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Optical properties of radiation defect centers involving single and paired Mn^{2+} centers in CaF_2:Mn

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Optical evidence of paired Mn^{2+} centers has been observed in CaF_2:Mn by time-resolved laser spectroscopy. The paired Mn^{2+} center is associated with a peak shift of the Mn^{2+} emisssion towards longer wavelength and a faster component of decay of 500 μs along with a slow decay of 48 ms due to a single Mn^{2+} ion. It appear that this center forms a Mn^{2+}-*F*-center-Mn^{2+} complex when the material is γ irradiated. This complex is associated with a thermoluminescence peak near 360 °C and an optical-absorption band near 300 nm. A conversion from a Mn^{2+}-*F*-center-Mn^{2+} complex to an *F*-center-Mn^{2+} complex is observed in phototransferred thermoluminescence and in photobleached optical-absorption spectra.

I. INTRODUCTION

Defect production in CaF_2 has been studied over the last three decades. By now it is well known that the colorability of undoped CaF_2 is quite inefficient compared to the alkali halides. Also, primary defects such as *F* centers, self-trapped hole centers (V_K centers), and *H* centers (holes trapped at interstitial anion sites) are unstable well below room temperature. However, on doping with trivalent rare-earth ions the colorability increases significantly[1] and some of these primary defect centers appear to be stabilized well above room temperature. For instance, V_K centers stabilized by cation vacancies can remain stable up to room temperature. Similarly, *F* centers stabilized by impurity centers are found to exist well above room temperature. Beaumont *et al.*[2] believe that nonparamagnetic hole centers can be stable to temperatures as high as 450 °C. It is the stability of these ionic defects which is thought to play an important role in the thermoluminescence (TL) mechanisms in Mn^{2+}-doped CaF_2. Mn^{2+}-doped CaF_2 is a widely used material in thermoluminescence dosimetry (TLD) with properties very desirable in a TLD system. This material responds to a low dose of 0.1 mGy and possesses a TL peak at approximately 285 °C which is stable at room temperature. However, the origin of this dosimetry peak and the recombination mechanism leading to the luminescence due to the ${}^4T_{1g}({}^4G)\rightarrow{}^6A_{1g}({}^6S)$ transition of Mn^{2+} ions is still unclear. A suggested[3] model involves the destruction of *F* centers by some types of hole centers which become unstable at this temperature, and subsequent transfer of released energy to Mn^{2+} leading to thermoluminescence at 285 °C. Another possible explanation could be that upon irradiation Mn^{2+} changes its charge state to Mn^{+} after capturing an electron and the hole that is left behind forms a trapped hole center. Thermal release of this hole occurs at ~285 °C and its recombination with the trapped electron at a Mn^{2+} ion leads to the Mn^{2+} thermoluminescence with associated TL peak at 285 °C. Although Alcala *et al.*[4] found evidence of Mn^{+} at low temperature, no evidence of Mn^{+} ions at room temperature or higher has been reported to our knowledge.

The validity of these models necessitates the stability of *F* centers or hole centers or both at this high temperature. McKeever and co-workers studied[5–8] this material extensively, and believe that *F* centers are stabilized by Mn^{2+} in CaF_2:Mn, and play a key role in the TL mechanism. However, the lack of clear knowledge about the TL mechanism, defect formation, and defect stability at high temperature is the primary reason why a problem that has been increasingly observed over the last decade in this system is not well understood. This problem, which has frustrated both the researchers and the users of this TLD system alike, is known as a zero dose problem. In the zero dose problem, TLD's without exposure to radiation read a dose of approximately 0.1 mGy or more above the natural background level when stored in the dark (dependent on the prior exposure history of the sample). Over the last few years much effort has been spent in identifying the cause of this chronic problem. Recently Chakrabarti, Sharma, and Mathur[9] identified a deeper trap which partially survives on heating the TLD's up to 400 °C. They have further shown that, unless this trap is completely depopulated, the 285 °C dosimetry peak is regenerated without further exposure to radiation, thus causing the zero dose problem. The exact mechanism of carrier transfer from the 400 °C trap to the dosimetry trap is not known at this time. Furthermore, it can be seen that by bleaching of this higher temperature trap by a 337-nm nitrogen laser [or the 266-nm fourth harmonic of a Nd:YAG (yttrium aluminum garnet) laser], carriers can be phototransferred to the dosimetry trap which indicates that both these traps are of similar nature. Once the high-temperature trap is depleted (optically or thermally), the zero dose problem is removed.

Optical absorption after irradiation of this material shows a broad absorption peak in the uv region, which

McKeever and co-workers[7,8] suggested is due to Mn^{2+} stabilized F centers which could not be annealed out by heating to 400 °C. We have seen that, with 337-nm laser bleaching followed by 400 °C annealing, this optical-absorption band can be destroyed. We explain all of these results in the light of Mn^{2+}-Mn^{2+} pairing in this material at high Mn^{2+} concentration. To our knowledge, this is the first evidence of Mn^{2+}-Mn^{2+} pairing in CaF_2:Mn by time-resolved spectroscopy. In dosimetric grade CaF_2:Mn, with 3% Mn^{2+} ions, paired Mn^{2+}-Mn^{2+} centers are significant enough to produce the high-temperature TL peak of greater intensity than the dosimetry peak at low doses of 1 mGy or lower. We observe a direct correlation between the Mn^{2+} concentration in the material and (1) Mn^{2+}-Mn^{2+} pairing, (2) thermoluminescence from the deep trap, and (3) optical absorption after irradiation. We propose a model based on the concept of paired Mn^{2+}-Mn^{2+} centers and Mn^{2+}-F-center-Mn^{2+} complexes which explains our observed TL and optical absorption in this material.

