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Luminescence of F and F^+ centers in magnesium oxide

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Time-resolved spectra of luminescence from F and F^+ centers in MgO excited at 248 nm are reported over 8 decades of time and intensity, from 20 ns to 2 s. The decay time of F and F^+ luminescence has been measured at temperatures ranging from 90 to 573 K. The luminescence yield and spectra were studied as a function of excitation-power density at 248 nm over a span of 10 decades, from 1 mW/cm^2 to 38 MW/cm^2. Higher pump-power density favors F luminescence over F^+ luminescence in thermochemically reduced crystals, and the luminescence yield saturates above about 50 kW/cm^2 of pump intensity. Transient absorption spectra were measured in the microsecond-to-seconds time range. The luminescence data show that the decay kinetics of excited F and F^+ centers are dominated by ionization from the excited state and charge recapture from traps which include the H^- center in thermochemically reduced MgO. It is furthermore inferred that electrons are the charge carriers having primary influence on kinetics of both F and F^+ centers. This implies that the F^+ first-excited state lies close to the conduction-band edge. We confirm that excitation at 248 nm also causes release of valence holes, and propose a mechanism which may explain the hole release, the increase of the F-to-F^+ intensity ratio with increasing pump intensity, and the saturation of luminescence with increasing pump intensity.

I. INTRODUCTION

It is generally agreed that the 530-nm luminescence band in MgO containing oxygen vacancies results from a $^1T_{1u} \rightarrow {}^1A_{1g}$ transition of the F center.[1,2] It is therefore both spin and parity allowed and should be expected to have a rather short lifetime. The decay of the luminescence at 530 nm is in fact observed to be very long, extending to several minutes in some crystals.[3-5] The apparent inconsistency between the phosphorescent F-center decay and the strongly allowed nature of the $^1T_{1u} \rightarrow {}^1A_{1g}$ transition was resolved by demonstrations that the persistence of the F-center phosphorescence is linked directly to the concentration of H^- ions (protons occupying F centers) in thermochemically reduced (TCR) magnesium oxide crystals.[3-5]

The relaxed F-center excited state lies only 0.06 eV below the conduction-band edge.[6] In the model of Refs. 3–5, it is therefore reasonable to assume that except near liquid-helium temperature most excited F centers ionize by electron release to the conduction band, followed by trapping of the electron at the most prevalent electron traps, among which are the H^- centers in thermochemically reduced crystals. Since the thermal depth of the H^{2-} center is itself only 0.56 eV, the electrons are mobile via trap-to-trap hopping at room temperature. Upon such an electron's encountering one of the ionized F centers (i.e., an F^+ center), there is some possibility of transient recapture into the luminescent F excited state and emission of delayed luminescence via $^1T_{1u} \rightarrow {}^1A_{1g}$. This sequence has been described and compared to experiment in Refs. 3–5. One of the purposes of this paper is to trace the F luminescence decay over the extended range from 10 ns out to the scale of seconds where the connection of phosphorescence decay kinetics with H^- ions in TCR crystals has already been established.[3-5]

The luminescence of F^+ centers occurs in a band at 390 nm and is of equal interest in this work. In fact, F and F^+ centers must be addressed together in MgO. Their absorption bands, with peaks, respectively, at 247 and 251 nm and widths of about 0.6 eV,[7,8] are so nearly coincident that one can hardly excite one without exciting the other. They are further related in that the F^+ is the ionized state of the F center, and we have already commented that excitation of F centers leads with high probability to ionization. F-to-F^+ conversion, and apparently F^+-to-F conversion, can both occur upon excitation in the 250-nm absorption bands.

Spectroscopy and decay kinetics of the F^+ center itself are of substantial interest. Theoretical treatment of the F^+ center in MgO involves large polarization effects and has so far yielded results less certain than for the F center.[9-14] In particular, the location of the F^+ ground and first-excited states relative to the valence- and conduction-band edges (and to the F ground state) in terms of binding energy of the electron is still a matter of debate. Recent theoretical treatments have predicted F^+ first-excited states ranging from deep in the band gap[12,13] to nearly degenerate with the conduction band.[11] Bartram, Swenberg, and La presented a theory of g shifts of F^+ centers in a number of oxides and sulfides involving admixture of a charge-transfer configuration in the F^+

ground state consisting effectively of a hole trapped on an anion adjacent to an F center.[15] The observation by Kemp *et al.* that illumination on the long-wavelength side of the F^+ bands in CaO produced photoconversion to F centers[16] was interpreted as hole release from the first-excited state in this charge-transfer model.[15] In MgO, excitation in the region of the F^+ absorption band produces V centers (trapped holes) and converts some F^+ centers to F centers, suggesting that F^+ excited states ionize by hole release in MgO as well.[17] Such conclusions seem to imply that the excited F^+ center introduces a vacant defect state (i.e., the vacant ground state at the configuration coordinates of the relaxed excited state) very near the valence-band edge. This idea is in keeping with generalization to MgO of the calculations presented by Choi and Takeuchi for Al_2O_3.[13]

On the other hand, the recent calculations of defect levels in MgO and CaO by Klein, Pickett, Boyer, and Zeller[11] place the first F^+ excited state (unrelaxed lattice) near or even degenerate with the conduction-band edge, consistent with the F^+ ground state lying roughly 5 eV below the conduction-band edge and therefore roughly 2.8 eV above the valence-band edge in MgO. In very recent Hartree-Fock calculations on the F^+ center in MgO, Pandey and Vail find that for their best O^{2-} basis set, the F^+ ground state lies above the valence band.[14] We believe the data of this paper provide important experimental evidence on the location of the F^+ levels. Nearly identical decay kinetics of the F and F^+ luminescence bands imply that electron release from the first-excited states of both centers is the dominant ionization mechanism in at least low-hydrogen TCR MgO. If so, then the F^+ excited state lies rather near the conduction-band edge. Optically stimulated hole release from the F^+ center or from the ionized F^+ center (F^{2+} in this view) will be shown to be consistent with this model as well, thus accounting for F^+-to-F and F^+-to-V photoconversion as observed.

