08) 2	(1.62±0.16) 2
Tm	0.21 ··· ···	··· (0.29±0.08) [1]	··· ··· ···	··· (0.80±0.16) 2	0.86 (1.08±0.11) 2	(1.31±0.13) 2
Avg	0.15±0.04 (0.16±0.03)	··· (0.34±0.11)	0.48±0.05 (0.54±0.11)	0.72±0.13 (0.72±0.15)	0.87±0.09 (0.98±0.12)	··· (1.47±0.15)

[a] Multiple peaks. [b] $\Delta > 0.1$.

[c] Error in measuring Eg with Arrhenius diagram is approximately 10 to 20%. This error is much larger for Sm peak No. 5 because of small size of peak.

for second-order processes. Here τ is the half-width (in °K) of the glow peak on the low-temperature side (i.e., $\tau+\delta=w$, where w is the full width at half-intensity), and $\Delta=2kT_g/(E_g)_i(i=1,\ 2)$. The choice of kinetics is determined by whether the ratio δ/w is larger (second order) or smaller (first order) than $(1+\Delta)/e$, where $e=2.718\cdots$.

The values for E_g calculated from these equations are listed in Table II in parentheses, along with the estimated uncertainty. First- or second-order kinetics are also indicated. However, the significance of designating a glow peak by first- or second-order kinetics is somewhat arbitrary and deals with the relative rates at which traps, electrons, holes and various types of centers recombine.

The accuracy of these calculations varies from 10 to 30%, for reasons that are discussed at length elsewhere.[20] However, several important pieces of information are contained in Table II. The order of magnitude of these energies has certainly been measured and will be useful for comparison with activation energies of known hole centers in CaF_2. Furthermore, a definite progression to higher energy with increasing glow peak temperature is apparent from these data. Such a progression is not necessarily expected *a priori*, since the energies depend on the shape of the glow curves as well as the peak temperatures. This discussion reveals that the shapes of the glow curves are consistent with the above-mentioned progression. Finally, these energies support the conclusion drawn above that the glow peaks are independent of the particular rare earth involved. This last point might be considered to be better made by the similarity of glow peak temperatures shown in Table I which are not influenced by the uncertainties and approximations involved in calculating the activation energies. To obtain better accuracy for activation energy measurements, additional experiments should be carried out, such as those already described in the literature.[16,42–44]

IV. SPECTRA OF THE THERMOLUMINESCENCE

Low-resolution measurements showed that the spectral distribution of the emitted light is characteristic of the rare-earth ion, not the host, and corresponds to the fluorescence of the trivalent rare earth. Photoelectric and photographic methods were used to study the spectra of the individual glow peaks at a resolution of less than 1 Å. The experimental procedures for these measurements are given in II, along with detailed results for each of the lanthanide rare earths. The important conclusions of this work have already been summarized,[45,46] and will be only briefly reviewed here.

The spectral data of the individual glow peaks presented in II form a consistent picture. For all of the glow peaks occurring below room temperature, the emission originates from a rare-earth ion in a cubic site, while the high-temperature glow peaks display a lower symmetry which is believed to be tetragonal. This is best seen for gadolinium, where the cubic and tetragonal spectra have been clearly identified. In some cases, the low-temperature emission from ions in cubic sites involves forbidden transitions; vibrational sidebands are then observed. These high-resolution spectral measurements confirm the fact that fundamental differences exist between individual glow peaks; the thermoluminescence is separated into at least two temperature ranges: 80–280°K (low-temperature range) and 280–450°K (high-temperature range). Different mechanism must be responsible for the emission in these two ranges.

V. ABSORPTION SPECTRA

The optical absorption spectra of divalent rare earths in CaF_2 have been given by McClure and Kiss.[7] These measurements were made at room temperature on crystals exposed to γ rays at room temperature. Similar results have been obtained in this laboratory. Weak absorption lines present in the unirradiated crystals due to the trivalent ions have also been monitored as a function of irradiation dosage. Very little decrease in the strength of these lines is observed while the broad divalent absorption bands appear and grow strong.[20,27,47] This is consistent with the interpretation that only a small fraction of the trivalent ions initially present can be reduced.

One of the main points of this work is that the charge reduction of the rare earths by irradiation is unstable, and the ions can be reoxidized by heating. Such reoxidation occurs even at room temperature, at a rate which differs for each rare earth. Moreover, the different absorption bands do not behave in quite the same way during this thermal reoxidation; some peaks bleach much faster at 300°K than others.[20] This suggests that, contrary to initial assumptions, some of these absorption bands may not be directly associated with the divalent ion.

A. X Irradiation at 77°K

The efficiency of the charge reduction increases when the irradiation is performed at liquid-nitrogen temperature. Low-energy x rays were used for these studies and the dosage was kept within the linear range of Fig. 5. The optical absorption of each of the rare earths in CaF_2 resulting from 1-h exposure to x rays at 77°K is shown in Fig. 7. Absorption was measured directly in optical density units on a Cary model 14 spectro-

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[43] Ch. B. Lushchik, Zh. Eksperim. i Teor. Fiz. **30**, 488 1956) [English transl.: Soviet Phys.—JETP **3**, 390 (1956)].

[44] V. A. Arkhangelskaya, Opt. i Specktroskopiya **18**, 92 (1965) [English transl.: Opt. Spectry. **18**, 46 (1965)].

[45] J. L. Merz and P. S. Pershan, Bull. Am. Phys. Soc. **11**, 72 (1966).

[46] J. L. Merz and P. S. Pershan, in *Proceedings of the Conference on Optical Properties of Ions in Crystals* (Johns Hopkins University Press, Baltimore, Maryland, 1966); (to be published.)

[47] Z. J. Kiss. Phys. Rev. **127**, 718 (1962).