II. EXPERIMENTAL DETAILS

Single crystals of CaF_2 doped with varied amounts of Mn^{2+} ions (0.1–5.0 mol %) in the melt were obtained from Optovac, Inc. and used in optical absorption and fluorescence studies. For thermoluminescence measurements these single crystals, as well as TLD chips which are nominally 3% Mn^2-doped CaF_2, were obtained from Victoreen, Inc. Neutron activation analysis on similar CaF_2:Mn crystal shows that, at concentrations of 3%, only half of the manganese concentration added to the melt is actually incorporated in the lattice.[10] Optical-absorption measurements were made by a Varian 2300 Spectrophotometer. Fluorescence measurements were made using an EG&G PARC model 1421 optical multichannel analyzer with a silicon diode array cooled to −25 °C. A nitrogen laser with a 10-ns pulse width and 0.3-mJ pulse energy was used for excitation. For laser bleaching of the deep trap and phototransfer of carriers, the same nitrogen laser source and also a Q-switched Nd:YAG laser of pulse width 10 ns and energy 6 mJ at its fourth harmonic were used. Thermoluminescence measurements were made using a Harshaw 4000 reader with heating rate 5 °C/s. X-ray photoelectron spectroscopy (XPS) was investigated by using a Kratos 300 instrument with a manganese anode and without an x-ray monochromator. The luminescence decay was detected by an EMI S20 photomultiplier tube in conjunction with an Instrument SA, Inc. monochromator. A ^{137}Cs source was used for γ irradiation.

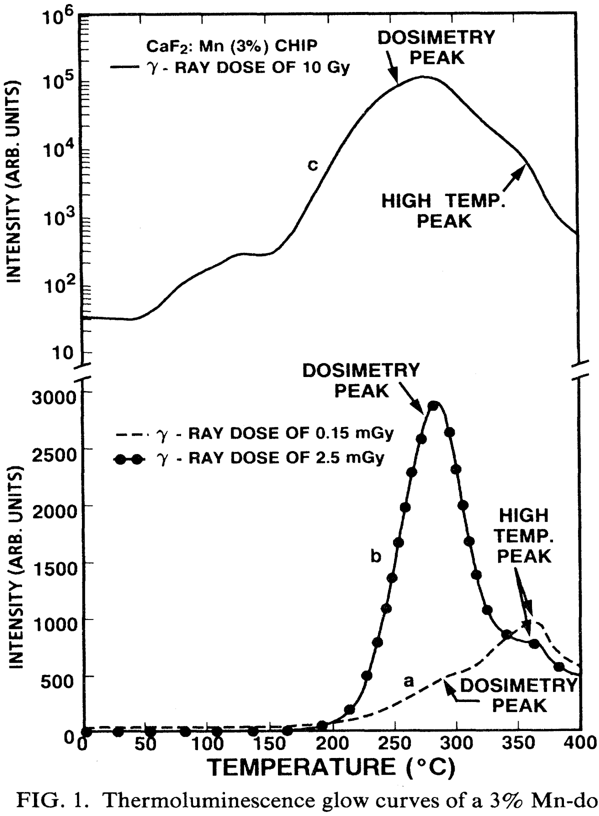

FIG. 1. Thermoluminescence glow curves of a 3% Mn-doped CaF_2 TLD chip after exposure of three different doses as given in the legend of the figure. One notes that only the high-temperature peak grows slowly with dose until very large doses are given, as is shown in curve c.

Time-resolved measurements were made in the gated mode of the optical multichannel analyzer (OMA) with an EG&G PARC model 1304 pulse amplifier optically triggered from the exciting laser source. The slow component due the single Mn^{2+} center was observed after a delay of 1 ms as by this time the fast component has already decayed. The faster component was measured with a 1-ms gate, and a 10-ns delay was given to avoid detection of the exciting laser which has a pulse duration of 6–10 ns.

