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Optical detection of a hydrogen complex responsible for the *F* phosphorescence in thermochemically reduced MgO crystals

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A hydrogen complex denoted as $[H_x{}^-]^0$ has been detected using optical-absorption techniques. The local mode of the hydrogen in the anion sublattice resonates at 1037 cm^{-1} and a broad absorption peaking at 400 nm characterizes the electronic transition of this complex. It is shown to be the predominant electron trap involved in the photoconversion process of $F \rightarrow F^+$ centers. It is metastable at room temperature, giving rise to the *F* phosphorescence (the thermoluminescence which peaks at 260 K). We further demonstrate that this complex is not the defect identified previously as an H^{2-} ion by electron paramagnetic resonance at low temperature.

I. INTRODUCTION

The origin of the green phosphorescence observed at 2.4 eV (520 nm) in thermochemically reduced (TCR) MgO crystals resulting from optical excitation in the *F* band at room temperature has been of experimental and theoretical interest for two decades.[1–5] Recently, it has been shown that this long-lived luminescence is unambiguously related to the presence of H^- ions (protons each with two electrons occupying O^{2-} ion sites) produced during the TCR process.[6–10] The following mechanism has been proposed: Absorption of 4.95-eV (250-nm) light excites electrons from the $^1A_{1g}$ ground state of the *F* center to its $^1T_{1u}$ excited state.[11] Since the excited state is close to the conduction band, the electrons are thermally ionized into the conduction band, resulting in conversion of *F* to F^+ centers. The released electrons are then trapped by the positively charged H^- ions and form the electrically neutral H^{2-} ions. The latter are metastable at room temperature, resulting in the reverse process causing the *F*-center phosphorescence.

Recently, an electron-paramagnetic-resonance (EPR) signal observed in thermochemically reduced MgO crystals (MgO:Mg) after photon excitation has been identified as due to H^{2-} (or perturbed H^{2-}) ions.[12] An optical identification of the H^{2-} ion in MgO has not been made. Furthermore, a direct optical connection of the H^- ions with the long-lived luminescence has not been demonstrated. In the present study we (1) performed optical studies of samples with high *F*-type and H^- concentrations between 77 and 295 K, and identified the local-mode vibration frequency and the electronic transition of an H^- complex containing an electron ionized from the *F* center. (We shall denote this complex as $[H_x{}^-]^0$.[13]) (2) We correlated the subsequent release of the electron with the *F*-center thermoluminescence (TL) and phosphorescence observed near room temperature; and (3) demonstrate unambiguously that this complex is not the H^{2-} species observed by Tombrello *et al.*[12] using EPR.

II. EXPERIMENTAL PROCEDURES

The samples used in this work were grown by the arc-fusion method using high-purity MgO powder.[14] A large concentration of hydrogen was obtained using MgO powder previously presoaked with water. The crystals contained cloudy regions due to the presence of voids containing high pressures of hydrogen gas. Thermochemical reduction was performed at high temperatures (~2400 K) under 4–7 atmospheres of magnesium vapor. This procedure produces high concentrations of *F* centers and H^- ions.

Absorption spectra were measured in a thin sample (0.4 mm) using a Cary 17D spectrophotometer for the uv-visible-ir range and a Perkin-Elmer 983 spectrophotometer for the ir region. Optical bleaching was produced with monochromatic light from a 1000-W Xe-Hg lamp in conjunction with a Bausch-Lomb monochromator. Suitable long-pass filters were used to avoid harmonic effects. Thermoluminescence measurements were made by raising the temperature of the samples at a rate of ~8 K/min. The temperature was measured using a calibrated copper-Constantan thermocouple. Emission was detected with an RCA 31034C photomultiplier.

EPR measurements were performed in an E-112 *X*-band Varian spectrometer. Isochronal annealings between 77 and 300 K were performed using a Varian E-257 continuous-flow cryostat.

