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Luminescence of the F^+ Center in MgO†

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A luminescence band with a half-width of about 0.6 eV at liquid-nitrogen temperature, which can be excited by uv light and x rays, has been observed in irradiated and additively colored MgO crystals at 3.13 eV. By combining ESR and optical studies, this emission band has been identified as due to F^+ centers (oxygen-ion vacancies each occupied by one electron). Furthermore, after resolving the F^+- and the F-band absorption in the vicinity of 5.0 eV, an analysis of the bands indicates that the oscillator strength of the F center is about 1.25, when the oscillator strength of the F^+ center is taken to be 0.8.

INTRODUCTION

An optical-absorption peak which is centered at about 5 eV is observed in MgO crystals which have been irradiated with neutrons,[1–3] electrons,[4] or in crystals colored in Mg vapor at high temperatures.[5] Henderson and King made a comparison of the neutron-dose dependence of this band with that of the electron-spin-resonance (ESR) signal of the F^+ center[6,7] (an oxygen-ion vacancy occupied by one electron) and attributed the absorption band to F^+ centers.[3] Recently, evidence has been presented that the absorption band for F centers (oxygen-ion vacancies each occupied by two electrons) also occurs near 5 eV in MgO.[8,9] This close proximity of the two bands was predicted previously[10,11] but has been difficult to show experimentally. In CaO crystals, Kemp *et al.*[12] have shown that it is possible under certain conditions to convert F centers to F^+ centers reversibly. Kappers and Hensley[13] state that by heating additively colored MgO crystals to temperatures above 400°C, F^+ centers convert to F centers. Conversely, by bleaching with intense uv light, especially at low temperature, conversion of F centers to F^+ centers occurs. Using these techniques, we have verified that the absorption band at 5 eV is actually a composite of two bands, the F and F^+, with slightly different half-widths and peak positions, and have obtained an oscillator strength of 1.25 ± 0.15 for the F center.

From an analysis of the temperature dependence of the half-width and the peak position of the 5.0-eV absorption band in neutron-irradiated crystals, Henderson *et al.*[14] suggested that F^+-center emission should occur at about 2.4 eV. Wood and Opik[11] predicted from a detailed theoretical calculation that this emission should occur at 3.4 eV. This paper reports the experimental evidence which shows that a luminescence band centered at 3.13 eV in electron-irradiated and additively colored crystals is due to F^+ centers in MgO.

PROCEDURE

The MgO crystals used in this study were obtained from W. & C. Spicer Ltd. and Muscle-Shoals Electrochemical Co. Unless specifically indicated otherwise, Spicer crystals were used for all the measurements. The impurity analyses of these crystals have been published.[15] The Spicer crystals contained <5-ppm Fe, whereas the Muscle-Shoals samples had 60-ppm Fe impurity.

Electron irradiations were carried out with a 2.0-MeV Van de Graaff accelerator to total doses of about 10^{19} electrons/cm^2 while the samples were kept near room temperature. Crystals were neutron-irradiated in the Oak Ridge Reactor Hydraulic Tube System No. 1-F-8 Tube 12, where the neutron flux (≥ 1 MeV) is about 2.3×10^{13} neutrons/cm^2 sec and the irradiating temperature is about 60°C. A crystal colored in Mg vapor at 1740°C at a pressure of 4300 Torr for 5 min was obtained through the courtesy of Hensley.[5] The samples were generally 0.1–0.2 cm thick and, for most measurements, both the optical and the ESR measurements were made on the same sample.

Optical-absorption data were taken with a Cary spectrophotometer model 14R. A Sulfrian cryostat was used for low-temperature measurements for both absorption and luminescence. The luminescence measurements were made using an EMI 9558Q multiplier phototube (cooled to dry-ice temperature to reduce the dark current) in conjunction with a $\frac{1}{2}$-m Bausch & Lomb monochromator. The emission data were corrected for

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monochromator and multiplier phototube response, and an estimate for the absolute magnitude of the emitted light was obtained by calibrating the detector system using a standard quartz-iodine lamp[16] with calibration traceable to the Bureau of Standards. A General Electric LC-90 industrial x-ray unit operating at 90 kV and 3 mA was used to stimulate luminescence. The output of this unit at these settings has been given previously.[15] A low-pressure Hg source passing through a $\frac{1}{2}$-m Bausch & Lomb monochromator set at 254 nm was also used as an excitation source. When uv excitation was used, the specimen in the cryostat was positioned at an angle of 45° with respect to both the detecting and the exciting monochromator.

