PHYSICAL REVIEW B VOLUME 23, NUMBER 4 15 FEBRUARY 1981

X-ray-induced thermoluminescence centers in CaF_2:Ho^{3+}

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(Received 11 July 1979)

The luminescence spectrum of as-received CaF_2Ho^{3+} at 77 K and the thermoluminescence spectra of the same crystal in the spectral region of 5300–5650 Å have been obtained. In a comparison between these spectra, it was found that the spectral compositions of the luminescence and the 328-K glow emission are essentially identical. A tentative physical model is proposed to explain this phenomenon. Based on this evidence, we conclude that the luminescence and the 328-K glow emission both originated from Ho^{3+} ions situated at the original symmetry sites in the host lattice, whereas the 152-K glow emission is due to thermoluminescence centers of distorted symmetry.

I. INTRODUCTION

Thermoluminescence (TL) properties of CaF_2 crystal doped with rare-earth ions have been previously reported in many publications.[1–7] One of the main features noted in those results is that the spectral composition of TL emission is temperature dependent. The low-temperature glow emission, in general, consists of more spectral lines than that of the high-temperature one (or the luminescence spectra). Various interpretations on the subject have been given by many authors.[1–5] Merz and Pershan have concluded that the rare-earth ions initially converted to the divalent state were in cubic sites.[1] The low-temperature glow peaks were characteristic of ions in cubic sites, while the glow peaks above room temperature were tetragonal. Schlesinger and Whippy, on the other hand, have suggested that the TL emission at low temperature originated from ions in sites other than cubic symmetry and at high temperature the compensators become mobile hence leaving the Ho^{3+} in a cubic environment.[2] For the CaF_2:Dy^{3+} system, Schlesinger and Kwan have further furnished an interpretation on the basis of a mixture of both cubic and other lower symmetry sites, from which they suggested that the luminescence spectral lines only constitute a subset of the corresponding TL spectrum.[3] A fourth conclusion was drawn from a study of the CaF_2:Er^{3+} system in which the authors have suggested, without clearly defining a physical model to support it, that the low-temperature TL emission is due to cubic and tetragonal sites, while at high temperature the TL emission is due mainly to cubic symmetry sites.[5]

Temperature dependence of TL spectral composition seems to be a common effect; its interpretations given by different authors, however, differ considerably. Each model seems to be capable of explaining certain phenomena, but none of them is adequate to account for all the observed results without encountering some difficulty (a detailed discussion of this will be given in Sec. III). There are several major questions left open and not yet fully understood.

(i) It has been frequently observed that the high-temperature glow emission is analogous to the luminescence spectrum of unirradiated samples whereas the low-temperature glow emission is distinctively different.[1–7] It is not quite clear whether or not these respective spectra originate from a similar physical mechanism, and what relationship exists between these respective processes.

(ii) By applying ionizing radiation, trivalent rare-earth ions in CaF_2 can be readily reduced to their divalent state and can also be reoxidized to their trivalent state by heating.[4] This phenomenon is well known and has been thoroughly investigated. However, little is known about the details of the electron-transfer mechanism that is responsible for the reduction and oxidation processes. As the $4f$ configuration represents the normal state for most of the divalent rare-earth ions, it has been generally asserted that during the reduction process the free electron captured by the trivalent rare-earth ion turns into a $4f$ electron of the divalent state. With this assertion some question arises. For example, during the oxidation process, how can a $4f$ electron of the divalent ion be so effectively removed from the $4f$ shell, as the $4f$ shells are known to be lying deeply inside the $5s^25p^6$ shells of the xenon structure and are well shielded by the latter.[8] On the other hand, if the free electron captured by the trivalent rare earth during the reduction process did not enter the $4f$ shell, then can it be in some excited orbital and remain there for a sufficiently long time without suffering spontaneous decay? Experimental results have shown that most divalent rare earths so produced in CaF_2 are relatively stable at low temperature.[1-5]