The decay of F^+ luminescence has been measured in SrO from 25 ns to 1 μs.[18] Concurrent with the present work, the decay of F and F^+ luminescence in CaO has also been measured in our laboratory over a broad time range.[19] However, with the exception of long-lived F-center phosphorescence,[3–5,20] little is known about time-resolved F and F^+ luminescence in MgO. (A preliminary report of the present work was presented in Ref. 21.) Compared with the phosphorescent decay of F centers in TCR MgO, the F^+ luminescence decay has been described only as "very rapid," i.e., not evidently phosphorescent in nature.[4] In this work, we have traced both F and F^+ luminescence decay over at least 8 decades of time and intensity from 10 ns to several seconds.

The pulsed excitation source we have used is a KrF excimer laser. As the data were accumulated under pulsed excitation for purposes of time resolution, it became apparent that even the time-integrated spectra did not always resemble the steady-state spectra measured with continuous low-level excitation. We thus undertook measurements of both efficiency and spectral distribution of luminescence as a function of the 248-nm pump power density over a range of 10 decades, from roughly 1 to 38 MW/cm^2. This has additional relevance in considering these crystals and defects for possible laser applications.

II. EXPERIMENT

The samples were high-purity MgO crystals grown by the arc-fusion method at Oak Ridge National Laboratory. For typical impurity analyses, see Refs. 22 and 23. Thermochemical reduction (TCR) in Mg vapor, also called additive coloration, was one of the methods used to introduce oxygen vacancies. Typical parameters for TCR as used here involved heating to 2200 K for 2 h in 6 atm of Mg vapor.[24] A consequence of such a strongly reducing atmosphere is the formation of a high concentration of oxygen vacancies. In the process, hydrogen present as an impurity diffuses (as H^+) throughout the crystal, and is trapped by F centers. An F center occupied by a proton is called a H^- center, i.e., a H^- ion substituted on an O^{2-} site. It is thus positive with respect to the lattice and can trap another electron. TCR crystals with three different concentrations of F centers and H^- ions were used in the work reported here. The crystals designated MgO-A and MgO-E were grown from predried starting material, taking steps to minimize water retention.[22] In contrast, crystal MgO-I was grown from starting material deliberately presoaked in water to introduce hydrogen into the melt.[22,25] Crystal MgO-I is the same high-hydrogen sample used in the study of F-center phosphorescence reported in Refs. 3–5. The low-hydrogen crystal MgO-A was additionally subjected to electric field sweeping prior to the TCR treatment to further reduce H^- concentration. Field sweeping, described in Ref. 26, involves heating the crystal to 1300 K while holding it in an electric field of 2000 V/cm. The neutron-irradiated crystal described in this work, designated MgO-C, was exposed to 5×10^{15} fast-neutrons/cm^2 at a temperature of 320 K. Pertinent data on the samples described in this paper are summarized in Table I.

The samples were excited by 248-nm, 18-ns pulses from a KrF excimer laser, producing energy fluence at the sample which was varied in the range from 0.02 to 700 mJ/cm^2 per pulse. Unless otherwise stated, pulse fluences of approximately 200 mJ/cm^2 were used for the time-resolved data reported. For the lowest power used in power-dependence studies, the monochromated light from a superpressure mercury arc lamp was used. For the power-dependence measurements, the spectra were integrated for 1 s following and including the laser pulse, or for 1 s under continuous excitation by the arc lamp.

Decay curves at a specific wavelength were recorded by passing the luminescence through a monochromator to a RCA 8575 photomultiplier and recording the signal in digital form with a LeCroy 100 megasample/s transient digitizer. To allow accurate measurement of low-level signals extending beyond 1 ms, the strong initial luminescence was shuttered to prevent overdrive of the photomultiplier and detection circuits. Because of the limited dynamic range of the instrumentation, the full 8-decade decay curve was not measured in a single shot, but in successive segments. These were sequentially normalized to fit smoothly together in overlapping regions.

TABLE I. Description of samples used in this study.

Sample	Preparation	n_F (cm^{-3})^{a}	n_H (cm^{-3})^{b}	o.d. (248 nm)
A	TCR, field swept	2×10^{17}	1.5×10^{17}	1.45
E	TCR, low H	2×10^{17}	$<5\times10^{16}$	4.3
I	TCR, high H, high F	1.6×10^{18}	3.3×10^{18}	16.5
C	neutron irrad., 5×10^{15} n/cm^2	1×10^{17}	$<5\times10^{16}$	1.4

[a] F-type–center concentration calculated from absorption coefficient at 4.95 eV.
[b] H$^-$-ion concentration calculated from absorption coefficient at 1053 cm^{-1}.

By deconvoluting the laser pulse width and photomultiplier rise time from the data, delay times down to about 10 ns could be resolved.

Optical spectra at specific delays after laser excitation were measured with an optical multichannel analyzer gateable to 20 ns. Specification of the decay time for a spectrum refers to delay introduced between the center of the 18-ns laser pulse and the center of the gate opening. That is, a spectrum labeled "0 delay" would have been measured when the gate coincided with the laser pulse. The spectra have not been corrected for the spectral response of the optical multichannel analyzer, which peaks at 450 nm and falls off toward the red, terminating at about 900 nm. Thus in our spectra the nominal 530-nm band appears to be at 510 or 520 nm.

Transient absorption in the range longer than a microsecond was measured by passing a 1-μs xenon flashlamp pulse through the crystal in synchronism with the existing laser pulse or after a delay.

The method of measuring excitation power-density dependence will be described as the results are presented.