Prior to the measurements of the luminescence intensities in irradiated crystals, the specimens were bleached with intense white light for about 30 min to reduce the V_1 concentration. Isochronal annealing was accomplished by heating the samples for 10 min at successively higher temperatures in an argon-atmosphere furnace.

The ESR measurements of F^+-center concentrations were made with an X-band homodyne spectrometer using 100-kHz field modulation. Measurements were made at both room temperature and liquid-nitrogen temperature (LNT) at low power (1–10 μW incident upon the sample cavity) to avoid saturation effects. The concentrations, which were determined by a comparison of the integrated intensity of the F^+-center signal to that of the Cr^{3+} resonance line in an MgO crystal of approximately the same size as the samples, are believed to be accurate within $\pm 25\%$. This MgO:Cr standard has been compared to the Varian pitch standards[17] and to a phosphorous-doped silicon standard,[18] and has been independently analyzed for total chromium content by neutron-activation analysis.

Because of the sensitivity of the samples to uv light, all ESR measurements were made immediately before or after the luminescence measurements, and the sample was kept in the dark at all times between the various treatments.

RESULTS

A comparison of the absorption-peak wavelength of the 5-eV band in additively colored crystals after a high-temperature anneal and again after a subsequent uv bleach, as shown in Fig. 1, indicates that the peak position and half-width differ after these treatments. After heating to 580°C for 15 min, no F^+ centers were detected by ESR, indicating an F^+-center concentration of less than 1×10^{14} centers/cm^3. The absorption peak was located at 5.01 eV, and the full width of the band at half-maximum was 0.77 eV. After bleaching at LNT using a mineral light source in conjunction with a 270-nm interference filter and a Corning 7-54 glass filter, the peak position shifted slightly to 4.92 eV, and the half-width became 0.62 eV. An ESR measurement indicated 7.7×10^{16} F^+ centers/cm^3. The concentration of centers N for a given defect is related to its optical-absorption coefficient α by Smakula's equation in its Gaussian form, $fN = 0.87\times 10^{17} n(n^2+2)^{-2}\alpha W_{1/2}$, where f is the oscillator strength, $W_{1/2}$ is the half-width, and n is the index of refraction. Assuming that the oscillator strength f of the F^+ center[3] is 0.8, the oscillator strength of the F center was determined to be 1.25 ± 0.15.

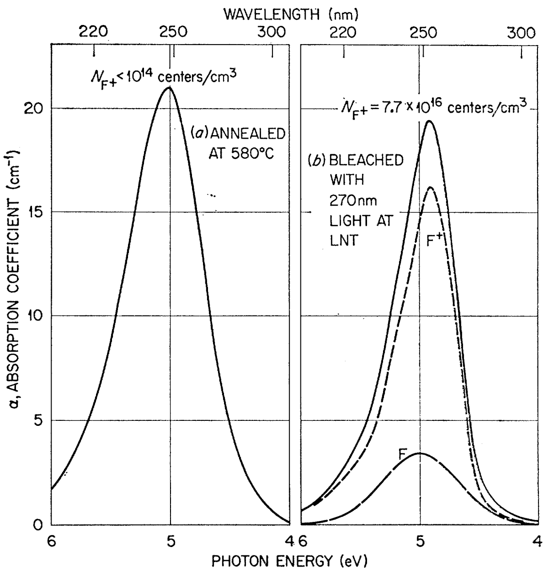

FIG. 1. Resolution of the optical spectra of the F^+ and the F band of an additively colored sample measured at room temperature. Experimental curve (b) was decomposed assuming a symmetric Gaussian with a half-width of 0.77 eV for the F center.

$F \leftrightarrow F^+$ conversions are also possible in electron-irradiated crystals, although not as complete as in the case of the additively colored crystal. Generally, both centers are present. Bleaching with uv light at room temperature favors the formation of F centers, and bleaching with uv light at LNT favors the F^+ center. These processes are reversible and normally gave a factor-of-3 variation in the F^+-center concentration, as measured by ESR. In neutron-irradiated crystals, however, a comparison of the peak position and half-width of the 5-eV band, especially in those crystals irradiated to high doses ($>10^{18}$ n/cm^2), suggests that most of the negative-ion vacancies are F^+ centers. Indeed, it was on this basis that Henderson and King obtained a value of 0.8 for the oscillator strength f of the F^+ center.[3]