III. EXPERIMENTAL RESULTS

Figure 1 shows thermoluminescence (TL) glow curves of a nominally 3% Mn^{2+}-doped CaF_2 TLD chip irradiated at different doses. Curve a is after a 0.15-mGy dose, curve b is after a 2.5-mGy dose, and curve c is after a dose of 10 Gy. At the low dose of 0.15 mGy, the high-temperature peak at 360 °C predominates the glow curve. The intensity of this peak remains roughly the same until a dose of 10 Gy or more is given. Then the high-temperature peak begins to grow again. The dosimetry peak, on the other hand, grows approximately linearly with dose. At a dose of a few mGy, the dosimetry peak completely masks the high-temperature peak and the TL glow curve appears to have only the dosimetry peak. Due to the unusual growth nature of the high-temperature peak and the fact that it remains masked by the dosimetry peak at a dose of few mGy, this peak has not been discussed by researchers so far. However, this peak plays a significant role in the understanding of the TL mechanism in this material. We propose that the zero dose problem encountered in using this material is due to the existence of this peak. As is seen in Fig. 1, a portion of the high-temperature peak continues beyond 400 °C, and heating in a standard TLD reader does not deplete this peak completely. This partially depleted high-temperature peak regenerates the dosimetry peak by transferring carriers to the dosimetry trap. In fact we

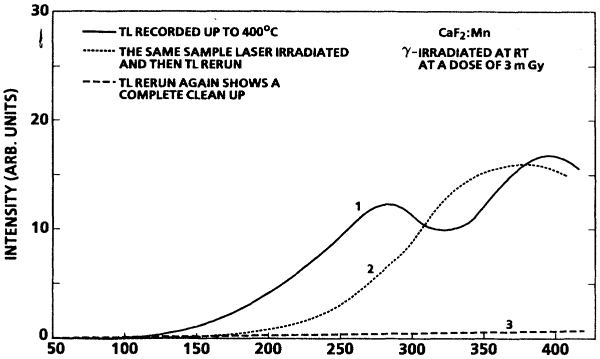

FIG. 2. TL glow curves of CaF_2:Mn showing the effect of laser bleaching. Curve 1 is a glow curve after a dose of 3 mGy. Curve 2 shows the effect of phototransfer caused by 337-nm laser light transferring carriers from a high-temperature trap which was not completely cleared in the TL run to 400 °C. Curve 3 shows that one more TL run to 400 °C following phototransfer cleans the TLD chip.

have observed immediate regeneration of the dosimetry peak after a TL readout, and with time the dosimetry peak is found to increase in intensity while the high-temperature peak decreases proportionately. However, the high-temperature trap can be depleted completely by phototransferring carriers to the dosimetry trap with the aid of a near-uv (337 nm) laser light. Once the phototransfer of carriers to the dosimetry trap takes place, one more TL readout to 400 °C cleans the glow peaks. Figure 2 shows these results. Figure 2, curve 2 shows the phototransferred thermoluminescence (PTTL) after the sample was exposed to 337-nm laser light subsequent to the first TL measurement (Fig. 2, curve 1). This PTTL glow curve shows the high-temperature peak at a slightly lower temperature and the dosimetry peak at a slightly higher temperature as compared to the glow curves in Fig. 1. It should be noted that the shifting of the high-temperature peak to lower temperature on optical irradiation enables one to clean the material of the deeper trap properly in the next readout to 400 °C. This is shown in Fig. 2, curve 3. Heating beyond 400 °C succeeds in cleaning a TLD of both the TL peaks, but repeated heating at high temperature changes the sensitivity of a TLD chip and the TLD cannot be reused. The phototransfer, being a cold process, is much more desirable.

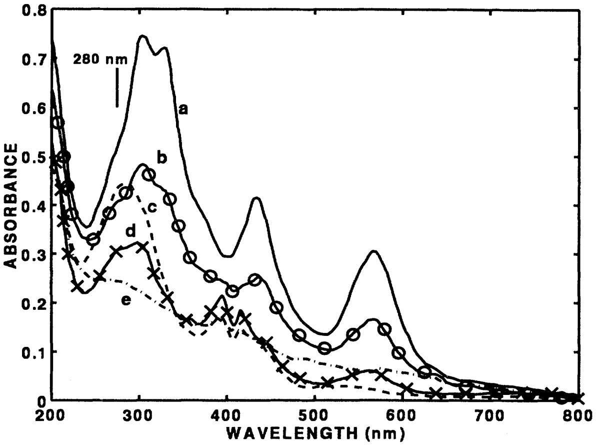

FIG. 3. Optical absorption of radiation-induced centers in 3% Mn-doped CaF_2. Curve *a* is the absorption after a γ-ray dose of 250 Gy. Curve *b* (open circles) is the absorption of the sample in *a* after bleaching for 45 min with the 337-nm laser. Laser bleaching followed by annealing to 350 °C (curve *e*, dot-dashed line) destroys the optical absorptions. The 280-nm absorption (as indicated) is not removed by the laser bleaching. Curve *c* shows the optical absorption after the dose of 250 Gy followed by annealing at 310 °C. The absorption peaks at approximately 300 nm are destroyed by heating to 310 °C. These peaks reappear on photobleaching by 337-nm laser light (curve *d*).