(iii) In the CaF_2 crystal various color centers may be created upon x irradiation of the sample. A review article on the subject has been given by Hayes.[4] Several authors have suggested that formation of color centers in CaF_2 is closely related to the presence of impurity ions in the host lattice.[1,9,10] Notable examples of this are[9,11] V_k centers in CaF_2:Tm^{3+} and photochromic (PC) centers ($R^{3+}-F^-$) in various rare-earth-doped CaF_2. Some common features between color centers and the TL centers from which these low-temperature glow emissions originated have been noted. They both can be created with ionizing radiation and are stable only at relatively low temperature. These similarities seem to suggest that some correlation may exist between them. An investigation of this possibility, however, is not to be found in the literature. The present investigation is an attempt to gain some better understanding of the questions raised above.

II. EXPERIMENT AND RESULTS

The experimental method employed in this work is similar to that used by previous authors, namely, analysis of both luminescence and TL spectra. However, in the present case, more effort was made to study the luminescence spectra so that direct information concerning the initial symmetry surrounding the R^{3+} in the as-received crystal could be obtained.

In order to have a direct comparison with some previous results, an identical sample of CaF_2:Ho^{3+} crystal to that used in Ref. 2 was chosen for the present study. The crystals were supplied by Harshaw Chemical Co. and they were grown by adding rare-earth trifluoride in the melt. The concentration of Ho^{3+} ions in these crystals is about 0.4 at. %. A cleaved crystal of about $10 \times 7.5 \times 4$ mm^3 was used in the experiments.

The luminescence spectra were obtained as follows. The sample was first cooled down to liquid-nitrogen temperature (LNT) in an Andonian cryostat. A 1-kW, Oriel C-60-50 xenon lamp was employed as the exciting source. The luminescence spectra were recorded by a homemade grating spectrograph. The observed spectra were calibrated by superimposing mercury lines on the same film. Various excitation energies, ranging from 3600 to 4600 Å, were used. It was found that luminescence spectra obtained by using different excitation energies were essentially the

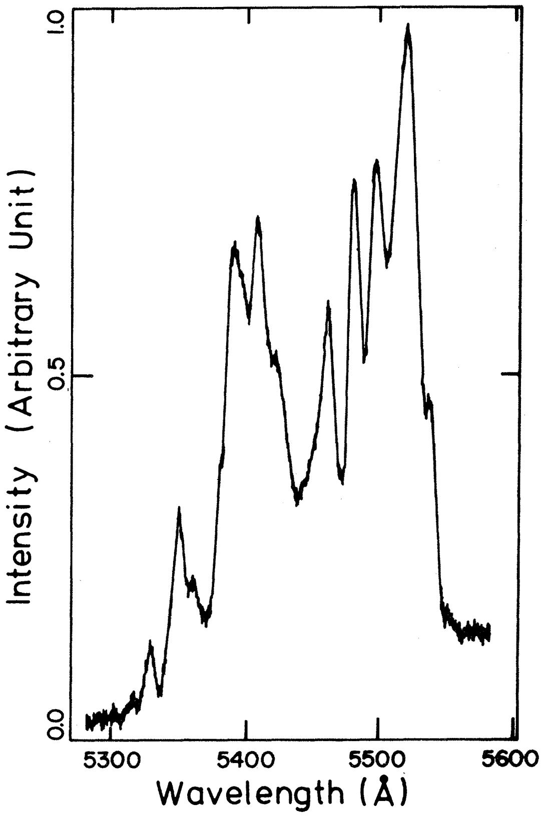

FIG. 1. Luminescence spectrum of as-received CaF_2:Ho^{3+} at 77 K, using 4447-Å light as exciting source.