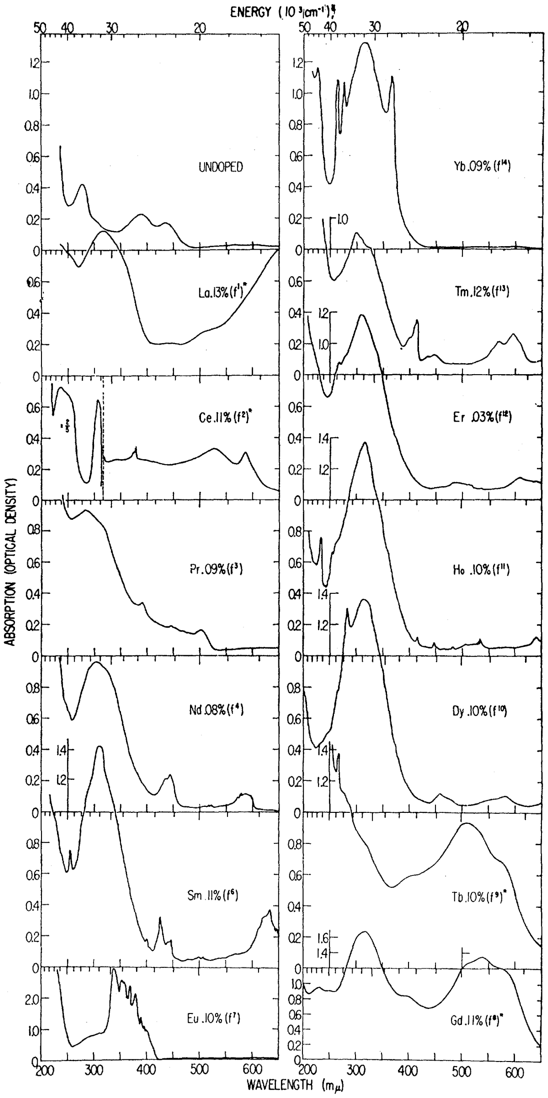

FIG. 7. Optical absorption of rare-earth–doped CaF_2 after x irradiation for 1 h at 77°K. Wavelength units (mμ) plotted below each graph; energy units (cm^{-1}) above. The number of electrons outside the La^{3+} core for each of the divalent ions is given in parentheses. *These ions are believed to have the $4f^{n-1}5d$ configuration in their ground state (Ref. 7).

photometer, so that comparison of the different ions can be made.[48]

Two significant features of the absorption are evident from Fig. 7. The first is the existence of the strong absorption band at about 3100 Å in nearly every case. Since this band appears with such regularity through the rare-earth series, it is believed to be an absorption by one of the hole centers formed during the irradiation, rather than a divalent rare-earth absorption. This interpretation is supported by the difference in thermal annealing behavior referred to above. The hole-absorption band is barely visible in the case of europium, which is consistent with the lack of thermoluminescence from this ion. In the case of cerium the hole absorption is masked by the strong *f* to *d* transition of Ce^{3+} at 33 000 cm^{-1} reported by Loh.[49] The only other ion where this band is not evident is terbium, where it may be present as a shoulder on the strong ultraviolet absorption.

The other important feature of these curves is the fact that further similarities are difficult to find. Each of the ions has its own characteristic spectrum from 3500 Å to longer wavelength. These absorption bands are believed to be due to the *f* to *d* transitions of the divalent rare earths themselves. For the low x-ray dosage and low temperature used here, the divalent absorption is generally much weaker than the hole band; this was not the case for γ rays at room temperature.

Four of the ions do behave somewhat differently than the others. The "divalent bands" at wavelengths longer than 4000 Å for La, Ce, Gd, and Tb are much stronger than the absorption bands in this region of the spectrum for the other ions. The similarity is most evident for gadolinium and terbium. These are also the four ions which are believed to include a 5*d* electron in the ground-state configuration. The existence of these anomalous bands, as well as the hole absorption at 3100 Å, casts some doubt on the blanket assertion that the radiation-induced absorption curves are due solely to the divalent rare earths.

The absorption bands in the undoped sample, also shown in Fig. 7, have not been positively identified. Traces of these same bands are found in several of the other samples, which suggests the presence of small amounts of impurities. However, it is clear that these effects are not the dominant ones of interest.

B. Thermal Bleaching of Absorption

Further information about the reduction-oxidation mechanism for the irradiated rare earths can be gained by examining changes in the absorption curves as the sample temperature is increased. If the thermoluminescence observed during heating is associated with the reoxidation of divalent ions, as has been suggested, then the absorption bands due to the divalent ions should bleach as each glow peak is emitted. For all the rare earths, measurements have been made of the absorption at 77°K before and after annealing each glow peak, using the following procedure. The absorption was first measured after irradiation and the cessation of transient afterglow, with the sample at liquid-nitrogen temperature. The sample was then heated to the thermoluminescence minimum between glow peaks

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[48] The low-energy x rays used for these studies did not penetrate more than 2 mm into the samples. This penetration depth therefore defines the effective thickness of the sample studied, and is the same for all rare earths at a given radiation dosage.

[49] E. Loh, Phys. Rev. **147**, 332 (1966).

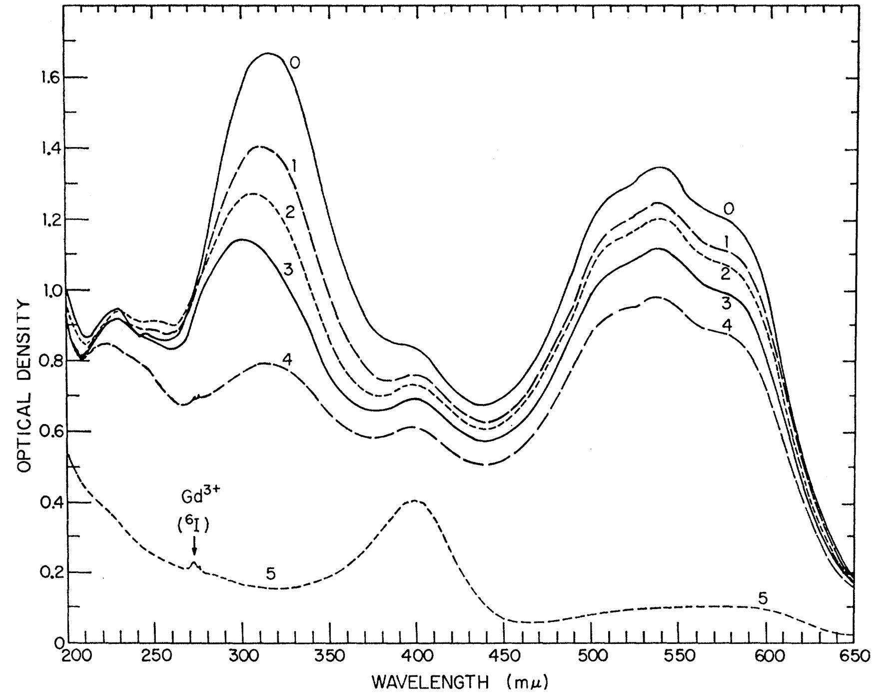

FIG. 8. Absorption bleaching of irradiated CaF_2:Gd 0.1%. Each curve is obtained by thermally annealing the glow peak identified by the curve number. Curve 0 is the absorption after irradiation at 77°K.

Nos. 1 and 2.[50] At this point the sample was recooled, and the absorption remeasured. This process was repeated so that each glow peak was thermally annealed, after which the resulting change in the optical absorption was measured at liquid-nitrogen temperature. The bleaching of the absorption accompanying the emission from each glow peak was measured between 2000 and 6500 Å in this way. The results of these experiments confirm the hypothesis of reoxidation.