III. RESULTS

The decay of luminescence in the F^+ band (390 nm) and F band (530 nm) of the field-swept TCR crystal designated MgO-A is plotted for room temperature in Fig. 1(a). It is remarkable that both the F and F^+ luminescence bands decay at almost the same rate over the 7-decade span from 200 ns to 2 s. In the nanosecond range, we find a fast-decay component ($t \approx 10$ ns) of the F^+ luminescence, but effectively no fast component for the F luminescence. The small fast-decaying component at 530 nm, about 10% of that at 390 nm, can be attributed simply to spectral overlap of the F^+ and F emission bands at 530 nm. Because of the 18-ns pulsewidth and 10-ns detector rise time, a component with $t<20$ ns could not be resolved directly, but would still be clearly seen as a 20-ns peak of intensity. We can say with confidence that the 530-nm band has no such fast component of significant strength relative to the slower components. Even for the F^+ band, the fast component comprises only about 14% of the time-integrated 390-nm luminescence, with the remaining 86% attributable to the slow-decay behavior which dominates Fig. 1(a). Similar decay curves for the remaining three crystals in Table I are shown in Figs. 1(b)–1(d).

Time-resolved spectra for the same four crystals are shown in Fig. 2. The data represent spectra recorded at successively greater delays after the laser excitation as labeled at the lower right-hand side of each spectrum. Spectra are shown normalized to the same height for display, with peak intensity relative to the earliest spectrum labeled as the dimensionless number at the lower right-hand side of each spectrum. From these parameters and the spectra, one can reconstruct the time dependence at any wavelength from 350 to 700 nm. It is evident from Figs. 2(a) and 2(b) for MgO-A and MgO-E that the 390- and 530-nm bands do not precisely follow each other over the full decay range. This is entirely con-

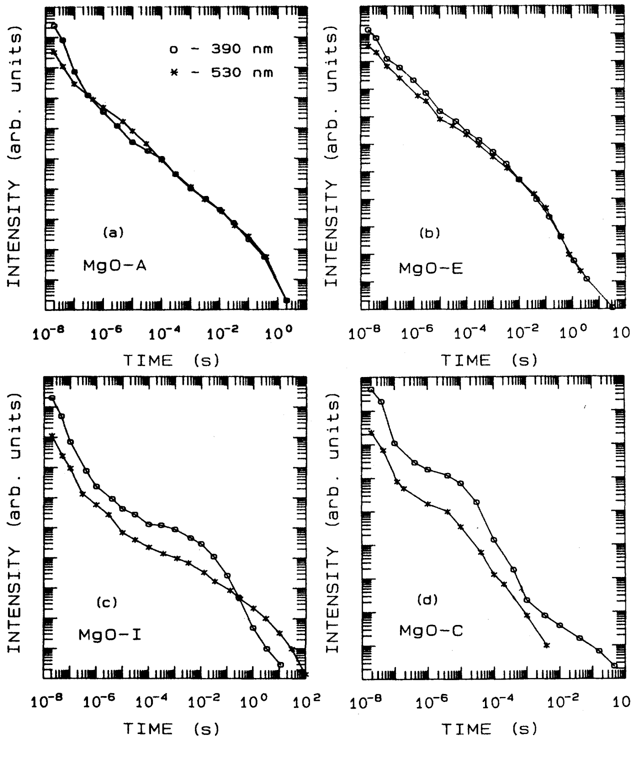

FIG. 1. For each of the four samples in (a)–(d) (see Table I), luminescence intensity from F^+ centers (390 nm) and F centers (530 nm) is plotted vs time following an 18-ns, 248-nm laser pulse. Both scales are logarithmic. The units of intensity are arbitrary, but relative intensities are meaningful. Measurements were made at room temperature.

sistent with Figs. 1(a) and 1(b), if the reader matches the small inequalities on the logarithmic decay curves with the relative heights of F and F^+ bands in the linear spectra of Figs. 2(a) and 2(b). Stated another way, the fact that the intensities of the two bands remain within about a factor of 2 of each other over 7 decades of decay indicates a remarkable correspondence of overall decay behavior. It is equally important to note that the 390- and 530-nm bands remain spectrally distinct throughout the full range of the decay. [See especially Fig. 2(b).] Without this proof of spectral distinguishability throughout the whole time range, Figs. 1(a) and 1(b) might only indicate that the signal measured at 390 nm is dominated by a tail of the 530-nm band extending to that wavelength, or *vice versa*. With the two distinct bands always visible, we can be confident that the F and F^+ decay kinetics are linked over the 7-decade span from 200 ns to 2 s.

The effect on the MgO-A decay curves of changing temperature over the range 90 to 573 K is shown in Fig. 3. The temperature-dependent changes of the logarithmic decay curves are rather complex, but remarkably, the F and F^+ luminescence bands continue to share the same overall decay characteristic at all temperatures except the lowest. At 90 K, the long-term component of F^+ luminescence falls significantly below that of the F luminescence.

The high-hydrogen crystal MgO-I exhibits a different behavior in Figs. 1(c) and 2(c). From 10 ns to 10 ms it yields the purest example of F^+ luminescence that we have seen in a TCR crystal. The F^+ luminescence is so dominant in this time range that we cannot resolve the F luminescence at all. Whatever F luminescence exists might follow the F^+ decay in this time range, but we have no evidence for or against it. However, the luminescence quickly switches character between 10 ms and 1 s, becoming almost pure F luminescence at 1 s and beyond, in agreement with the phosphorescence measurements of Refs. 3–5.

The initial luminescence is predominantly F^+ in all crystals studied. One generalization of the data for TCR crystals is that increasing the H^- concentration seems to