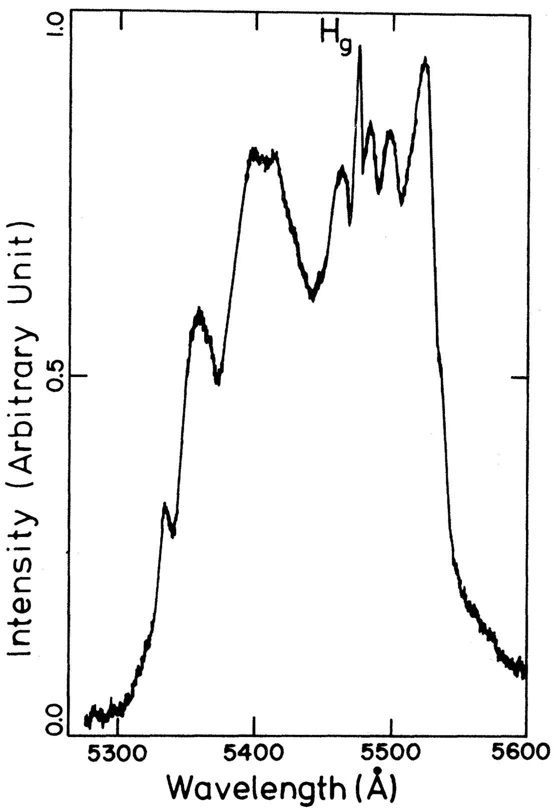

FIG. 2. Luminescence spectrum of as-received CaF_2:Ho^{3+} at 300 K, using 4447-Å light as exciting source.

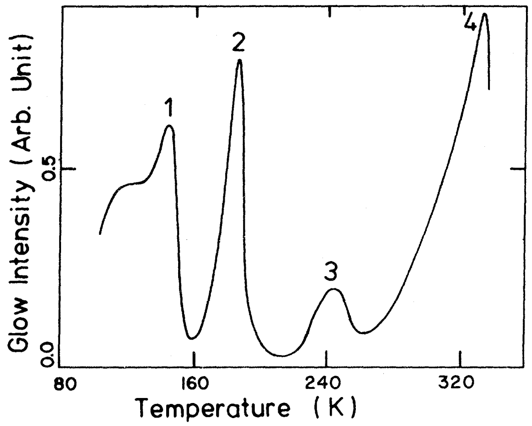

FIG. 3. Thermoluminescence glow curve of CaF_2:Ho^{3+}, x irradiated for 1 h at 77 K with heating rate of 11 K/min.

same except for some variation in the relative intensities. One of the typical results so obtained is shown in Fig. 1. Figure 2 is a similar spectrum obtained at room temperature.

The TL spectra and its glow curve were taken simultaneously in the following way. The sample was held in the crystal holder of a vacuum cryostat. It was first cooled to LNT then irradiated with x rays for one hour. The x-ray tube which had a copper target was operated at 40 kV and 20 mA. The crystal was heated with a Nichrome resistance heater, the

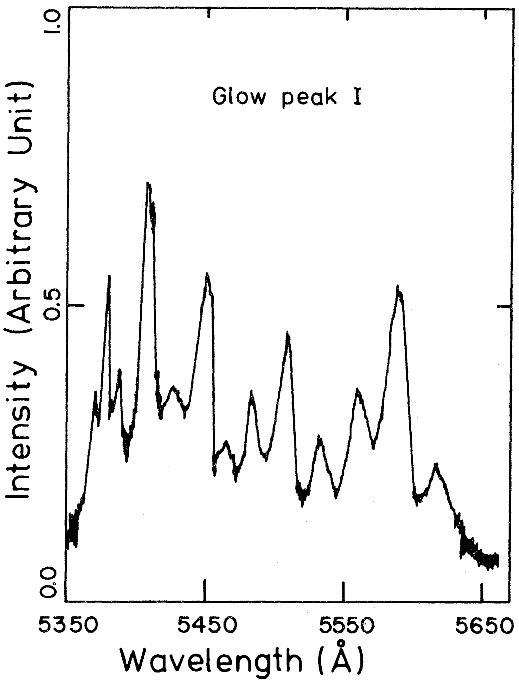

FIG. 4. Spectral composition of the thermoluminescence glow peak at 152 K (peak 1, Fig. 3).