The absorption curves for 0.1% Gd grown from G & S CaF_2 are shown in Fig. 8. The upper curve is the absorption after irradiating for 1 h at 77°K; this is identical to the Gd curve in Fig. 7. Each succeeding curve corresponds to the absorption after annealing each glow peak. As each glow peak is annealed, the decrease in the absorption band at 5400 Å is proportional to the intensity of that glow peak, to within the 10% accuracy involved in measuring the glow peak. This proportionality means that either the 5400 A band is actually an absorption due to Gd^{2+}, or it is caused by another center that anneals in proportion to the divalent ions. However, the peak at 3100 Å decreases much faster than the 5400 Å band. This is further evidence that the band at 3100 A is not a divalent ion absorption, and instead can be associated with the hole center formed during the irradiation. Weak absorption by the ^6I multiplet of Gd^{3+} is also seen in the figure.

Anomalous effects are observed in conjunction with the glow peaks at highest temperatures. As mentioned above, the high-temperature glow peaks no longer behave similarly for different rare earths. Associated with these high-temperature peaks, an absorption band is found at 4000 Å which is observed only in the four ions having strong absorption in the red: La, Ce, Gd, and Tb. By comparing results from crystals grown from various sources of CaF_2, it was found that this band is much more sensitive to growth conditions and impurity level than the hole centers responsible for the more dramatic effects discussed above. This 4000 Å band disappears after bleaching the highest-temperature glow peak, at 340°K. Irradiation with light at this wavelength has also been found to bleach this band, with the growth of a new band at lower energy.[51]

Comparison of Figs. 9 and 10 reveals the difference in the relative ease with which two of the rare earths, Sm and Tm, can be reduced. Appreciable concentrations of Sm^{2+} can be obtained by growing the crystal in a reducing atmosphere[52]; this was not done for the crystals studied here in order to minimize the number of divalent ions before irradiation. Nevertheless, some absorption due to Sm^{2+} in the unirradiated sample (U) is seen at 4250, 4470, and 6350 Å. Irradiation produces a large increase in these bands and the hole absorption becomes a dominant feature of the spectrum, while the Sm^{3+} peaks at approximately 4000 Å are hardly affected.

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[50] The fast heating rate shown in Fig. 2 was used for these measurements. Glow peaks Nos. 1, 1a, and 1b are therefore unresolved, and are designated here as No. 1.

[51] These effects were first pointed out to us by Z. J. Kiss (private communication). Some optical bleaching experiments, and their effect on the glow curves, have been discussed by one of us (JLM) in Chap. IX of Ref. 20. The production of a new paramagnetic center by UV bleaching has been reported by B. W. Faughnan, Z. J. Kiss, and D. L. Staebler, Bull. Am. Phys. Soc. **12**, 41 (1967).

[52] W. Kaiser, C. G. B. Garrett, and D. L. Wood, Phys. Rev. **123**, 766 (1961); D. L. Wood and W. Kaiser, *ibid.* **126**, 2079 (1962).

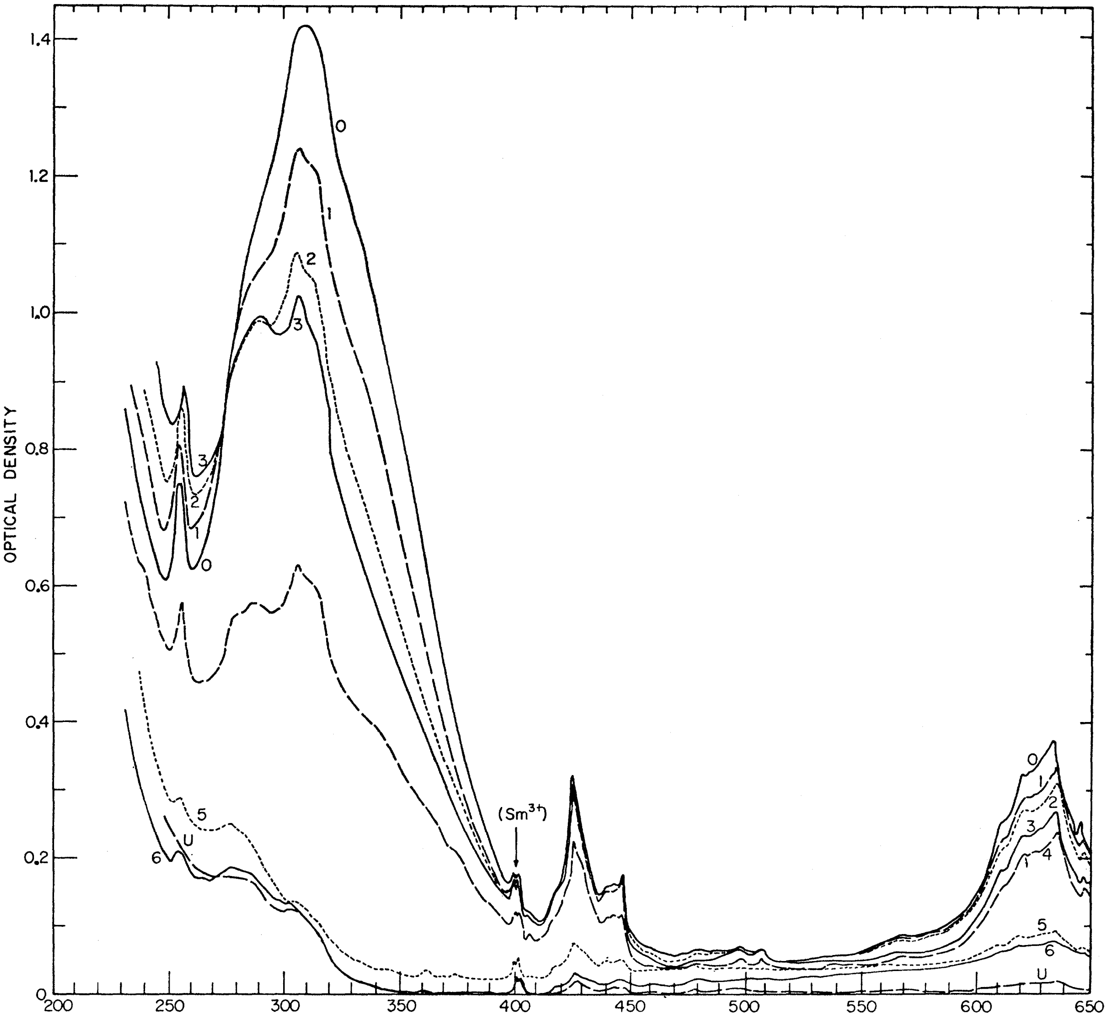

FIG. 9. Absorption bleaching of irradiated CaF_2:Sm 0.1%. Curve numbers as in Fig. 8. Curve U is for unirradiated sample.

After annealing all of the glow peaks, the crystal returns nearly to its unirradiated condition. This is not the case for Tm, which is more difficult to reduce (cf. Fig. 10). The unirradiated crystal shows no sign of Tm^{2+}. However, once produced by irradiation, Tm^{2+} is relatively stable, since a significant absorption is still present after heating the crystal to 450°K. The hole absorption band near 3000 Å has been bleached by this process, so the remaining Tm^{2+} ions must be acompanied by another, deeper-lying hole trap. This is borne out by the high-temperature thermoluminescence experiments of Fong,[16] who measured a glow peak at 214°C which he attributed to electron rather than hole activation.