Allen and McKeever[8] observed PTTL earlier. However, they did not identify the TL peak from which the phototransfer to the dosimetry peak takes place. Chakrabarti, Sharma, and Mathur[9] observed two more TL peaks in this material at 450 and 512 °C. However, they observed that the phototransfer takes place from the peak at 360 °C (as much as 30 °C peak shift to higher temperature has been observed depending on the heating rate, thickness of the crystal, and the TLD chip used). This 360 °C peak is referred to as the high-temperature peak in this paper. The dosimetry peak regenerates at the expense of this peak only. Figure 3 shows optical-absorption spectra of a single crystal of CaF_2 doped with 3% Mn^{2+} after γ irradiation and after laser bleaching and annealing. Curve *a* is the optical-absorption spectrum after the crystal is irradiated to a γ-ray dose of 250 Gy. The optical absorption observed at 280 nm and its relation to our TL data is the focus of this study. After the first optical-absorption measurement, the sample was bleached by the 337-nm nitrogen laser for 45 min and the absorption measurement was then performed. Curve *b* represents the result. The same crystal was then annealed to 350 °C for 45 min and the optical-absorption measurement was made again. The absorption bands disappeared, as shown by curve *e*. Figure 3, curve *c*, shows the optical absorption of a different 3% Mn^{2+}-doped crystal (cut from the same boule) and γ irradiated at a dose of 250 Gy followed by annealing to 310 °C for 10 min. Annealing to 310 °C, just over the dosimetry TL peak, reduces the two-peak (280 and 300 nm) structure of the optical-absorption (OA) bands to one peak at 280 nm. The crystal was then exposed to the 337-nm laser light for 30 min. The second band reappeared at 300 nm, as is seen in Fig. 3, curve *d*. In Fig. 4 we show similar optical-absorption results, except this time the 266-nm Nd:YAG laser was used for photobleaching. The wavelength of the 266-nm laser is closer to the 280-nm OA band than the 337-nm nitrogen laser.

On optically exciting a γ-irradiated CaF_2:Mn crystal with the 337-nm laser, we observe Mn^{2+} emission which persists for several minutes even after the laser is turned off. Once the excitation is removed the luminescence intensity I is found to decay following approximately second-order decay kinetics with the set point for the start of the second process depending on the Mn^{2+} concentration in the sample. This can be represented in a convenient way by plotting $I^{-1/2}$ versus time. For a

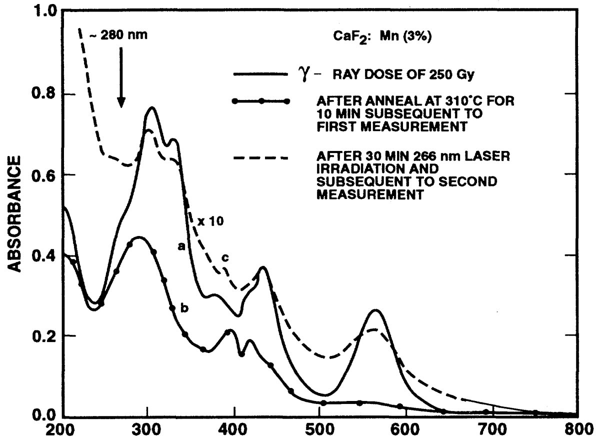

FIG. 4. Optical-absorption spectra showing annealing effect and photobleaching by 266-nm laser light.

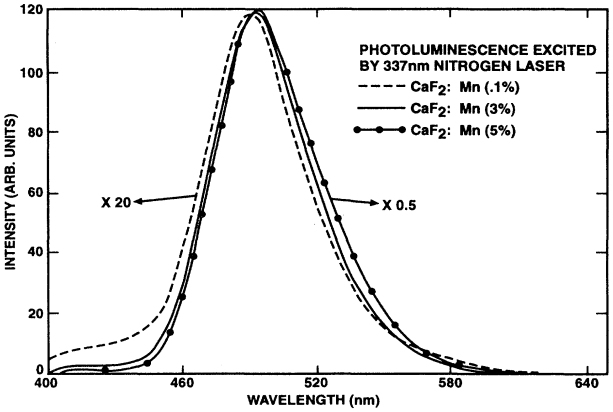

FIG. 6. Photoluminescence spectra of CaF_2:Mn showing peak shift of emission with Mn^{2+} concentration.

second-order decay such a plot would be a straight line.[11] Figure 5 shows the results of 3% and 0.1% Mn^{2+}-doped single crystals after they were irradiated to a dose of 720 Gy and excited by 337-nm laser light. A convenient way to establish a characteristic time for the second-order behavior to be apparent is the time at which the extrapolated straight line part of the $I^{-1/2}$-versus-t curve deviates by more than approximately 2% from the actual decay curve. As the Mn^{2+} ion concentration is increased from 0.1 to 3% in the sample, this characteristic time for the start of the second-order process is delayed from approximately 110 to 200 s. This result indicates that the manganese concentration in the material directly influences the trapping and retrapping mechanisms. Figure 6 shows the manganese emission for various Mn concentrations and the peak emission shifts to longer wavelengths by approximately 5 nm for higher Mn concentration. Time-resolved emission spectra of dosimetric grade 3% Mn^{2+}-doped CaF_2 is shown in Fig. 7. By the proper choice of gating, fast and slow components of the emission have been separated in the time-resolved spectra. We have observed a fast component with a decay of 500 μs compared to the slower component of 48 ms.