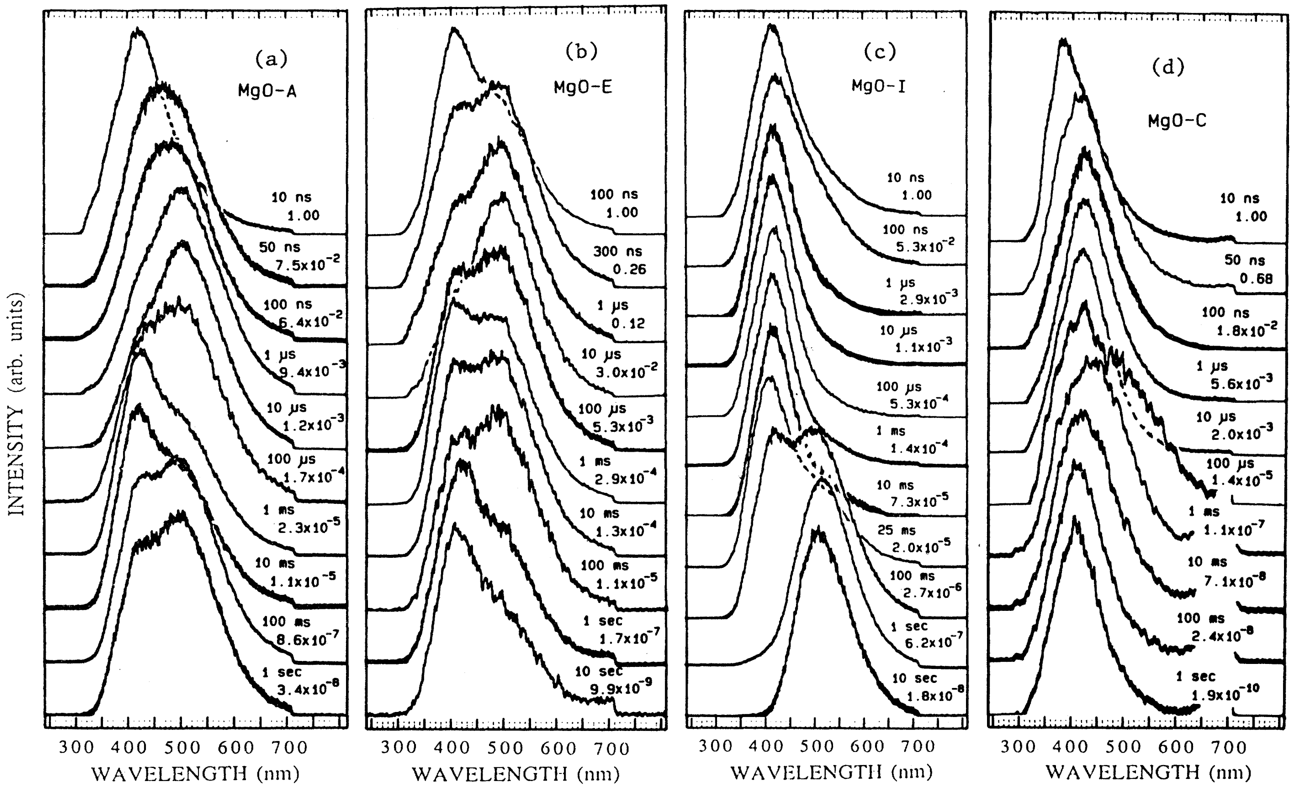

FIG. 2. For each of the four samples in (a)–(d), luminescence spectra are shown corresponding to delay times after 248-nm excitation as labeled by the first number at the lower right-hand side of each spectrum. All spectra are normalized to the same height and displaced vertically relative to one another for display. The second number (unitless) at the lower right-hand side of each spectrum gives the ratio of the peak intensity at that time to the peak intensity at the earliest time shown. In some cases the peaks may be at different wavelengths. The units of intensity are arbitrary. The measurements were made at room temperature.

delay the first transition from F^+ to F character. It has already been noted that in the low-hydrogen crystals the F and F^+ luminescence bands decay together with only minor differences, while in the high-hydrogen crystal the major trend is the switch from initial F^+ to long-term F character. Notice also in Fig. 2 that both low-hydrogen TCR crystals start initially with F^+ luminescence the stronger of the two bands, switch quickly to F dominance, and then back to F^+ dominance.

Time-resolved luminescence spectra for a neutron-irradiated sample, MgO-*C*, are shown in Fig. 2(d). The luminescence dies more quickly, but is still protracted over at least 1 s as seen in Fig. 1(d). The band appearing at about 700 nm is due to Cr^{3+} impurity luminescence.[27]

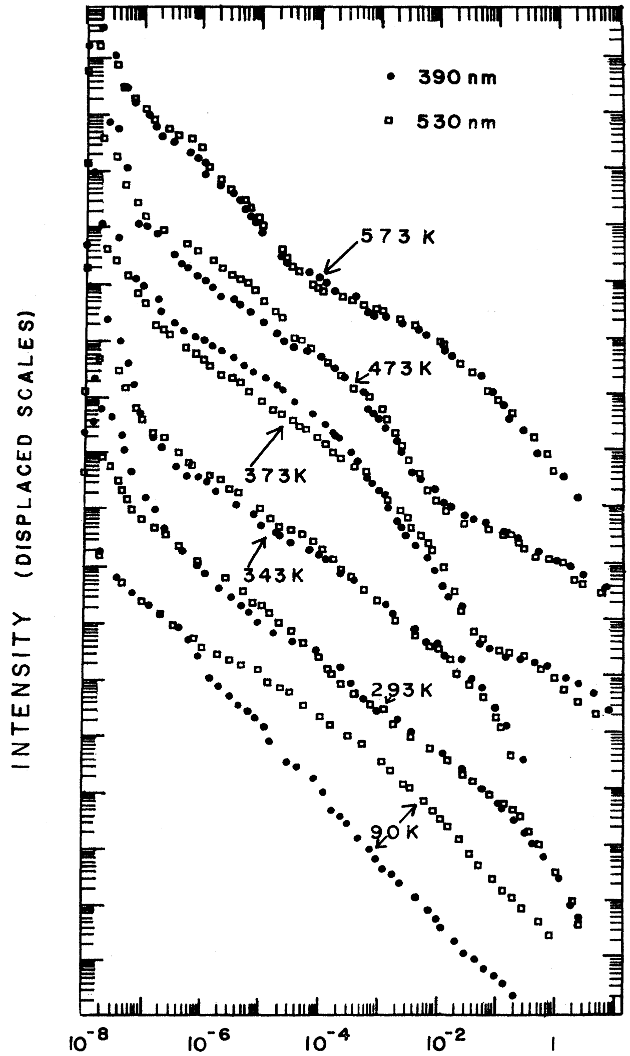

FIG. 3. Luminescence decay curves are plotted on logarithmic scales (displaced vertically for display), for temperatures from 90 to 573 K in the low-hydrogen TCR crystal MgO-*A*. Data for the F^+ center (390 nm) and F center (530 nm) are shown. The units of intensity are arbitrary.