In both these cases the hole absorption band at approximately 3100 Å is much stronger than the divalent rare-earth bands after irradiation at 77°K. Chemically reduced Sm behaves somewhat differently. For Sm-doped crystals grown in a reducing atmosphere, the Sm^{2+} bands at 4250, 4470, and 6350 Å are of comparable intensity to the 3100-Å hole band. The production of this hole band by irradiation is also seen for Eu, the most stable divalent ion of the lanthanide series. The absorption bleaching of CaF_2:Eu 0.1% is shown in Fig. 11. Feofilov and co-workers[53,54] have studied the absorption of Eu^{2+} and observed the same spectrum as that shown for the unirradiated sample (U) in Fig. 11. However, exposure to x rays produces additional absorption around 3000 Å, and the concentration of divalent ions increases slightly. Since very little glow emission can be seen from europium even at the fast heating rate, the sample was arbitrarily heated to 300°K (curve 4 in Fig. 11) and the absorption measured again at 77°K. This bleaches both the hole absorption near 3000 Å and the Eu^{2+} absorption. Further heating of the crystal to 420°K (curve 6) bleaches the remaining effect of irradiation, so that the crystal was identical

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[53] P. P. Feofilov, Opt. i Spektroskopiya **1**, 992 (1956).

[54] A. A. Kaplyanskii and P. P. Feofilov, Opt. i Spektroskopiya **13**, 235 (1962) [English transl.: Opt. Spectry. **13**, 129 (1962)].

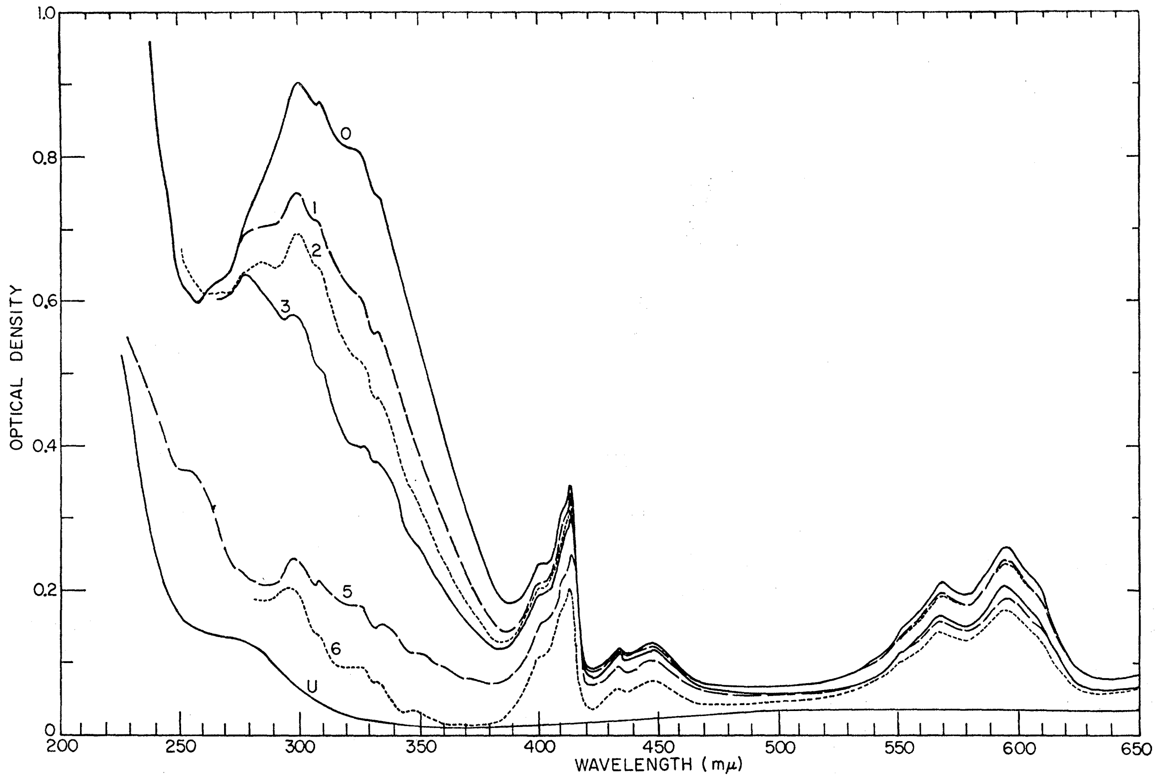

FIG. 10. Absorption bleaching of irradiated CaF_2:Tm 0.1%. Curve numbers as in Fig. 8.

with the unirradiated one. The changes produced by irradiation are small, however, because most of the reducible europium is already in the divalent state before irradiation.

The absorption bleaching curves for Er, published elsewhere,[46] are consistent with the results described above. In the case of Er and Ho, which behave similarly, the ratio of the hole absorption to the divalent ion absorption is even larger than for the other ions studied. The remaining lanthanide ions have also been studied,[20] and the same sort of bleaching effects occur as the glow peaks are annealed. In a few cases the thermal treatments appear to produce another, unidentified center in the vicinity of 4000 Å. In all cases, however, the hole absorption at approximately 3100 Å and the divalent ion bands bleach as the temperature is increased, but at different rates.

C. Color Centers in CaF_2

The presence of the strong absorption bands reported above in irradiated CaF_2 doped with rare earths necessitates a few remarks about the formation of color centers in pure CaF_2. Several review articles and books have dealt with this subject,[13,55–57] but the situation is still not clearly understood and no direct analogy appears to exist with the more widely studied alkali halides. In general, two different types of absorption spectra have been observed in CaF_2, depending on the treatment of the crystal. When the crystals are additively colored and quenched, the two-band Mollwo spectrum is usually seen.[58] When crystals are exposed to ionizing irradiation, four bands are observed.[59,60] This Smakula-type spectrum can also be produced additively if the temperature is kept sufficiently low.[61] In general, however, it has been found to be relatively difficult to produce color centers in the pure material, especially by irradiation. The formation of F centers or other typical color centers requires high dosages[60,62] or certain specific temperature ranges.[63,64] The presence of impurities enhances the probability of formation of these centers, especially if the impurity has a different valence state than the ion it replaces, such as Y^{3+} replacing Ca^{2+}.[59,65] The absorption bands for the undoped crystal

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[55] K. Przibram, *Irradiation Colours and Luminescence* (Pergamon Press, Ltd., London, 1956).

[56] K. Przibram, Z. Physik **154**, 111 (1959).

[57] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, New York, 1962).

[58] E. Mollwo, Nachr. Gesell, Wiss. Gottingen **6**, 79 (1934).