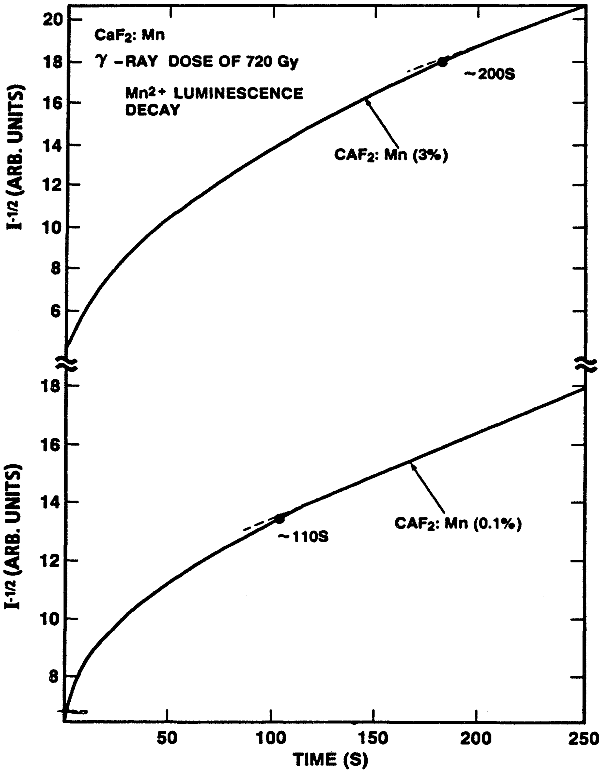

FIG. 5. The inverse square root of the Mn^{2+} luminescence decay intensity ($I^{-1/2}$) as a function of time. A characteristic time at which approximately second-order behavior becomes apparent is indicated for each curve.

IV. DISCUSSION

In order to understand the defect production and the origin of the dosimetry peak of CaF_2:Mn, McKeever and co-workers studied[5–8] optical-absorption spectra of γ-irradiated CaF_2:Mn. They observed a broad optical-absorption band similar to the one shown in Fig. 3, curve *a*. McMasters, Jassemnejad, and McKeever[5] observed OA bands at 325, 385, and 560 nm in undoped γ-irradiated CaF_2 crystal. The 325- and 385-nm bands are due to the V_K and F centers, respectively, probably stabilized by rare-earth impurities present[5] in the so-called undoped CaF_2 crystal. The presence of rare-earth impurities in this material produces photochromic centers[12] on irradiation which are divalent rare-earth ions with an F center in a [111] direction. The ~560-nm OA band is due to the M centers or impurity-associated M centers. They observed[5–8] additional OA bands at 280, 300, and ~425 nm in γ-irradiated CaF_2:Mn crystal. McMasters, Jassemnejad, and McKeever[5] observed that the optical absorption in CaF_2:Mn due to all other centers is suppressed when the Mn concentration in the material is increased. Both the 280- and 300-nm OA bands, particu-

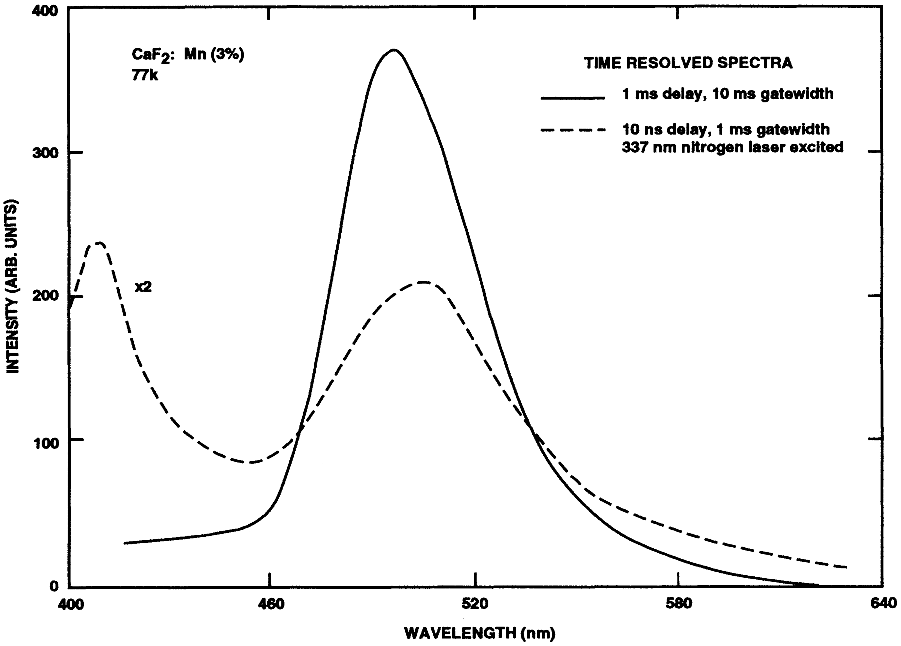

FIG. 7. Time-resolved spectra of 3% Mn^{2+}-doped CaF_2.

larly the 280-nm band, continue to exist on annealing the material to 400 °C, when the concentration of Mn in the material is increased to 1% or greater. McKeever and co-workers[7,8] assigned this broad OA band near 300 nm to an F_A center or an F center perturbed by the presence of a nearby Mn impurity. If the same F_A center is responsible for the dosimetry peak, then the OA band would disappear once the material is annealed over the dosimetry peak at 285 °C. Our studies show that the optical absorption observed after γ irradiation can be destroyed if the sample is bleached with nitrogen laser light for 45 min, and heated to 350 °C (just above the dosimetry peak). This is shown in Fig. 3, curves *a* and *b*. This result has a direct correlation with our results for laser-induced phototransfer followed by annealing of the TL traps (Fig. 2). After phototransfer of the carriers from the deeper trap to the dosimetry trap, all TL peaks can be destroyed by heating to 400 °C. Similarly, after laser bleaching of the OA band, this 280-nm band can be destroyed by heating to 350 °C. We believe that the center responsible for the high-temperature ~360 °C peak also has an OA band in the uv region, and it appears that the 280-nm OA peak is due to this center.