In unirradiated Spicer crystals, either as-grown or slow-cooled in argon gas from 1000°C, an x-ray-stimulated luminescence peak occurs at ~3.2 eV (388 nm), with a half-width of ~1.2 eV. When quenched from 1000°C, these crystals exhibit a peak at ~3.6 eV

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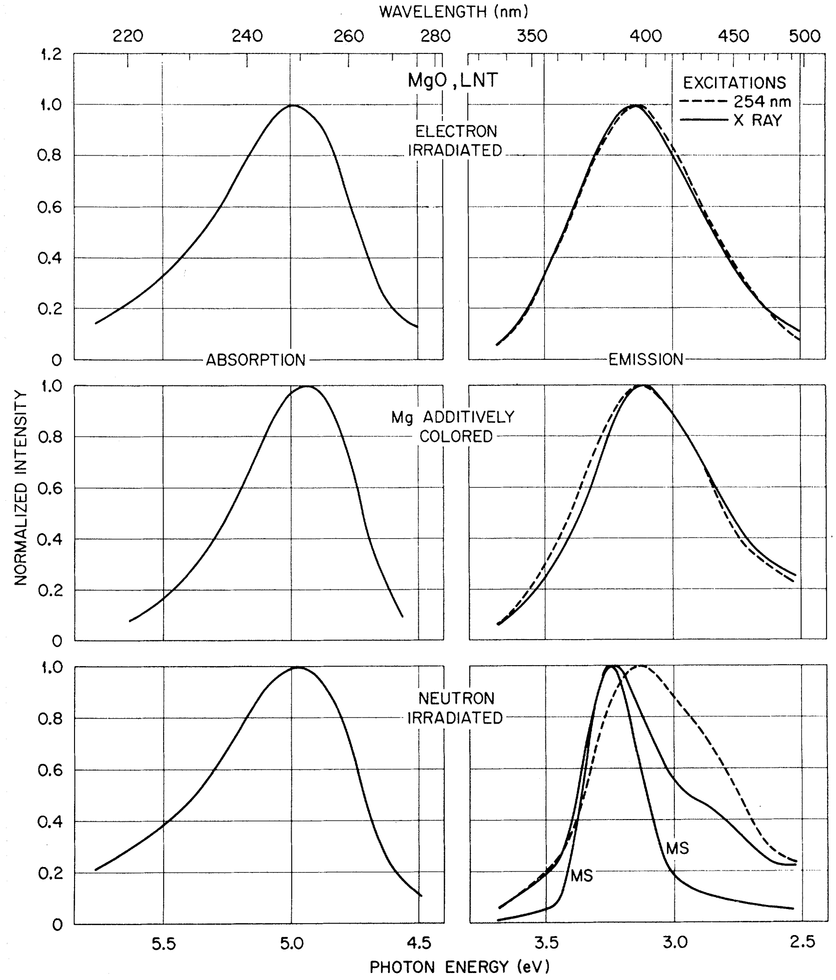

FIG. 2. Normalized absorptions at 5.0 eV and x ray and uv-stimulated emission near 3.1 eV for electron-irradiated, additively colored, and neutron-irradiated crystals. The emission spectra have been corrected for monochromator-phototube response. Corrections have also been made for self-absorptions for the broad V_1 band (540 nm) in the electron-irradiated crystal and the 353-nm band in the neutron-irradiated crystal.

(345 nm), with a similar half-width. The intensities of these bands which have been observed and studied in the past[19–21] have a weak temperature dependence. In the case of Muscle-Shoals crystals which have been slow-cooled, no impurity luminescence is observed.[22] After irradiation, either by electrons or neutrons, all impurity luminescence in the range of 300–600 nm disappears when the absorption coefficient of the 250-nm absorption band, α_{250}, reaches ~ 2 cm^{-1} ($\sim 1\times 10^{16}$ defects/cm^3). Meanwhile, a luminescence band which can be excited by x rays or by 254-nm uv light appears at 3.13 eV (396 nm). The quantum efficiency of this band is strongly temperature-dependent, with the intensity at LNT being more than a factor of 10 greater than that at room temperature.