[59] A. Smakula, Phys. Rev. **77**, 408 (1950); **91**, 1570 (1953).

[60] W. J. Scouler and A. Smakula, Phys. Rev. **120**, 1154 (1960); D. Messner and A. Smakula, *ibid.* **120**, 1162 (1960).

[61] F. Lüty, Z. Physik **134**, 596 (1953).

[62] L. A. Lisitsyna, Opt. i Spektroskopiya **19**, 295 (1965) [English transl.: Opt. Spectry. **19**, 167 (1965)].

[63] V. V. Ratnam, Phys. Status Solidi **16**, 549, (1966); **16**, 559 (1966).

[64] T. Kamikawa, Y. Kazumata, A. Kikuchi, and K. Ozawa, Phys. Letters **21**, 126 (1966).

[65] J. R. O'Connor and J. H. Chen. Phys. Rev. **130**, 1790 (1963).

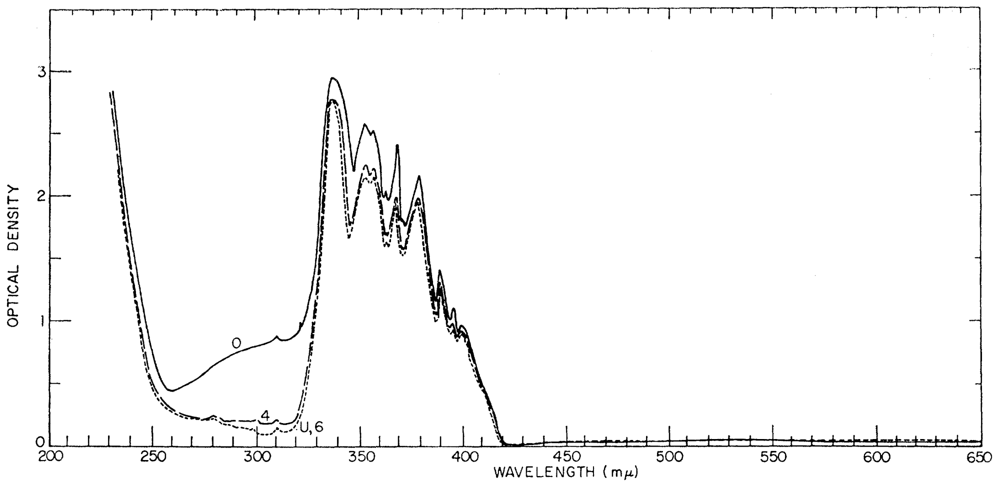


FIG. 11. Absorption bleaching of irradiated CaF_2:Eu 0.1%. Curve numbers as in Fig. 8.

in Fig. 7 may well be due to some unspecified impurity; they do not coincide with the bands found in the Mollwo or Smakula-type spectra. However, in all the other crystals rare-earth impurities have been intentionally added in sufficient concentrations to determine the majority of centers that can be formed. The situation of interest in this work therefore seems to be the simplest case: The trivalent rare earths replace divalent calcium and act as electron traps. The most likely centers that will be formed during irradiation are those that can supply electrons to the rare earths. One would therefore expect large concentrations of filled hole traps after exposure to x rays, rather than F centers or other electron traps. An example of such a filled hole trap, the V_K center, has been observed by Hayes and Twidell in Tm-doped CaF_2.[8]

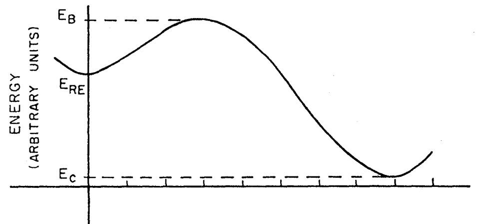
VI. DISCUSSION

In the data presented above, three facts about the charge reduction of rare earths by irradiation have been established: (1) The irradiation of rare-earth–doped CaF_2 reduces trivalent rare-earth ions in cubic sites to the divalent state; (2) subsequent heating reoxidizes the ions with the emission of light; (3) the temperatures at which this emission occurs are independent of the particular rare earth studied. As quoted above and discussed in II there is a fourth fact, namely the spectra of the thermoluminescence corresponds to the fluorescence of the trivalent ion in sites of cubic symmetry for the low-temperature glow peaks, and tetragonal symmetry above room temperature. The following simple model is proposed to explain these phenomena.

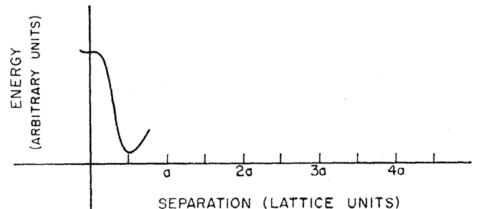
A. A Model

For a trivalent rare-earth ion with a nearby (localized) compensator, the position of lowest energy for the extra electron is on the compensator rather than on the rare earth. The situation is not so simple if the rare earth is left in a site of cubic symmetry because its compensator is nonlocal. The evidence presented in the literature, and the experimental data given above, then imply that another energy minimum (i.e., a metastable one) for the compensating electron is located at the rare earth. A rare-earth ion in a cubic site can therefore be stabilized in the divalent state. In this case, a potential barrier probably exists between the rare earth and the nonlocalized compensator, so that an activation energy is needed to transfer the electron from the compensator to the rare earth and back again.

An idealized diagram of such a situation is shown in Fig. 12. The position coordinates of the rare-earth ion



(a) NON-LOCAL COMPENSATION



(b) LOCAL COMPENSATION

FIG. 12. Potential energy between trivalent rare earth and interstitial fluoride compensator. Interstitial fluoride separation from rare earth is plotted along horizontal axis in units of lattice constant $a=5.45$ Å.

are taken as the origin in this diagram; the abscissa represents the distance of the charge compensator from the rare earth. Part (a) of the figure is for the case of nonlocal compensation. Energy minima occur at the sites of the rare earth and the compensator, with a potential barrier of height $(E_B - E_{RE})$ between them. The height of this barrier is a strong function of the rare earth, since it is determined by the ionization potential of the rare-earth ion, modified by the lattice environment. The figure is drawn so that the position of lowest energy is at the compensator $(E_{RE} > E_C)$; this is not necessarily the case, and may depend on both the particular rare earth and type of charge compensation involved. In either case, it is known that only trivalent ions are found in the crystals as grown (except for the three special cases of Eu, Sm, and Yb), so that the electron must initially be bound to the compensator. Irradiation frees electrons from these compensators or from normal lattice positions, and the free electrons may eventually be trapped at the trivalent rare-earth site. Since some of the ions exhibit room-temperature thermoluminescence characteristic of the thermal ionization of the divalent rare earth, the potential barrier E_B is probably not very high, and the position of lowest energy is most likely at the compensator, as drawn.