An extremely short-lived luminescence component is seen at about 370 nm in the neutron-irradiated sample. The earliest spectrum in Fig. 2(d) resembles the steady-state luminescence spectrum of a neutron-irradiated sample reported in Ref. 28. However, in the time-integrated or steady-state spectrum of MgO-*C*, the 370-nm component is negligible.

The dependence of the luminescence spectra on excitation power density at 248 nm is shown in Fig. 4. Plots of log intensity versus log power density for the 390- and the 530-nm bands are shown in Fig. 5. In all cases the luminescence is measured as the time integral from the excitation pulse to 1 s later. All spectra in Fig. 4 except the lowest power density were excited by a 248-nm excimer laser pulse, imaged to a rectangular spot of uniform intensity and constant size. Attenuation was achieved by introduction of calibrated ultraviolet neutral density filters. The lowest power density (mW range) was achieved by substituting a monochromated (248 nm) superpressure mercury lamp for the laser, keeping the same image spot size on the sample.

Several trends are readily apparent in all the samples. Increasing the excitation power density forces the spectrum toward F-center dominance in every TCR crystal studied. Furthermore, the total luminescence yield saturates strongly with pump power in the TCR crystals for power densities above 50 kW/cm^2. As shown in Table I, the optical densities at 248 nm are sufficiently large in all the samples that the excitation light should be almost completely absorbed. We tested for increased transmittance of 248-nm light at high incident power densities, up to 38 MW/cm^2. There was no significant increase in transmittance. We thus conclude that we are seeing a real decrease in efficiency, defined as luminescence photons emitted per 248-nm photon absorbed, as excitation power density increases above a threshold level, typically about 50 kW/cm^2. Above that threshold, the luminescence efficiency drops by 2 orders of magnitude in some cases. Reasons could include a quenching mechanism that comes in at high excitation density; preexisting, underlying 248-nm absorption by nonluminescent centers whose ground states rapidly repopulate; or similar nonluminescent 248-nm absorption which is itself induced by the 248-nm excitation. We will examine these possibilities in the discussion to follow.

The optical-absorption spectra registered by passage of a 1-μs xenon lamp flash through the MgO-*I* crystal at the indicated delays after laser excitation are shown in Fig. 6.

IV. DISCUSSION

The data have shown that most of the F and F^+ luminescence in MgO decays slowly, i.e., in times greater than 1 μs. Since the radiative transitions themselves are allowed, it seems clear that we are seeing primarily the luminescence controlled by charge transport between traps and the F and F^+ centers. In addition, the close similarity of decay rates for the two luminescence bands over at least 7 decades in MgO-*A* and MgO-*E* leads us to conclude that the *same* charge traps govern the luminescence of both F and F^+ centers. It is widely accepted

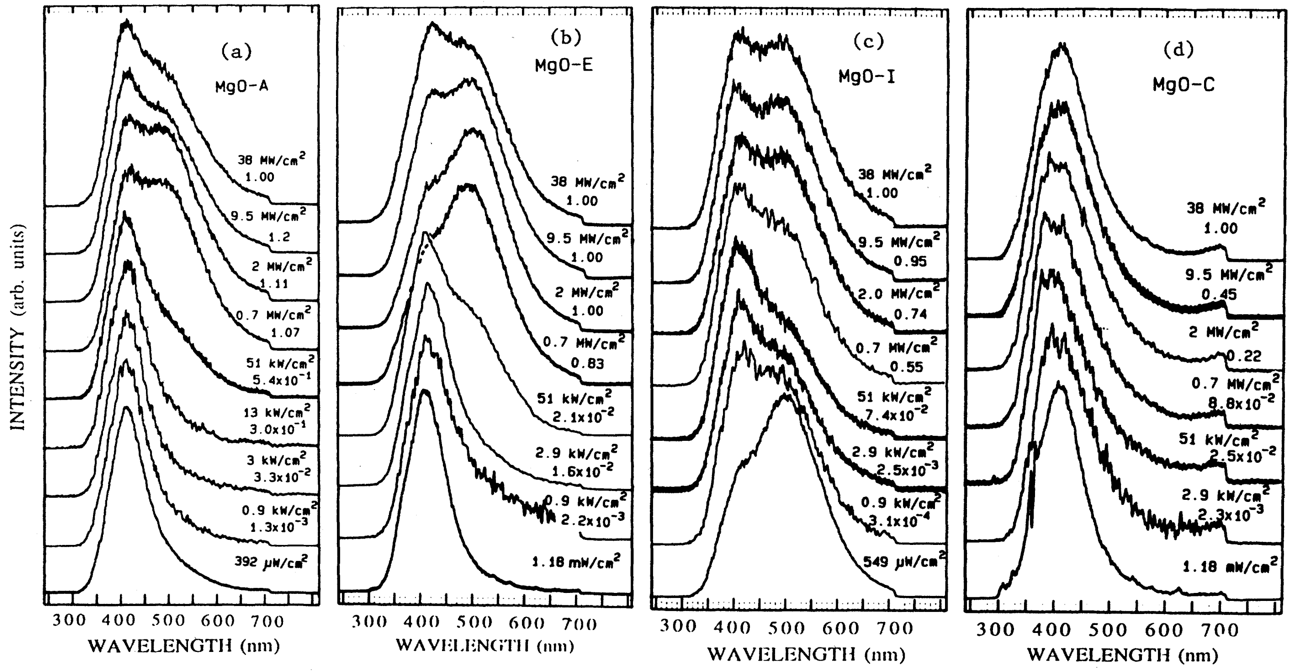

FIG. 4. For each of the four samples in (a)–(d), luminescence spectra are shown corresponding to different power densities of the 248-nm excitation light, as labeled by the first number at the lower right-hand side of each spectrum. All spectra are normalized to the same height and displaced vertically relative to one another for display. The second number (unitless) at the lower right-hand side of each spectrum gives the ratio of the peak intensity at that time to the peak intensity at the earliest time shown.