The normalized absorption and emission spectra for electron-irradiated, additively colored, and neutron-irradiated crystals are shown in Fig. 2. Base-line corrections have been made for the 250-nm absorption spectra. The emission data have been corrected for both monochromator-photomultiplier response and self-absorption by some of the bands induced by radiation, viz., the 355-nm band in neutron-irradiated crystals and the broad V_1 band centered at 540 nm in irradiated crystals. It should be pointed out that after heavy doses of electron irradiation, the maximum V_1 concentration that could be obtained by subsequent γ irradiation nearly doubled, and the thermal stability increased from a decay half-life of several hours[22] to days. It can be seen from Fig. 2 that the emission spectra for both x-ray and uv excitation are very similar in electron-irradiated and additively colored crystals. The peak photon energy was 3.13 eV,[23] and the half-width was about 0.6 eV. This is not true in the case of the neutron-irradiated crystals, where it is observed that the peak position and half-width of the x-ray-induced emission

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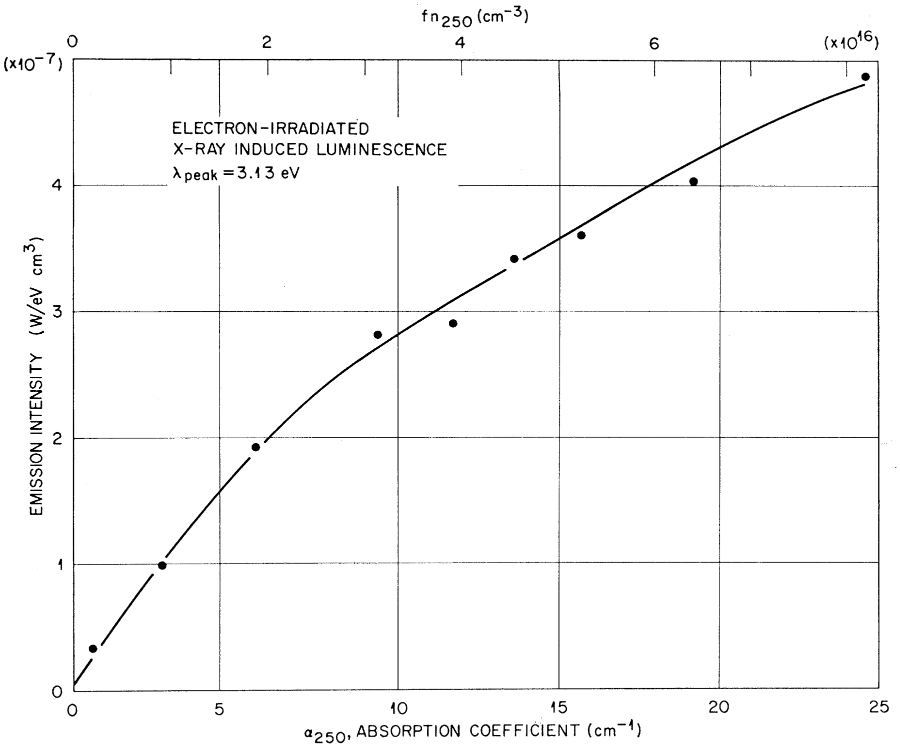

FIG. 3. Peak emission intensity at 3.13 eV excited by x ray as a function of the absorption coefficient of the 5.0-eV bands for an electron-irradiated crystal. Crystal was bleached with white light prior to measurements.

varied between the nominally pure Spicer crystal and the impure Muscle-Shoals crystals.

In order to see whether the 3.13-eV emission was related to either F or F^+ centers, the dependence of the emission intensity at 3.13 eV on the absorption coefficient of the 250-nm band for an electron-irradiated crystal was measured. The results are illustrated in Fig. 3. Because the optical absorption at 5 eV increased with radiation dose, excitation with 5-eV light would result only in surface emission. Therefore, for uniform penetration independent of electron damage, x-ray excitation was used, under constant experimental conditions, i.e., white-light bleach prior to all measurements. An estimate of the concentration of negative-ion vacancies, F^+ centers as well as F centers, based on Smakula's equation, is also shown.

Another method of determining whether there is a relation between the 3.13-eV emission and F or F^+ centers is by a study of the annealing characteristics of both absorption and emission in irradiated and additively colored samples. Therefore, the normalized absorption band at 5.0 eV and emission intensities at 3.13 eV, along with the ESR-measured F^+-center concentration of an electron-irradiated and an additively colored crystal, are plotted in Fig. 4 as a function of annealing temperature. For the MgO:Mg crystal, the emission intensity and the ESR values for each annealing point were measured after the crystal had been bleached with uv light in order to maximize the F^+-center concentration. It can be seen that in the electron-irradiated crystal, the optical absorption, ESR signal, and the photoemission decay together to a near-vanishing point by 550°C. On the other hand, in the MgO:Mg crystal there is little if any decay even at 740°C.