The case of localized compensation is portrayed in Fig. 12(b). Here the minimum is definitely at the site of the compensator, and the potential barrier, if it exists, is small compared to kT even at liquid-nitrogen temperature. The electron is always found at the site of the compensator, and the rare-earth ion cannot be reduced.

The rare-earth ions initially converted to the divalent state are therefore in cubic sites; the electrons come from compensators located far enough away so that their perturbation of the local cubic symmetry is small, or from distant lattice fluoride ions. Electron deficient centers, or holes, are left behind. The electron energy-level diagram therefore probably resembles Fig. 12(a), with the electron trapped at the rare-earth ion. The height of the potential barrier $(E_B - E_{RE})$ is large compared to kT, for T running from the irradiation temperature (77°K) to at least 350°K, since the divalent rare earth is not thermally ionized in this temperature range. Instead, as the temperature is increased, the hole centers become free to diffuse through the crystal. When a hole approaches a divalent rare-earth ion, it captures the extra electron, leaving a trivalent ion in an excited state. In the energy picture of Fig. 12, this corresponds to a continuous transition from case (a) to case (b), with the exception that the diffusing hole is not necessarily an ionized charge compensator, but instead can be a hole formed in the otherwise perfect CaF_2 lattice. In either case the potential barrier between the rare earth and the approaching hole center is no longer large compared to kT (where T is now the activation energy for diffusion of the hole center), so the electron recombines with the hole. This process leaves the trivalent rare-earth ion in an excited state; the decay of this excited trivalent rare earth to its ground state results in the observed thermoluminescence.

For the low-temperature glow peaks, this diffusing hole center must leave the rare-earth ion in a cubic site. An example of such a center is the V_K center or self-trapped hole observed by Hayes and Twidell in irradiated CaF_2. This center anneals at 138°K and its formation can be enhanced by the presence of impurities such as the rare earths. Similar lattice holes may exist in a number of configurations. For example, they could be trapped at different impurities or crystal imperfections, or there could be pairs of self-trapped holes (i.e., a neutral fluorine molecule); each of these configurations would have a different activation energy, and thus lead to a different glow peak. However, when a hole of this type recombines with the electron trapped at the rare-earth site, the lattice fluorides relax to their undistorted positions, leaving the excited trivalent rare earth in a cubic environment.

The most obvious explanation of the high-temperature peak is the diffusion of interstitial F^0 atoms which had been far from the rare earths. When they approach the divalent ion, they provide the tetragonal symmetry during the electron recombination process. These high-temperature glow peaks may well constitute a good measurement of the energy for diffusion of an F^0 atom through the CaF_2 lattice.

It should be emphasized that two different types of hole diffusion are included in this model. The self-trapped hole involved in the low-temperature peaks is simply an electron missing from a fluorine; distortion around that position traps the hole. The center is then equivalent to an F_2^- molecule. As the temperature is increased, the hole diffuses by hopping from site to site. A hole hop corresponds to a nearby electron being captured by the hole. However, the diffusion occurring for the high-temperature glow peaks actually involves the motion of an interstitial neutral fluorine through the lattice, which would require a higher activation energy.

The similarities in the general form of the glow curves for the different rare earths tend to confirm the model described above. In particular, the glow peak at 330°K ascribed to the diffusion of interstitial F^0 atoms is usually dominant, as might be expected from simple energy considerations. It requires less energy to remove an electron from an interstitial fluoride ion than from a lattice fluoride. It is then not surprising that the concentration of F_{int}^0 holes should exceed that of each configuration of lattice holes contributing to the low-temperature peaks. This is borne out by comparing the glow curves for the undoped crystals with those containing rare earths. The relative intensity of peak No. 5 is much larger for the doped samples than for the undoped ones, where interstitial compensation is unnecessary. (Compare Figs. 3 and 4.) It is also interesting to note that this glow peak is comparatively small for the ions which are known to be most stable in the divalent state.

In general, the ions in the first half of the lanthanide series are more difficult to reduce. This was noted in the glow curve data, and seems to be related to the difference in ionic radii of the rare-earth ions and the Ca^{2+} they replace. The ions in the first half of the lanthanide series are much larger than the Ca^{2+} ion, and are usually not found in cubic sites.[21] There is evidence that these rare earths are more closely associated with their charge-compensating ions. In a study of the infrared and vibronic spectra of adjacent rare-earth and H^- ions in CaF_2, Yatsiv and co-workers[66] never found the hydrogen ion in a cubic site for crystals doped with La, Ce, Pr, and Nd; instead, H^- was associated with the trivalent rare earth.

The model proposed above also suggests that differences may be observed in the glow curves resulting from subsequent irradiations of a given sample. The reason for this is the diffusion of atomic fluorine postulated for peak No. 5; these atoms diffuse toward rare-earth sites, changing their role from nonlocal compensators to localized ones. During the next irradiation of the sample, fewer trivalent ions would be found in cubic sites, so that charge reduction would not be as complete. This would be expected to affect peak No. 5 most severely, since the nonlocal compensators which contribute to this peak in the initial run are no longer available for subsequent runs.

However, such differences were not noted in successive irradiations. Instead, the glow curves were generally reproducible for the same sample to within 10% for the peak intensities. One argument that can be offered to counter this objection is that after each glow curve run, the crystal relaxes to an equilibrium distribution of localized and nonlocal compensators. This means that after recombination, a number of the local interstitial F^- ions are capable of diffusing away from the trivalent rare earth, during the period when the sample is still warm from the previous run. The charge compensators may achieve nearly the same distribution through the lattice each time, and the minor differences between runs might contribute to the scatter shown in the reproducibility.

B. The Self-Trapped Hole

The V_K center, or self-trapped hole, was first observed in CaF_2 by Hayes and Twidell by paramagnetic resonance after exposing the crystal to x rays at liquid-nitrogen temperature.[8] The center is aligned along a (100) direction, and decays when the sample temperature is raised to 138°K. The hole is formed by the removal of an electron from a normal lattice site. The resulting electrostatic forces cause a displacement of neighboring anions. This distortion traps the hole at a specific site in the lattice. The hole is shared predominantly by a pair of anions displaced towards each other; the configuration is therefore a form of the X_2^- molecular ion, where X refers to the anion. The center is "self-trapped" since it does not rely on the presence of an impurity or crystal imperfection to lower its energy at a particular position in the crystal. The presence of trivalent impurities in the crystal enhances the formation of V_K centers, since these impurities provide effective electron traps. Most of the studies of this center have been made in the alkali halides, where it is aligned along the (110) direction. It was first identified and studied in detail by Castner, Känzig, and Woodruff.[67] The bleaching of the V_K center in the alkali halides is accompanied by thermoluminescence characteristic of the impurities present.