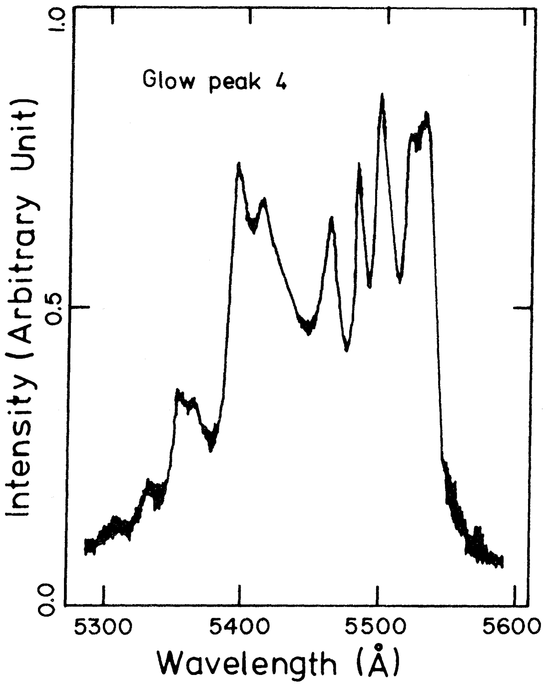

FIG. 5. Spectral composition of the thermoluminescence glow peak at 328 K (peak 4, Fig. 3).

TABLE I. Wavelengths (Å) of emission lines in thermoluminescence and luminescence spectra of CaF_2:Ho^{3+}.

Thermoluminescence Peak 1, 152 K	Thermoluminescence Peak 4, 328 K	Luminescence, 77 K
	5311	5313
	5330	5325
	5351	5346
5370	5363	5360
5382		
5389	5394	5387
5406		
5410	5414	5404
5428		5418
5452		
5466	5466	5466
5484	5483	5478
5510	5500	5496
	5519	5518
5531	5532	5534
5560		
5590		
5618		

heating rate being kept constant at 11 °C/min. TL spectra were taken photographically by placing one of the cryostat windows against the entrance slit of spectrograph. The opposite window of the cryostat was placed against an EMI6256 photomultiplier. The photocurrent was first fed to a Keithley micromicrometer and then recorded by a Hewlett-Packard chart recorder. The glow curve of $CaF_2:Ho^{3+}$ in the temperature range between 77 and 330 K is shown in Fig. 3. The spectral compositions of the TL associated with glow peaks No. 1 and No. 4 in Fig. 3 are shown in Figs. 4 and 5, respectively. TL spectra from glow peak No. 2 is similar to that of peak No. 1 but its resolution is poorer. For peak No. 3, its intensity is too weak to be measured. A summary of the wavelengths of the observed spectral lines in the TL and luminescence spectra are given in Table I.

III. DISCUSSION

In the comparison of Fig. 1 with Fig. 5 of this paper and Figs. 2(c) and 4 of Ref. 2 one can readily notice that, except for some variations in relative intensities, the compositions of the four spectra are essentially the same. This striking similarity indicates that they all originated from similar physical mechanisms. As luminescence spectra were obtained prior to x irradiation of the crystal, they must originate from Ho^{3+} ions situated at sites of original symmetry whatever that may be. This led us to conclude that the high-temperature thermal glow emission (Fig. 5) must originate from those Ho^{3+} whose immediate environment remains unchanged after x irradiation. A further comparison between Figs. 1 and 4 show that the luminescence spectrum from the unirradiated crystal is distinctively different from that of the low-temperature thermal glow emission. The former has 12 emission lines whereas the latter consists of at least 14 recognizable lines, but nevertheless, they both cover almost the same spectral region. This low-temperature thermal glow emission cannot be arising directly from color centers that may be present after x irradiation, as all the known spectra of color centers in CaF_2 cover quite different spectral regions.[4] Furthermore, they are all of a structureless broad-band nature, whereas in the present case, numerous structures are present. It seems that the only reasonable conclusion one may draw is that, upon x irradiation of the sample, certain environmental changes surrounding some Ho^{3+} ions in the host lattice occurs. As a result the original symmetry surrounding these Ho^{3+} ions is distorted. During the TL process, those ions whose immediate environment has been distorted, therefore yield spectra of a character different from that of the unaffected sites. Details of the distorted symmetry are not known. However judging from the number of spectral lines present in each of the spectra, we believe that these new sites created by x irradiation have a symmetry lower than that of the initial ones.