In order to determine which center, F or F^+, is responsible for the 3.13-eV emission, a series of annealing/bleaching runs was made. Figure 5 depicts a series of emission spectra from an additively colored crystal stimulated by uv excitation. The emission spectrum after annealing at 440°C, when the ESR measurement showed a low F^+-center concentration, is illustrated by the bottom curve. After uv bleaching at either LNT or room temperature, both the ESR and the luminescence intensities increased. Similar results for both the F^+-center signal and uv-excited luminescence are observed in electron-irradiated crystals, and the results are reversible. It should be mentioned that the uv-bleaching light is much more intense than the uv-excitation source and, although small changes can be observed because of bleaching after repeated excitations, the effect is negligible.

DISCUSSION

It is clear from the above data that the 5-eV absorption band in irradiated or additively colored crystals is seldom a single band. Although it is possible to convert nearly all of the F^+ defects to F centers in an additively colored crystal annealed at high temperature, and therefore obtain essentially a pure F-center

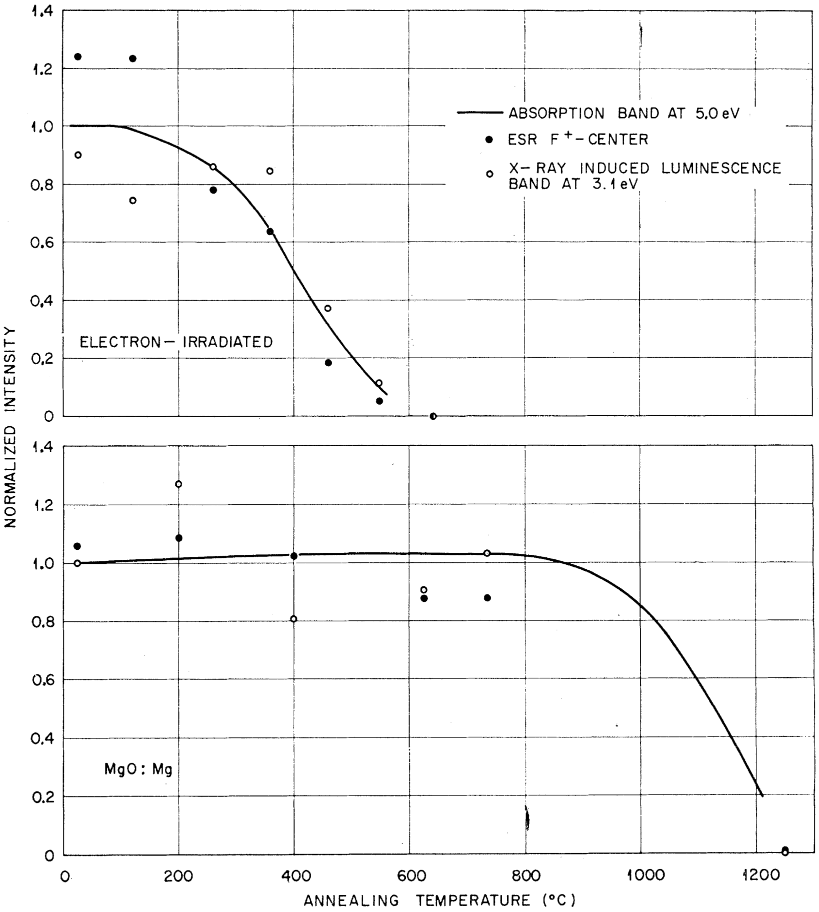

FIG. 4. Normalized annealing of the 3.13-eV emission band, ESR F^+ center, and the 5.0-eV absorption bands for an electron-irradiated and an additively colored crystal. Bleaching with intense uv light preceded the luminescence and ESR measurements for the additively colored crystal.

absorption band, complete conversion to the F^+ band cannot be assured[13] even after a prolonged uv bleach at low temperature. The absorption band of the F center in the additively colored crystal used in determining the oscillator strength represented about 9×10^{16} centers/cm^3 according to Smakula's formula. However, even after a prolonged LNT uv bleach, the F^+-center concentration measured by ESR was only 7.7×10^{16} centers/cm^3. In the determination of the oscillator strength, therefore, the 5-eV band was assumed to be a composite of both F and F^+ after the uv bleach, and the decomposition then gave the final result for the MgO :Mg and the electron-irradiated crystals.