A number of other centers related to the V_K have also been studied. The V_1 center can be considered as a pair of V_K centers forming a X_2 molecule, while a X_2^- molecular ion situated at a single halogen site [and therefore introducing an extra halogen between two halides in the (110) direction] is called an H center.[57] Another example which has been found in alkali halides is the V_F center; this was identified by Känzig[68] as a F_2^- molecular ion associated with an alkali vacancy, with the molecular bond "bent" because of the vacancy. Sierro[69] has also found this center in natural CaF_2 containing a higher concentration of Ca^{2+} vacancies than the synthetic crystals. This center was stable up to about 330°K, so it is not certain whether it is associated with glow peak No. 5 or with the low-temperature peaks.

This discussion makes plausible the existence of several types of centers in CaF_2 which are minor variations of the V_K center. They could be trapped at different lattice imperfections or at impurity sites, and each would be expected to have a different thermal activation energy for diffusion. Many of these centers could provide cubic symmetry at the rare-earth site during recombination. The production of these centers should be very sensitive to impurities and growth conditions of the samples. This sort of sample dependence has been seen for the thermoluminescence of undoped samples, shown in Fig. 3. The peak temperatures are largely unaffected by the source of CaF_2, whereas the intensities of the different peaks (hence the concentration of the centers responsible for them) differ considerably for the different sources shown. A similar sample dependence is also observed for the erbium-doped samples grown from different sources of CaF_2, although the dependence is not so extreme as in the undoped case. The presence of the trivalent rare earth may therefore tend to favor the formation of certain centers and not others.

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Similarly, the differences noted in the dependence of the low-temperature and high-temperature glow peaks on rare-earth concentration could originate from the different types of holes proposed in the model above. The task remains, however, to identify the actual constituents and orientation of the center associated with each glow peak. This could possibly be done by magnetic resonance, and should be done on the same samples used for thermoluminescence experiments.

The mechanism for diffusion of V_K centers has been elucidated by the work of Keller and Murray[70–72] on the alkali halides. They showed that the centers diffused by reorientation through 60° jumps where only one anion is involved. The thermal activation energy for this type of diffusion varied from 0.15 to 0.54 eV for the materials studied. In particular, for three alkali iodides the activation energies were found to increase with iodine separation. The possibility that other, more complicated configurations of V_K centers may also occur has been suggested by Kiss and Staebler.[30] They also found that thermoluminescence indicative of cubic symmetry was observed from CaF_2:Dy after γ irradiation at 77°K and heating to room temperature. The same emission was obtained if the sample was exposed to infrared radiation instead of heating. The complex time dependence of this luminescence could be explained by assuming that two Dy^{2+} ions recombined with an F_2 molecule in two steps, each of which involved recombination with an F^0 hole.

Optical absorption bands in the region from 3500 to 4500 Å have been observed[71,73] for the V_K center in many of the alkali halides. The identification of this band as an F_2^- molecule in CaF_2 has recently been confirmed by the work of Arkangelskaya and Alekseeva.[74] The peak wavelengths of the V_K absorption bands are compared in Table III with the interatomic spacing of the X_2^- molecule for all the known cases. The trend is clear from this table: As the spacing increases, the band peak moves to longer wavelength. LiF and NaI appear to be exceptions, but the inconsistency for LiF may result from the difference in polarizability of the NaCl- and CaF_2-type lattices. The absorption is believed to result from an electronic transition from the ground state ($^2\Sigma_u^+$) to the first excited state ($^2\Sigma_g^+$) of the X_2^- molecular ion.[73] This transition is σ-polarized (electric vector parallel to the molecular axis), which accounts for the preferential orientation of V_K centers which can be achieved by illumination with polarized light.[70]

TABLE III. Effect of X_2^- spacing on V_K optical absorption.

Crystal	Lattice constant (Å)	X_2^- spacing (Å)	Absorption (mμ)	Reference
KHF_2	5.67	2.26[a]	302	[d]
CaF_2	5.45	2.73[b]	310	This work
			315	74
LiF	4.01	2.83[c]	348	73
SrF_2	5.86	2.93[b]	325	74
BaF_2	6.18	3.09[b]	345	74
KCl	6.28	4.44[c]	365	73
NaI	6.46	4.57[c]	432	71
KBr	6.59	4.66[c]	385	73
KI	7.052	4.98[c]	400	73
RbI	7.33	5.18[c]	405	71

[a] F-F spacing is through hydrogen; cf. R. W. Wykoff, *Crystal Structures* (Interscience Publishers Inc., New York, 1960), Vol. II, p. VIa1.

[b] For CaF_2 lattice: X_2^- spacing $=a/2$.

[c] For NaCl lattice: X_2^- spacing $=a/\sqrt{2}$.

[d] F. B. Otto and O. R. Gilliam, Phys. Rev. **154,** 244 (1967).

Although the two types of hole centers postulated to explain the glow peaks below and above room temperature diffuse differently, they both involve configurations of the F_2^- molecular ion. This is clear for the V_K center, and the interstitial F^0 hole would also tend to associate with one of its neighboring lattice F^- ions. However, the transition probabilities between the appropriate electronic states of the F_2^- molecule need not be identical for different configurations of this center, since the relative spacing of the fluorine atoms and the influence of environment may be different. For this reason the rapid bleaching rate of the hole absorption band compared to the divalent rare-earth absorption is not unexpected.

C. Diffusion of Interstitial Fluorides

Several independent measurements of the activation energy for the diffusion of interstitial F^- ions in rare-earth–doped CaF_2 have been made. By studying the diffusion narrowing of the NMR linewidth of F^{19}, Veigele[75] estimated $E=0.63$ eV. Lysiak and Mahendroo[76] obtained $E=0.53$ eV from the temperature dependence of the spin-lattice relaxation time in samarium-doped CaF_2. Southgate[77] studied the anelastic and dielectric loss in Y-doped CaF_2; he found that the dielectric losses are dominated by the dc conductivity, with an activation energy of 1.16 eV. This was hypothesized to be due to F_{int}^- diffusion, although part of this energy (e.g., 0.26 eV) might be needed to free the F_{int}^- from a Y^{3+} ion, leaving 0.9 eV for diffusion. The ionic conductivity measurements of Ure[78] do not agree very well with the results quoted above; he found an activation

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energy of 1.65±0.35 eV. However, all these results are for the diffusion of F^- ions, while F^0 atoms are believed to be responsible for glow peak No. 5 measured in this work. Such activation measurements have not been made, but the diffusion of $H_{\text{int}}{}^0$ has been studied by Welber.[79] He found an activation energy of 1.2 eV and a jump frequency factor of 1.5×10^{15} sec^{-1}. Considering the scatter of the results quoted above, the value of 0.87±0.09 eV obtained from glow peak No. 5 (cf. Table II) is not unreasonable.

D. Divalent Rare-Earth Ions

The model proposed above depends heavily on the assumption that only rare-earth ions initially in cubic sites can be reduced to the divalent state. The evidence for this has been discussed in Sec. II. However, these measurements usually involve detecting the rare earth as a divalent ion after the irradiation. It is possible that a more complicated mechanism could occur, where rare earths in noncubic sites are reduced, immediately followed by diffusion of the compensating ion away from the rare-earth site. Low[34] does not reject this possibility, allowing for a relatively high mobility of the change compensator. The activation energies for diffusion discussed above make this seem unlikely at 77°K, unless a significant fraction of the x-ray energy can be transferred to the vibronic excitations of the rare-earth-compensator complex.