Recently, Lewandowski and Wilson[13] carried out lattice-embedded multiconfigurational self-consistent-field (SCF) calculations of the Mn-perturbed F-center complex in CaF_2:Mn. These calculations predict a group of localized levels that are responsible for absorption in the region of 298–341 nm. Our optical absorption (Fig. 3) does exhibit two strong absorption bands at approximately 300 and 320 nm. (One also notes that Lewandowski and Wilson's work does not include photon interactions.) The optical absorption we observe at 280 nm may therefore be due to a different defect complex. We attribute this to a Mn^{2+}-F-center-Mn^{2+} complex due to the possibility of Mn^{2+} aggregation.

It can be argued that since the phototransfer is associated with regeneration of the dosimetry peak (Fig. 2, curve 2), one should observe a regeneration of the OA associated with this center which McKeever and co-workers[7,8] suggested as an F_A center. In order to investigate this we performed a methodical annealing and laser bleaching of the OA spectra. Figure 3, curve *c* shows optical absorption of a 3% Mn-doped CaF_2 crystal γ-irradiated at a dose of 250 Gy, then annealed at 310 °C for 10 min to remove the dosimetry peak but not the high-temperature peak. On annealing the irradiated crystal, the 300-nm OA peaks as observed in Fig. 3, curve *a*, is destroyed along with the 325-nm OA band also observed[5] in undoped CaF_2. But the peak at 280 nm survives. The crystal was then laser bleached with the 337-nm nitrogen laser for 30 min. The peak at 300 nm now reappears (Fig. 3, curve *d*). This result can be correlated with the regeneration of dosimetry peak (Fig. 2, curve 2) by the phototransfer process which strongly indicates that the second peak at 300 nm in irradiated CaF_2:Mn is due to the same center that is responsible for the dosimetry peak in the TL glow curve.

Since the center responsible for the deeper trap (360 °C peak) has OA peaking at 280 nm, it is expected that the use of 280-nm light should cause efficient phototransfer. We have chosen 337-nm laser light for phototransfer from this broad band (Fig. 3, curve *b*) as the 337-nm laser light can bleach the chip penetrating through the glass bulb which encapsulates a chip in a dosimeter. For wavelengths shorter than 337 nm, the light is heavily absorbed by the glass envelope and one has to break the glass bulb to ensure sufficient irradiation of the sample. When we use the 266-nm Nd:YAG laser light for photobleaching, we observe a growth of the 300- and 325-nm OA bands similar to the 337-nm laser as expected. (One also notes that the overall intensity of all the OA bands is reduced markedly on using the 266-nm laser light.) This is shown by Fig. 4, curve *c*.

In γ-irradiated CaF_2:Mn, excited by 337-nm laser light or uv light in the range of 280–340 nm, we observe long-lived optically stimulated luminescence (OSL) at room temperature. The decay of this OSL is influenced by the concentration of Mn^{2+} present, as shown in Fig. 5. The OSL could very well result from the electron-hole recombination at the Mn^+ ions. The holes being released by the uv laser form the trapped hole centers. It should be noted that Merz and Pershan observed[12,14] a broad OA band from 280 to 350 nm due to the hole centers in various rare-earth-doped γ-irradiated CaF_2. It is known[5,15] that CaF_2 usually contains rare-earth impurities. Either due to the presence of these impurities or to the Mn^{2+} ions or both, the hole center may exist in this material even at high temperature. We believe that on optically exciting the γ-irradiated CaF_2:Mn with uv light, two processes are initiated: (1) the phototransfer process from the deep trap to the dosimetry trap, and (2) the hole release process from the trapped hole centers. The released holes recombine with all the various electron centers, therefore no appreciable increase in the F_A-center OA is observed following the laser irradiation. Thermoluminescence being a much more sensitive process than optical absorption, a smaller change can be observed through this process. This type of competitive electron and hole release process involving *F* centers and V_K centers has been observed in CaF_2:Dy at low temperature by Chakrabarti *et al.*[16]