It can be seen from Fig. 2 that by exciting the defects responsible for the 5-eV band, an emission band at 3.13 eV occurs in all three types of crystals: electron-irradiated, MgO :Mg, and neutron-irradiated. It is also observed that, in the case of electron-irradiated and additively colored crystals, the emission excited by x rays is very similar to that obtained from uv excitation, indicating that impurity luminescence in the visible region has apparently been quenched by the radiation.

In Fig. 3 the emission intensity was found to increase

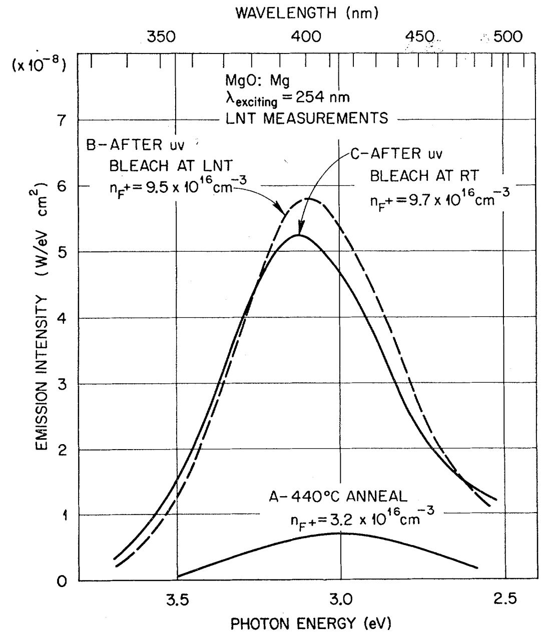

FIG. 5. Effect of uv bleaching on the F^+ concentration and emission intensity in a crystal which had been annealed at 440°C.

monotonically with the absorption coefficient of the 250-nm band. The departure from linearity at high defect concentration can be attributed to concentration quenching of the luminescence intensity.[24] The annealing curves indicate that the emission intensity of the 3.13-eV luminescence band in these crystals has the same annealing behavior as the 250-nm absorption band and/or the ESR F^+ center. In irradiated crystals, F and F^+ centers disappear near 500°C, but they do not anneal out until temperatures above 1000°C in the additively colored crystals.[25] It has been proposed that in irradiated samples the disappearance of F and F^+ centers at 500°C is due to oxygen interstitials recombining with the immobile vacancies.[25]

Up to this point, the evidence provided by studies of the 254-nm excited luminescence, irradiation-dose dependence, and the annealing of the emission band indicates that either the F or the F^+ center is responsible for the emission band at 3.13 eV. It is possible, using the annealing/bleaching technique discussed above, to show that there is a correlation between the F^+ center and the emission band. The data for one of the crystals examined are shown in Fig. 5 and illustrate that the emission band is due to F^+ centers. When the F^+-center concentration is low, the uv-excited luminescence intensity is small. When the F^+-center concentration increased by a factor of 3 as measured by ESR, the emission intensity increased nearly tenfold. Although in most crystals the quantitative agreement was much better than this, some difference in these measurements is not surprising. For example, because of self-absorption of the bleaching light in the crystal, some of the F centers in the interior of the crystal are probably not converted to F^+ centers, and therefore are not detected by ESR measurements, which probe the whole volume of the sample, whereas the uv-stimulated emission occurs primarily at the surface where the bleaching treatment is most effective. At this point, it should be noted that even though, in irradiated crystals, the uv-excited luminescence gave a reasonable correlation with the ESR-measured F^+-center concentration due to $F^+ \leftrightarrow F$ conversions, the x-ray-induced luminescence did not. This may be due to the presence of other centers in irradiated crystals such as V_1 centers or interstitial ions.

In summary, the results of this work in conjunction with earlier ESR and optical-absorption studies may be presented as follows:

(i) The 5-eV optical-absorption "band" in irradiated or additively colored crystals is generally a composite of the F band centered at 5.01 eV with a half-width of 0.77 eV and the F^+ band centered at 4.92 eV with a narrow half-width of 0.62 eV, measurements being made at room temperature.

(ii) The oscillator strength of the F band is determined to be 1.25 ± 0.15, if the oscillator strength of the F^+ center is assumed to be 0.8.

(iii) The luminescence band of the F^+ center, which theoretically has been predicted to be near 3 eV, is experimentally found to be centered at 3.13 eV, with a half-width of ~ 0.6 eV at LNT in either electron-irradiated or additively colored crystals.

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