These results also show that not all the optical absorption bands seen in these crystals are due to the divalent rare earths, as had previously been asserted. The question remains whether any of these bands have been proven unambiguously to be divalent ion absorption. The evidence is certainly compelling that the lowest-energy absorption bands seen in Fig. 7 are due to the divalent ions. The same bands are produced by the different methods of charge reduction, and they differ from one rare earth to another as might be expected. McClure and Kiss[7] have made a theoretical calculation of the expected onset of the f to d absorption for the lanthanide series ions, and their results are in reasonable agreement with the data. Other theoretical and experimental determinations of the divalent configurations show absorption in the same wavelength regions as seen here.[80–82]

Conflicting information is found in the literature. Arkhangelskaya[15,44] studied the thermoluminescence of CaF_2 and its isomorphs doped with Er, Ho, Tm, and Dy, using a fast heating rate (24°/min). His glow curves were consistent with the results in Sec. III. He also states that the optical absorption induced by irradiation did not bleach until the crystals were heated to 260°C. This is in obvious contradiction to the data presented in Sec. V. However, the irradiations reported by Arkhangelskaya were performed at room temperature, usually with heavy dosages of x or γ rays. In such cases the amount of damage to the crystal can be considerable, and the sample temperature is often higher than 300°K. This encourages the diffusion of interstitial fluorines and decreases the probability of a stable reduction of the rare earths according to the mechanism associated with glow peak No. 5. This behavior is actually found by Ratnam and Bose,[83] who found that the glow curve above room temperature differs considerably if the x-ray temperature is increased by 30°K, because of interstitial F^0 diffusion. It is quite likely, therefore, that none of the effects studied in this work between 80 and 350°K are included in the absorption measurements of Arkhangelskaya, and that only the more complicated high-temperature phenomena take part in his absorption bleaching data.

Contradictions are also found in the literature from paramagnetic resonance studies. Hayes and Twidell found no noticeable reduction in the concentration of Tm^{2+} after heating an irradiated crystal to the temperature at which the V_K centers bleached (138°K); instead, the divalent ions were annealed by heating the crystal to 550°C.[8] On the other hand, Sabisky observed that the concentration of Ho^{2+} produced by irradiation at 77°K was reduced by 50% after heating the sample to room temperature.[27] The reconciliation of these apparent contradictions must be found in differences in samples, techniques, or even rare earths. The crystals used by Hayes and Twidell may favor the formation of the centers responsible for higher temperature glow peaks, so that the change in concentration of Tm^{2+} at 138°K is small and difficult to detect. This is consistent with the fact that glow peak No. 5 is usually much larger than any of the peaks occurring below room temperature. Furthermore, the relative stability of Tm^{2+} to well above room temperature has already been encountered in Sec. V,B.

VII. CONCLUSION

From the experimental studies reported in this work, important information was revealed concerning the process of charge reduction of rare earths in irradiated CaF_2. Foremost was the fact that the peak temperatures of the glow curves were not characteristic of the particular rare earth, but instead were common to all the ions. Six or seven glow peaks were usually observed between 77°K and room temperature, and the temperatures at which they occurred were identical for each ion to within a few degrees. Most ions also displayed a large glow peak at approximately 300°K.

The emission spectrum of each glow peak will be presented for most of the rare earths in II, where it will be shown that the data can be interpreted in a consistent manner. Since the nature of the hole will

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determine the symmetry at the rare-earth site during the recombination event, it has been possible to formulate a model which assigns particular properties to the different hole centers. The absorption data demonstrated that these hole centers definitely exist and the holes and divalent ions bleach simultaneously as the temperature is increased. The model described in the Introduction was then shown to explain most of this absorption and thermoluminescence data. Additional evidence was cited from the literature to support this model. The centers proposed to be responsible for these effects involve different configurations of the F_2^- molecular ion, but the model does not attempt to describe the actual configuration associated with each glow peak. Detailed studies of the V_K and related centers in CaF_2 are still to be pursued. It would be interesting to study the implications of the phenomena described here to the theory of small polarons. This has also been pointed out by Keller and Murray for the case of KI.[70]

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Charge Conversion of Irradiated Rare-Earth Ions in CaF_2. II. Thermoluminescent Spectra*

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High-resolution emission spectra are observed for individual glow peaks from all the lanthanide ions in CaF_2. The crystals are irradiated with x rays (or γ rays) at 77° and subsequently heated. For a given ion, identical spectra are observed for all glow peaks below 300°K. In all cases where the spectra can be interpreted, the ions responsible for these glow peaks are in sites of cubic symmetry. For some of these ions this is the first time that cubic emission has been seen without the complication of accompanying emission from sites of lower symmetry. The emission above room temperature is always from ions of axial symmetry, which for Gd^{3+} has been identified as tetragonal. Comparison is also made between Gd^{3+} in CaF_2, SrF_2, and BaF_2. In the last two cases both cubic and trigonal symmetry are observed below room temperature.

I. INTRODUCTION

THE preceding paper[1] (henceforth to be denoted as I) described studies of the x-ray-induced (or γ-ray-induced) reduction of trivalent rare-earth ions in CaF_2 single crystals at 77°K and their subsequent thermal oxidation on heating. Changes in optical absorption spectra that accompanied peaks in the "glow curves" were monitored and a model of the electronic processes was proposed. To a large extent that model made use of the emission spectra to be reported in this paper.

Unusually high-resolution thermoluminescent spectra were obtained for low-radiation dosages by using a slow heating rate and a cooled photomultiplier. The spectra of individual glow peaks could be recorded by heating the crystal slowly (after irradiation) and scanning the spectrometer through each glow peak one or more times. For all but the weakest of peaks several passes could be made and the results of each compared. Since the total emission of the glow peak, integrated over wavelength, was being monitored at the same time, relative changes in the intensities of emitted lines during the course of a single glow peak could be monitored, as well as changes from one glow peak to the next. When the spectra for several passes through the same glow peak were normalized to a standard value (usually the maximum of the integrated glow peak), no changes in the spectral distribution of the emission were seen, to within the accuracy of the intensity measurements (approximately 10%). Thus, the spectra were found to be relatively "pure"—different species of ions emitting at different rates were never found within a single glow peak. However, important differences in the spectra were found from one glow peak to another. In general, these were differences in the site symmetry of the emitting trivalent rare-earth ion. For most of the glow peaks below room temperature the rare earth is found in a cubic site. In some cases, where the transition probability for such emission is strongly forbidden, all the emission consists of vibrationally induced transitions. The large glow peak that is found for most of the rare earths at about 330°K consists of trivalent

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