that excited F centers are easily ionized by electron release to the conduction band. It has often been assumed that F^+ ground and excited states should lie at substantially lower energies than their F-center counterparts. In that case, thermal release from the excited state (F^{+*}) to the conduction band would be unlikely, and F^+ ionization might be expected to occur instead by release of a hole to the valence band. This receives support from the observation that exciting MgO near 250 nm produces

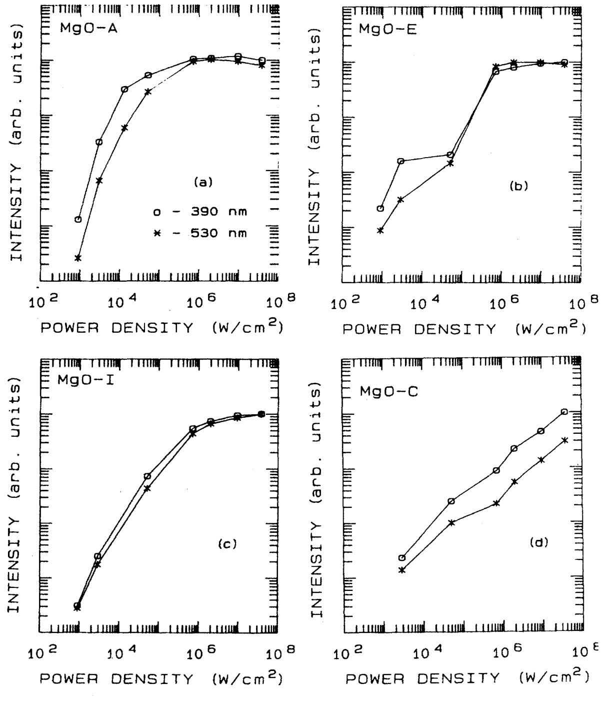

FIG. 5. For each of the four samples in (a)–(d), luminescence intensity from F^+ centers (390 nm) and F centers (530 nm) is plotted vs power density of the 248-nm excitation light. Both scales are logarithmic. The units of intensity are arbitrary.

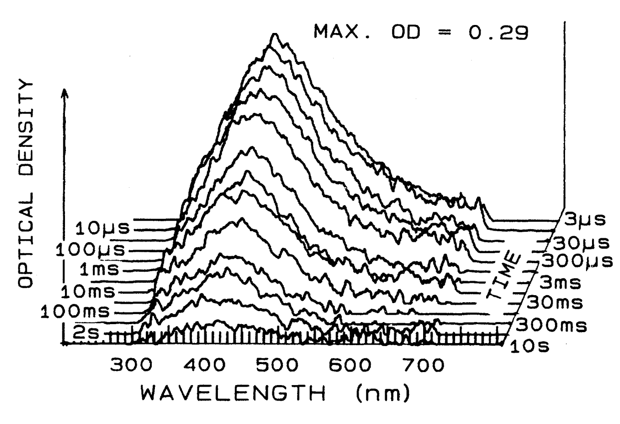

FIG. 6. Transient absorption spectra measured at the indicated delay times after excitation of sample MgO-I by a 248-nm laser pulse at an energy density of 200 mJ/cm^2.

V-type trapped hole centers and converts some F^+ centers to F centers.[17] However, with regard to the present data, it is extremely unlikely that independent electron traps and hole traps would interact almost identically with F and F^+ centers, respectively, to produce almost identical decay kinetics over a wide range of both time and temperature, as is observed. We propose that the same charge carriers must be responsible for long-lived luminescence in both bands.

The concept of F^+ photoionization by electron release is borrowed from results of photoconductivity in SrO. Feldott and Summers showed that electrons are the dominant charge carriers released upon excitation in the F^+ band of SrO.[29] Furthermore, they determined that the activation energy for thermal release of the electron from the F^+ excited state is 0.12 eV. The concept of electron release from the F^+ excited state is also consistent with the recent theoretical calculations of Klein *et al.* who found the first F^+ excited state to be close to or degenerate with the conduction-band edge in MgO and CaO.[11]

In the simplest scenario for the electron trapping and recombination, we envision the laser pulse as placing both F and F^+ centers in states which ionize by electron release to the conduction band. In the process of recombination with those electrons, F and F^+ centers alike would see the same time-dependent flux of conduction electrons, and so would exhibit the same decay kinetics of recombination luminescence. However, the spectral data make it clear that there are small (factor of 2) differences in F and F^+ luminescence intensity over the 7 decades from 200 ns to 2 s. The decays should be exactly proportional if the entire source of recombining electrons were free electrons in the conduction band. The subtle differences lead us to propose that a significant number of the recombinations occur by tunneling from nearby traps to the ionized F or F^+ centers. Such a tunneling process depends on the wave-function overlap between the trap level and the F- or F^+-center excited states, and therefore can introduce some distinction between the two centers into the decay kinetics. The process is similar to the donor-acceptor pair model developed for defects in semiconductors,[30] which has been used to describe the decay of V-center luminescence in MgO.[31]

The dominant electron trap controlling F-center phosphorescence beyond 1 s in TCR MgO has previously been identified as the H^- center.[3-5] This is also probably true for most of the F-center luminescence decay we have seen between about 1 μs and 1 s, and therefore, by the above arguments, for F^+ luminescence as well. It is probable that other kinds of electron traps can influence portions of the decay curve, especially in neutron-irradiated MgO. Formation of H^- centers is principally expected in thermochemically reduced crystals. Therefore the absence of the longest-lived components of F and F^+ luminescence in neutron-irradiated MgO lends indirect support to the importance of H^- centers in stretching the decay time.

Edel, Henderson, and Romestain had earlier suggested that the role of electron traps in delayed F-center luminescence might be fulfilled by F centers themselves, through a postulated $F^\dagger$ state which decays to an F^+ center and a released electron.[20] The free electron would then recombine with an ionized F center to produce delayed F-center luminescence, in close similarity to the process we have described. While the role of H^- centers as electron traps has been established by Chen and coworkers,[3-5] there is as yet no direct observation of an $F^\dagger$ state playing such a role. Almost any shallow electron trap in MgO is a reasonable participant in persistent F-to-F^+ luminescence, however.