III. RESULTS

The crystals used in this study contain primarily *F* centers and H^- ions. The concentrations are 1.6×10^{18} and 3.0×10^{18} cm^{-3}, respectively. A small concentration of residual F^+ centers is also present as indicated by EPR and a luminescence band at 3.1 eV (400 nm).

A. Optical studies

At 77 K these MgO:Mg crystals exhibit infrared-absorption bands at 1056, 1034, and 1027 cm^{-1} (Fig. 1, top). These bands have been attributed to different species of H^- ions. A second-harmonic absorption at 2601 cm^{-1} was also observed. In the uv region, a strong absorption band at 4.95 eV due to electronic transitions of both F and F^+ centers is also present. Optical pumping into the F band (using 235–270-nm light) at 77 K decreased the 1027-cm^{-1} local mode and created a new band at 1037 cm^{-1}. No such effect was observed when pumping in the blue region, 400–430 nm. Figure 1 (center) illustrates the spectrum during the optical pumping and Fig. 1(c) (bottom) shows the enlarged differential spectrum. During excitation into the F band, an electron is released into the conduction band and captured by one of the H^- species, referred to as $[\mathrm{H}_x{}^-]^+$, and form the $[\mathrm{H}_x{}^-]^0$ species.[13] We attribute the 1027- and 1037-cm^{-1} bands as due to the local modes of $[\mathrm{H}_x{}^-]^+$ and $[\mathrm{H}_x{}^-]^0$ ions, respectively, for reasons which we shall describe later. The photoconversion process can be described by the following equations:

$$F+h\nu\ (4.95\ \mathrm{eV})\rightarrow F^*\rightarrow F^+ + e^-\ , \tag{1}$$

$$e^- + [\mathrm{H}_x{}^-]^+ \rightarrow [\mathrm{H}_x{}^-]^0\ . \tag{2}$$

The 1037-cm^{-1} vibrational mode resulting from F-band excitation at 77 K was attended by a yellow-brown color in the sample. (Again this coloration was not produced when exciting with blue light.) This coloration is due to a broad optical-absorption band peaking at 400 nm. Figures 2(a) and 2(b) illustrate the optical-absorption spectra of the same MgO:Mg crystal before and after pumping with F light, respectively. The differential spectrum, illustrated by the solid curve, shows that the peak occurs at ~400 nm. The band is very broad. The band shape below 400 nm could not be accurately measured because of the overlap with the intense F and F^+ bands. The production and thermal stability of this band indicate that it is correlated with the infrared absorption at 1037 cm^{-1}. Therefore we attribute this 400-nm absorption band to the electronic transition of the $[\mathrm{H}_x{}^-]^0$ complex.

Both the $[\mathrm{H}_x{}^-]^0$ complex, as monitored by the local mode at 1037 cm^{-1}, and the electronic transition at 400 nm, were stable at 77 K. At this temperature, the sample did not exhibit the characteristic long-lived green phosphorescence observed when excited at 295 K. In fact, exciting the sample with F light at 295 K and quenching rapidly to 77 K produced the same $[\mathrm{H}_x{}^-]^0$ optical characteristics. The green phosphorescence which prevailed during excitation at 295 K was quenched when the sample was cooled down.

The process described by Eqs. (1) and (2) was reversed when the sample warmed to 295 K. The thermal destruction of the $[\mathrm{H}_x{}^-]^0$ complex was attended by a very brilliant green TL glow which peaked at 260 K (Fig. 3), indicating that the electrons were released and returned to the F^+ centers, giving rise to the phosphorescence. This TL glow was reported previously in MgO:Mg crystals.[9] The correlation between the presence of the $[\mathrm{H}_x{}^-]^0$ complex and the green phosphorescence has been established in various samples. Furthermore, the local mode at 1037 cm^{-1}, the absorption peak at 400