As the trivalent rare earths enter the fluorite lattice by substituting divalent Ca^{2+} ions, additional negative charge compensators are required. Several different types of charge compensation have been reported in the past. However, based on theoretical calculation[12] as well as recent experimental investigations,[13–16] many authors have concluded that the trivalent rare earths in CaF_2 are found predominantly at tetragonal sites, and charge compensation is provided by interstitial F^- ions. There is little doubt about this conclusion. Thus we make the same assumption. Recent studies[14,15] have also shown that as the rare-earth concentration increases, formation of ion-defect clusters in CaF_2 becomes very pronounced. One of the main features of clustering is that the spectra consist of generally broader lines. In view of our observed spectra as well as the Ho^{3+} concentration employed in the present case, it seems that some degree of clustering in our sample is very likely. However, for this investigation, we believe that the effect of clustering on our results is not significant.

Attempts were made to interpret the present results by using models suggested by previous authors. However, considerable inconsistencies exist between the observed data and those models. Notable examples of this are given in the following. If the original symmetry sites associated with R^{3+} in the as-received crystal were cubic as suggested by Merz and Pershan,[1] then according to their model, it would be difficult to explain why their fluorescence spectra such as in the cases of $CaF_2:Er^{3+}$ and $CaF_2:Tm^{3+}$ showed tetragonal symmetry, since neither x irradiation nor electron-hole recombination are involved in the fluorescence process. On the other hand, if one assumes that the original symmetry sites associated with R^{3+} were not cubic as suggested by Schlesinger and Whippy,[2] then from Fig. 1 of this paper and Fig. 2(c) of Ref. 2, one can readily recognize that the original symmetry sites associated with R^{3+} are identical to that associated with the 333 K glow peak of Ref. 2, which the authors have claimed to be cubic. This is obviously inconsistent since according to the model, such cubic sites are formed only after the compensators have moved away from the R^{3+} sites. Finally, if the original symmetry sites were a mixture of both cubic and other lower symmetries,[3,5] again it would be difficult to understand why in the luminescence spectra (see Figs. 2 and 3 of Ref. 3 and Figs. 3 and 4 of Ref. 5) only a portion (subset) of the total emission was observed. In view of the various discrepancies, it is apparent that an alternative model is essential in order to have a consistent explanation of the observed results. Based on analysis of the experimental results of this and previous works, we propose the following physical model as a qualitative explanation of the observed effect. However, we should point out that the proposed model is only tentative. For a quantitative and more comprehensive interpretation of the results, further theoretical and experimental studies of the subject are obviously needed.

IV. PHYSICAL MODEL

The original symmetry sites associated with the R^{3+} ions are predominantly tetragonal with interstitial F^- ions as charge compensators. Substitution of divalent Ca with trivalent rare earth leads to the presence of electron traps in the host crystal. Upon x irradiation of the sample at LNT, two different types of TL centers are created. One type is formed following the usual reduction process, namely an electron is trapped at the R^{3+} and the latter is reduced to a metastable R^{2+} state. We define this as a type-I center. Another type of center is formed when an F center is created at the nearest-neighbor positions of some R^{3+} and subsequently an electron is trapped in the vicinity of the R^{3+} in question. X-ray-induced F centers in CaF_2 have been observed previously by several authors.[4,17] In the present case, we assume that some of the F centers so formed are at positions immediately next to an R^{3+} ion. Thus, a complex, consisting of an F center and an R^{2+} is formed.