If the excited F^+ center ionizes by electron release as we have proposed, then the resulting defect is an F^{2+} center (bare oxygen vacancy) and the F^+ luminescence results from the recombination event

$$F^{2+} + e^- \rightarrow F^+ + h\nu(390\ \text{nm})\ . \tag{1}$$

Since the recombination evidently takes as long as several seconds to occur, the F^{2+} center must be recognized as existing for finite times if Eq. (1) correctly describes F^+ luminescence. The F, F^+, and trap levels corresponding to our hypothesis are summarized in Fig. 7.

Within the picture introduced above, we may presume that an intense laser pulse ionizes F to F^+ and F^+ to F^{2+}, consistent with the observation that all the crystals have displayed initial F^+ luminescence spectra, regardless of the steady-state spectrum. If F^{2+} centers can also absorb 248-nm photons (mechanisms discussed below), then we should consider the possible consequences in luminescence, absorption, and charge release.

Our model of the F^{2+} energy levels is based on the idea that the excited F^+ center (F^{+*}) lies very near the conduction-band minimum in its unrelaxed excited state.

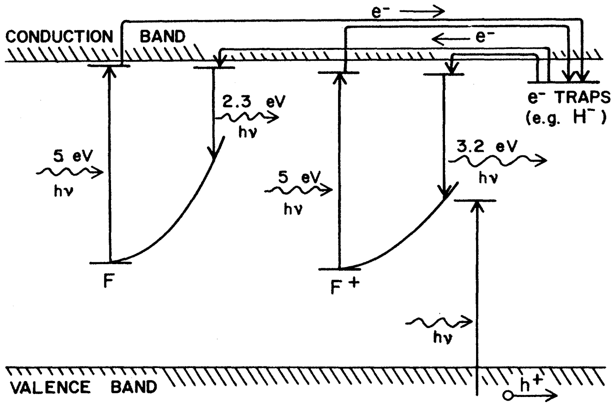

FIG. 7. Schematic representation of the trap and defect levels that we have suggested to account for the correspondence of F and F^+ luminescence decay times. The conduction-band edge is taken as a constant reference energy for purposes of this diagram, so that Stokes shifts appear almost entirely as a rise in the ground-state energy. Although it is not known how the band gap may be influenced locally by the defects, the valence-band edge is assumed flat on this diagram. At the lower right-hand side, we represent the optical excitation of an electron from valence states into the empty ground state of a relaxed F^{+*} (or F^{2+}) center, which we suggest can account for observed hole release and for F luminescence dominance and saturation of luminescence at high excitation power density.

Then the unrelaxed F^{+*}, and the nearly equivalent unrelaxed F^{2+}, present two vacant defect electron levels about 5.1 eV below the conduction-band minimum and therefore about 2.7 eV above the valence-band maximum. After the lattice relaxation accounting for the 2-eV F^+ luminescence Stokes shift, the F^{+*} ground state or F^{2+} will have risen about 2 eV relative to the conduction-band edge. Then 5-eV (248-nm) photons should be able to excite electrons from valence states into the empty F^{+*} or F^{2+} levels. Or, in other words, holes are optically excited from the F^{+*} and F^{2+} into the valence band. The result of such an optical hole excitation is an excited *F center* (F^*) in the first case, or an ionized F center (F^+) in the second case, accompanied by a hole in the valence band and (in the latter case) an electron in the conduction band or in a trap. Upon recombination with the excited electron, both cases give *F-center luminescence.* Thus in this model an intense laser pulse first produces mostly F^{2+} centers which emit F^+ luminescence upon recombination with an electron, but continued excitation of the F^{2+} centers may give predominantly F-center luminescence and valence holes. This agrees with our observations of (a) initial F^+ luminescence, (b) tendency toward F luminescence with increasing excitation power density, and (c) holes which must evidently be released by 248-nm excitation in order to account for the growth of V centers which is observed (even in some of the Mg-rich TCR crystals).

However, in a very intense laser pulse, we may expect that after optical excitation of a *hole* from F^{2+}, the resulting F^+ center can absorb another photon, exciting the resident *electron* to the photoionizing state near the conduction band, and thus creating the F^{2+} charge state again. This two-step cycle can be repeated many times in an 18-ns pulse since no recombination times are involved. What we have, then, is a state near midgap which can turn a high flux of 248-nm photons into a stream of holes and electrons by successive absorption events. If the electrons and holes can mutually annihilate, e.g., by exciton recombination, this process will effectively consume 248-nm photons while producing no additional F^+ or F luminescence. This is just the kind of mechanism that could account for the saturation behavior shown in Fig. 4.

One possible weakness of this optical hole excitation model is uncertainty over the strength of optical transitions from the valence band into the localized F^{2+} vacant levels. However, because of the extremely large electronic polarization which the F^{2+} (bare oxygen vacancy) is expected to induce on surrounding oxygen ions, the valence states of those ions may be considered quasilocalized states degenerate with the valence band. This could in turn lead to significant enhancement of the optical transition matrix elements between the locally perturbed valence band (i.e., the polarized neighboring oxygen ions) and the F^{2+} (or F^{+*}) vacant levels. The resulting absorption would be analogous to charge-transfer bands of trivalent transition metals in oxide hosts, but probably even stronger because of the double positive charge with respect to lattice neutrality in the case of the F^{2+} center.