The exact origin of the remaining OA band at 425 nm is not clear. Alcala *et al.*[4] observed a broad optical-absorption band near 450 nm in x-ray-irradiated CaF_2:Mn which they assigned to the Mn^+ center. In the case of Mn^{2+}-doped CaF_2, no evidence of a change in the charge state of Mn^{2+} ions has been reported at room temperature or higher. However, our x-ray photoelectron spectroscopy (XPS) data show evidence of a reduction of Mn^{2+} ions to a Mn^{1+} charge state upon *x* irradiation. In Fig. 9, the peak in the XPS spectrum of CaF_2:Mn identified with the manganese 3*d* shell is reduced in intensity. This is interpreted to mean that the 3*d* shell of the ensemble of Mn^{2+} ions in the material is losing electrons, with some of the manganese ions being reduced to a 1+ charge state. This XPS result and the influence of OSL decay by Mn^{2+} concentration in the material show evidence of participation of Mn^{2+} in charge trapping in this material following exposure to ionizing radiation at room temperature. However, it appears that in CaF_2:Mn the trapping mechanism is much more complex and involves *F* centers. The fact that 337-nm laser light causes the *M*-center (*F* aggregate center) OA band at 560 nm (Fig. 3, curve *d*) to reappear after it is destroyed on annealing the γ-irradiated material to 310 °C, gives us very valuable evidence that the *F* centers are released by the laser light. Some of these released *F* centers form *M* centers known to be stable at room temperature in this material. A released *F* center can also be stabilized by a nearby Mn^{2+} ion, forming a so-called F_A center.[7] Regeneration of the dosimetry peak and the second OA band in the 300-nm region by the nitrogen laser in the annealed CaF_2:Mn sample suggests that the dosimetry peak and this OA band are both due to an F_A center. From our phototransfer TL data we can argue that the *F* centers are released from the center responsible for the deep trap with the TL peak ~360 °C peak. Evidently, this center is also due to a complex involving an *F* center. Our further studies suggest that it is possibly due to an *F* center perturbed by a Mn^{2+}-Mn^{2+} pair.

Mn^{2+}-Mn^{2+} pairing

It is well known that in Mn^{2+} pairs are formed in other Mn^{2+} doped phosphors.[17–20] We looked for such pairs in as-grown samples and indeed found optical evidence of the formation of such pairs. Figure 6 shows photoluminescence spectra of three CaF_2:Mn single crystals with Mn^{2+} concentrations of 0.1%, 3%, and 5%, respectively. The luminescence is observed by exciting the ${}^6A_{1g}({}^6S)\rightarrow{}^4T_{2g}({}^4D)$ transition of the Mn^{2+} ion with the 337-nm nitrogen laser. Evidently, the luminescence peak is redshifted as the concentration of Mn^{2+} ions in the material is increased. Ginther[21] observed this peak shift in cathode-ray-excited emission spectra of CaF_2:Mn. He noted that the samples with Mn concentrations for 0.5% to 1% have an emission peak at 490 nm. With increasing Mn concentration, the emission peak shifts to longer wavelength. At 5% Mn concentration, the peak is at 500 nm, and at 10% Mn concentration he observed the peak shifting to 510 nm. However, he gave no account of the cause of this peak shift with Mn concentration. In ZnS:Mn, thorough studies[17,18] of the peak shifts of Mn^{2+} transitions have been performed, and the shifts attributed to the formation of manganese pairs in the material at higher concentrations. Recently, peak shifts due to paired Mn^{2+} centers have also been observed in Mn^{2+}-doped CaS (Ref. 19) and Zn_2SiO_4 (Ref. 20) phosphors.

It is known that a paired Mn^{2+} center is associated with a faster decay component than the single Mn^{2+} center.[19] This is attributed to the fact that the Mn^{2+} pairs have lower local symmetry than the single Mn^{2+} centers. In the time-resolved spectra of Fig. 7, one only sees the fast (500-μs lifetime) component with a 10-ns delay. With a 1-ms delay, only the slow (48 ms) component is observed. One notes that this emission of the fast component is shifted to longer wavelengths as is the higher Mn^{2+} concentration sample shown in Fig. 6. Thus the fast component is due to the Mn^{2+} pairs.

Our results show strong evidence of the formation of paired Mn^{2+}-Mn^{2+} centers in 3% Mn-doped CaF_2, and supports the possibility of a Mn^{2+}-*F*-center-Mn^{2+} complex in CaF_2:Mn irradiated by ionizing radiation, as sug-

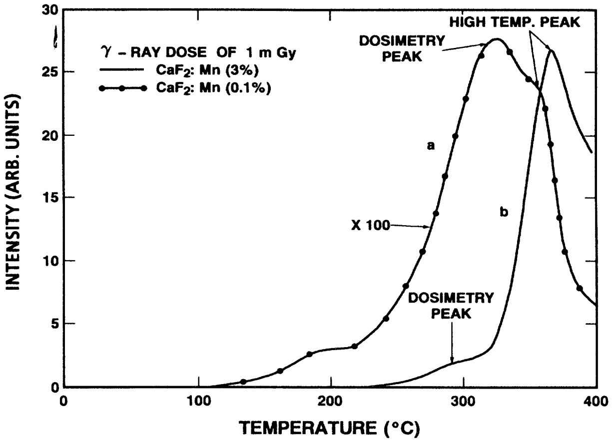

FIG. 8. Thermoluminescence glow curves of 3% and 0.1% Mn^{2+}-doped CaF_2 at a dose of 1 mGy showing different ratio of intensities of high temperature to the dosimetry TL peak.