The presence of an F center in the immediate vicinity has two effects on the neighboring R^{2+}. First, it alters the regular environment and hence distorts the original symmetry surrounding the R^{2+} in question. Secondly, the binding force between the trapped electron and the R^{3+} is believed to be weakened. In the complex, we assume that there is only weak interaction between the F centers and the R^{2+}, therefore the essential character of each constituent is still preserved, i.e., the F-center electron interacts principally with four nearest-neighboring cations (three Ca^{2+} and one Ho^{3+}) and six F^- ions[18] and the rare-earth-trapped electron is still essentially bound to the Ho^{3+} ion. Such a complex is defined as a type-II center. Similar complexes such as photochromic (PC) color centers have been observed in several rare-earth-doped CaF_2 crystals.[11,19] However, in the present case the proposed F center-R^{2+} complex is not identical to a PC center.

The proposed complex differs from a PC center in several respects. It is known that in rare earths the effective potential energy of the $4f$ electrons possess two minima.[20] One of the minima, corresponding to the potential energy of a normal f electron, is a narrow, deep valley that lies inside the $5s^25p^6$ closed shells of the xenon structure. The second minimum lies outside the closed shells and is a shallow one. The two valleys are separated by a high potential barrier. Because of the presence of a high potential barrier between them, the chance for a slower free electron to be trapped at the second valley is considerable. Based on experimental results as well as the above consideration, we conclude that, during x irradiation, some electrons released from F^- ions are subsequently trapped in the second potential valley of the $4f$ configuration of the rare earth in question. In order to distinguish these electrons which are trapped at the second valleys from those normal f electrons which are associated with the inner valleys, we tentatively call the former "metastable f electrons" and denote them as f^*. As the depth of the second valley is only about 1 eV (Ref. 20), the release of a metastable f^* electron from the R^{2+} is understandably easy and requires considerably less energy than the release of an electron trapped in the inner valley. Experimental results have, in fact, shown that for most rare earths, the third ionization potentials are well above 20 eV,[21] whereas during the TL process, the thermal energy available for oxidation of R^{2+} to R^{3+} is only a fraction of an electron volt.

Judging from the rapid heating rate, and the intense TL emission, the mechanism that is responsible for the TL process appears to be quite effective. It is very unlikely that during the process, a normal $4f$ electron could be so effectively removed from the inner f shell with thermal energy of only a fraction of an electron volt. Undoubtedly, the presence of nearby holes will have certain effects on the process. However there are some 3 orders of magnitude difference between the third ionization potential and the thermal energy available during the TL process. It is still difficult to understand how the process can occur. In the case of PC centers, the situation is different. Where the rare earth involved is required to have a single d electron in the divalent crystal-field ground state, so that during the reverse photochromic process the $5d$ electron can be readily removed from the $4f^n5d$ configuration. In the present case, since all the divalent rare earths under consideration have the same $4f$ configuration as their ground state, we therefore propose that the TL process in the present case is accomplished by the removal of an f^* electron from the metastable $4f^{10}f^*$ configuration rather than from the normal $4f^{11}$ configuration of the divalent Ho. In addition, experimental results also show a considerable difference between a type-II center and a PC center in their thermal behavior. The former are only stable below 180 K, whereas the latter can be stable up to 300 K.[11]

In summary, the observed results of TL in CaF_2:R^{3+} may be described as follows: Upon x irradiation of the sample at LNT, two types of TL centers were created. Type-I centers were formed following the usual reduction process by reducing R^{3+} to the R^{2+} state. X rays also induced F centers in the host lattice. Some of the F centers were formed at positions immediately next to an R^{3+} ion and subsequently an electron was trapped at the R^{3+}

TABLE II. A summary of TL and luminescence spectra observed in $CaF_2{:}R^{3+}$.