If the optical cycle of the F^+-to-F^{2+} system described above does channel high-intensity 248-nm excitation into copious electron and hole production, one might expect to see a resulting increase in the exciton emission line at 7.65 eV.[32] This is beyond the spectral range of our current instrumentation, but should be observable in a vacuum-ultraviolet spectrometer. One might also look for the F^{2+} absorption band. We have looked for general transient absorption induced by 248-nm excitation, and found the spectrum reported in Fig. 6 for MgO-*I*. If the F^{2+} absorption were to be observed, it should have the lifetime governed by the electron traps that determine F^+ luminescence in MgO-*I*, i.e., several seconds. Within the model that we have suggested, the relaxed energy levels of the F^{+*} should be approximately as represented on the lower right-hand side of Fig. 7. We have seen that the ground state of F^{+*} rises about 2 eV relative to the conduction-band edge in the relaxed configuration. Thus if the band gap[33] remains roughly constant in the presence of the defect, the F^{2+} level may lie about 3.7 eV above the valence-band maximum. The charge-transfer absorption band would be broad because the initial set of states is comprised of the valence band. We simply point out that the spectra have about the right lifetime, energy, and width. In this model, optical hole release would follow from the sequence of first absorbing light in the F^+ band to create an F^{2+} center (after thermal ionization), and then absorbing another 5-eV photon in the high-energy wing of the broad F^{2+} charge-transfer (hole) absorption band.

Presumably it is also possible to optically excite electrons from the valence band directly into the F^+ ground state, creating a ground-state F center and free hole. However, this might be much weaker than the transition into the F^{2+} because of smaller polarization of the valence states and consequent small transition matrix elements to the localized defect. It should be possible to test some of these concepts by using double-pulse excitation by 5-eV photons in combination with lower-energy photons tunable around the anticipated F^{2+} absorption spectrum.

Extreme electronic polarization induced by the F^{2+} center on the surrounding ions might cause spontaneous generation of a bound exciton from the valence band. That is, the F^{2+} might pull almost one electron of charge from the near-neighbor oxygen ions, leaving the equivalent fraction of a hole shared among them and bound to what is then effectively an F^+ center. Release of the bound hole might be possible with only thermal energy.

V. SUMMARY

The following experimental observations are reported without regard to any assumed model other than that the 390-nm band is F^+ luminescence and that the 530-nm band is F luminescence.

(1) Both the F^+ and F luminescence bands have long persistence times, out to at least 1 s. This is true in all thermochemically reduced MgO and at least for the F^+ center in neutron-irradiated MgO. In neutron-irradiated crystals, F^+ luminescence is so dominant that it is

difficult to ascertain the F luminescence decay.

(2) In the low-hydrogen thermochemically reduced crystals studied, the F and F^+ luminescence decay curves correspond very closely over 7 decades of time and intensity, from 200 ns to 2 s.

(3) Within the above-noted correspondence of decays, there are small variations of relative F and F^+ intensity, of order 50%, viewed against a factor-of-10^7 overall decay.

(4) At high excitation intensities, the initial luminescence spectrum is that of the F^+ center in all TCR MgO crystals.

(5) At a later time, F luminescence contributes significantly. The time at which the F luminescence first contributes significantly is delayed for the crystal with higher H^- concentration in the group we have studied.

(6) As the 248-nm excitation power density increases, F luminescence increases relative to F^+ luminescence in TCR samples. Even crystals which exhibit pure F^+ luminescence under low-level continuous excitation assume significant F character at power densities above 50 kW/cm^2.

(7) Both F and F^+ luminescence intensities saturate strongly as excitation power density increases above 50 kW/cm^2. The absolute intensities even decrease in some crystals as the power density approaches 38 MW/cm^2. We checked for increased transmittance of the crystals at 38 MW/cm^2 and found nothing significant, even though the luminescence efficiency at that power was at least 2 orders of magnitude smaller than at low power.

(8) The neutron-irradiated crystal does not show as strong a saturation behavior as the thermochemically reduced crystals. It exhibits primarily F^+ luminescence, its initial luminescence is significantly more intense than in the TCR samples, and the luminescence is not as persistent although still lasting almost 1 s.

(9) Excitation at 248 nm induces a V-center optical absorption band (associated with a magnesium vacancy trapping a hole, possibly with charge-compensating impurities). This was expected in the neutron-irradiated sample. Surprisingly, it was also found in some thermochemically reduced samples, especially MgO-E. The main significance of this is confirmation that some holes are released upon excitation at 248 nm. It is a surprise that there are enough magnesium vacancies in the thermochemically reduced sample to produce an observable V band.

Within the context of the model we have suggested, the following conclusions are drawn.

(1) Because the luminescence decay is so much slower than expected from the allowed transitions assigned to both F and F^+ luminescence, we conclude that charge trapping and transport govern the decay kinetics. It follows that both F and F^+ centers readily ionize (above about 100 K) from the excited states reached by 5-eV excitation.

(2) Because the F and F^+ luminescence bands decay together over a wide time range and temperature range in all low-hydrogen TCR MgO studied, we conclude that the charge carriers whose transport and trapping govern the decay kinetics are the same for both luminescence bands. Since photoionization of F centers is known to occur by electron release, we therefore propose that excited F^+ centers also ionize predominantly by electron release and that it is the recapture of an electron which initiates the 390-nm luminescence. This picture implies that the F^+ excited state lies close to the conduction-band edge and that the ground state lies about 5.1 eV below the conduction-band edge, i.e., the F^+ ground state is only slightly below the F ground state.

(3) If the excited F^+ center ionizes by electron release, then the F^{2+} center (bare oxygen vacancy) must be recognized as existing until radiative recombination restores the F^+ ground state.

(4) From our observations in this work, as well as other work,[17] we also must allow that holes are released into the valence band upon excitation in the F^+ band. We propose that the F^+ and F^{2+} levels lie near midgap and can participate in electron transitions both from valence states into empty defect levels and from filled defect levels to (or near) the conduction band.

(5) These charge-transfer transitions from the neighboring oxygen ions into the F^{2+} center are consistent with a number of our observations. Such a transition restores the F^+ center, which yields F luminescence upon recombination with an electron, in qualitative agreement with our observation that high excitation intensity favors F luminescence over F^+. Furthermore, having the F^+ and F^{2+} near midgap provides a way to channel large numbers of photons into electron and hole production rather than defect luminescence, in agreement with the extreme saturation behavior we have observed as excitation intensity increases.

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