gested by McKeever.[6] We calculated the ratio of paired centers compared to the single Mn^{2+} center, and found that to be only 0.001. Therefore, it is unlikely that the Mn^{2+}-*F*-center-Mn^{2+} complex is the origin of the dosimetry peak. Our results indicate that in 0.1% Mn-doped CaF_2 (where the number of paired centers should be approximately 0.0001%) the high-temperature peak is smaller than the dosimetry peak (Fig. 8, curve *a*) even at a low dose of 1 mGy. Curve *b* shows that at the same dose in 3% Mn^{2+}-doped CaF_2, where the number of paired centers are much larger, the high-temperature peak is of higher intensity. As discussed earlier, the high-temperature peak saturates even at this small dose, indicating that the number of centers responsible for this peak is small compared to the centers responsible for the dosimetry peak which grows linearly with dose. The fact that the ratio of the intensity of the high-temperature peak to the dosimetry peak falls drastically when the Mn^{2+} concentration is decreased to 0.1% suggests that the paired centers may be responsible for this peak. Second, we have observed that the OA band at 280 nm cannot be annealed by heating to as high as 400 °C unless it is bleached by the 337-nm laser prior to annealing, i.e., until the deep trap is depleted. Also, phototransfer by the 337-nm laser light in a partially annealed sample regenerates the dosimetry peak with an associated optical-absorption band at 300 nm. All these results strongly show a correlation between (1) the pair formation and the deep trap, (2) annealing of the dosimetry trap and the OA band at 300 nm, and (3) their regeneration by the laser light. We, therefore, suggest that there is a complex center involving paired Mn^{2+} that is formed in the sample irradiated by ionizing radiation. We also propose that this complex is the origin of the high-temperature peak which has not been known until recently.[9] This complex is thoroughly depleted by heating the material to well over 400 °C or by optical bleaching by 337-nm laser light. Once the deeper trap is thoroughly depleted, regeneration of the dosimetry peak cannot be observed without further irradiation.

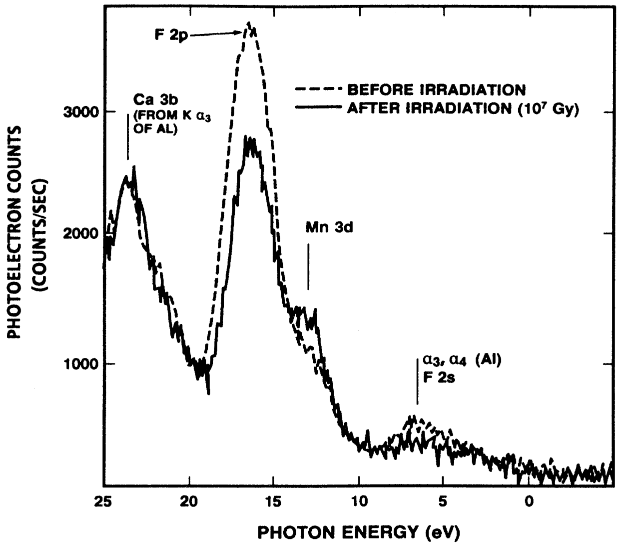

FIG. 9. XPS spectrum of CaF_2:Mn, before and after a γ-ray dose of 10^7 Gy showing that, at least in the vicinity of the surface, the counts of fluorine atoms decrease with respect to those of Ca and Mn atoms.

It is also noteworthy that the photoconversion process of the Mn^{2+}-*F*-center-Mn^{2+} complex to the Mn^{2+}-*F*-center complex by 337-nm laser light (with associated regeneration of the 300-nm optical-absorption band and the dosimetry peak) and the thermoluminescence processes involve mobility of *F* centers in the lattice. Figure 9 shows a large decrease in the relative intensity of the fluorine 2*p* XPS peak upon *x* irradiation with respect to the calcium 3*p* peak in 3% doped CaF_2:Mn. This shows a deficiency on the order of 20% of fluorine ions after 10^7 Gy of irradiation of the material, and indicates that *x* irradiation does cause fluorine migration. One should note that XPS only sees approximately 50 Å into the surface of the sample, and that this fluorine reduction may be a surface effect. However, *F*-center mobility does require fluorine migration.

V. SUMMARY

We have observed paired Mn^{2+} centers in CaF_2:Mn at high manganese concentration. This aggregate center may stabilize an *F* center, forming a Mn^{2+}-*F*-center-Mn^{2+} complex when the material is exposed to ionizing radiation. Our results of thermoluminescence and optical-absorption measurements in γ-irradiated CaF_2:Mn indicate that the ~360 °C peak may be due to this complex while the TL ~285 °C peak is due to an *F*-center-Mn^{2+} complex, as suggested earlier.[6,7] Unless the Mn^{2+}-*F*-center-Mn^{2+} complex is thoroughly destroyed, an *F* center may be released from this complex which can be stabilized by a single Mn^{2+} ion forming an *F*-center-Mn^{2+} complex with an associated dosimetry TL peak at 285 °C without any further exposure to ionizing radiation. A photoconversion of a Mn^{2+}-*F*-center-Mn^{2+} complex to an *F*-center-Mn^{2+} complex is also observed in optical absorption and thermoluminescence.

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