Trivalent rare earth	Spectral region (Å)	No. of component in low-temp. glow emission	No. of component in high-temp. glow emission	No. of component in luminescence emission	Normal config. of R^{2+}	Third ionization potential (eV)	Ref.
Pr^{3+}	4700–5000	28 (110 K)[a]	16 (400 K)	16 (LNT)	$4f^3$	20.96	1,6
Dy^{3+}	4700–5900	30 (149 K)	Two broad bands[b] (410 K)	15 (LNT)	$4f^{10}$	21.83	3,7
Ho^{3+}	5300–5650	16 (155 K)	11 (328 K)	11 (LNT)	$4f^{11}$	22.10	2 and this work
Er^{3+}	5300–5650	18 (114 K)	8 (300 K)	8 (LNT)	$4f^{12}$	23.00	1,5
Tm^{3+}	4350–4600	15 (150 K)	? (320 K)	6 (LNT)	$4f^{13}$	24.10	1

[a] All figures in brackets are the temperature at glow peak.

[b] The peaks of the two bands coincide approximately with the respective centroids of the spectra shown in Figs. 3(a) and 3(b) of Ref. 3.

ion in question thus reducing it to its R^{2+} state. Through their weak interaction, the R^{2+} and the F center form a complex. However, the essential characters of each constituent in the complex are still preserved. Such a complex is defined as a type-II center. In both types of centers, the process of reduction of R^{3+} to its R^{2+} state is believed to be accomplished by trapping a free electron into the shallower potential valley which lies outside the closed $5s^25p^6$ shells of the R^{3+} ions, rather than in the inner $4f$ shell as was generally suggested. The presence of an F center in the immediate vicinity has two effects on the R^{2+} ion. It distorts the original symmetry surrounding the R^{2+} and weakens the binding force between the trapped electron and the R^{3+} in question. Because of the latter effect, the type-I center is relatively more stable than the type-II center. Upon heating the crystal, electrons trapped at R^{2+} in type-II centers are released first and leave behind them an excited R^{3+} state. Following this the excited R^{3+} undergo transitions to their ground states and hence give rise to the observed emissions characteristic of R^{3+} situated in a symmetry site that differs from the original one because of distortion produced by the nearby F center. As the temperature increases, the population of the type-II center decreases rapidly and at the same time more thermal energy is now available for the release of electrons trapped at R^{3+} in type-I centers. As no distortion is present in the type-I center, only those emission lines, which originated from those R^{3+} associated with the original symmetry sites, were observed in the high-temperature glow. This explains why the spectral composition of the high-temperature glow emission has the same character as that of the luminescence spectra. Such examples can be seen from Figs. 1 and 5 of this paper, Figs. 3(b) and 4(b) of Ref. 5, and Fig. 7 of Paper II in Ref. 1. One can also notice in these figures that the number of components in the high-temperature glow emission are considerably less than that of the low-temperature case, indicating that the symmetry in the latter case is indeed lower than the original one as we suggested. A summary of similar effects observed in various rare-earth-doped CaF_2 is given in Table II.

Another point in support of the present model is the spectral composition of room-temperature (RT) phosphorescence as shown in Fig. 4 of Ref. 2. Its spectrum is essentially identical to that presented in Figs. 1 and 5 of this paper. As the spectrum was obtained by x irradiation of the sample at RT, it is clear that because of the relative instability of the type-II centers, creation of such centers at RT is no longer possible and only those type-I centers associated with the original symmetry are therefore still sufficiently populated to give rise to observable emissions.

In conclusion we should like to emphasize that the physical model presented in this paper is tentative. Our experimental results are insufficient to draw a definite conclusion and further investigation on the subject is obviously needed. The main aim of this paper is on the one hand, to present our experimental results, and on the other, to point out some of the existing problems on the subject and hopefully to serve the purpose of stimulating some interest among other investigators in the field. As most of the previous investigations have been experimental and of a qualitative nature, some fundamental studies of the basic mechanism would be much desired.

ACKNOWLEDGMENT

One of us (S.T.P.) wishes to thank Dr. M. Schlesinger for his valuable guidance and suggestions during the course of the first stage of this work.

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