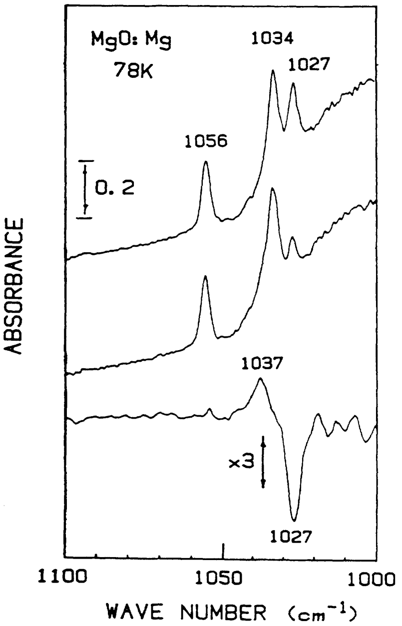

FIG. 1. Infrared spectra of a thermochemically reduced MgO crystal at 78 K (top), during F excitation (center), and the differential spectrum (bottom). The bottom curve is enlarged by a factor of 3.

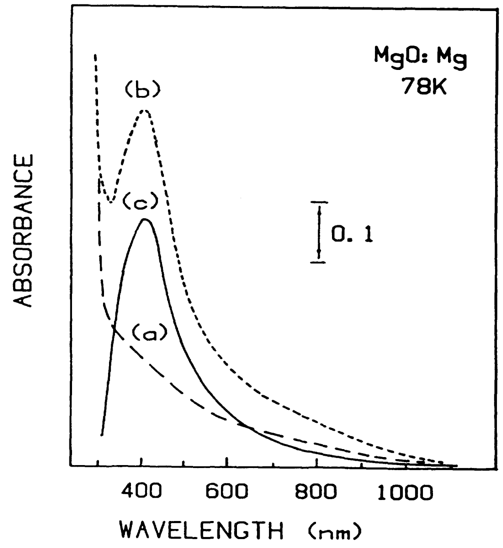

FIG. 2. Spectra of a thermochemically reduced MgO crystal at 78 K before [curve (a)] and after [curve (b)] excitation with F light. The differential spectrum is shown in curve (c).

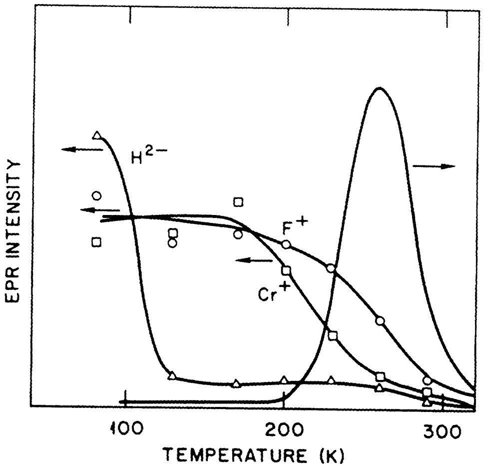

FIG. 3. Right ordinate: *F*-center thermoluminescence of a thermochemically reduced MgO crystal previously irradiated with *F* light at 7 K. Left ordinate: Isochronal annealing of the EPR signals of a similar crystal irradiated with *F* light at 77 K. The values given for H^2, F^+, and Cr^+ do not scale with one another. The ordinates are in arbitrary units.

nm, and the green phosphorescence are all identified with hydrogen-rich regions in different samples. Some crystals have an inhomogeneous distribution of hydrogen, as indicated by the presence of some cloudy regions due to scattering from voids containing high-pressure hydrogen gas. Associated with these hydrogen-rich regions are the strong H^- infrared absorptions. After excitation with *F* light at 295 K, these regions exhibited intense green phosphorescence. When excited at 77 K, these same regions exhibited the yellow brown coloration. All these effects were subdued in the clearer regions of the samples. Therefore we associate the 1037-cm^{-1} local mode, the 400-nm absorption band, and the long-lived green phosphorescence with the presence of hydrogen.

The $[H_x{}^-]^0$ complex, as characterized by the two absorptions (1037 cm^{-1} and 400 nm), and the *F* phosphorescence can be produced only in samples in which both the *F* band and the 1027-cm^{-1} local mode are present. In a sample in which the $[H_x{}^-]^+$, characterized by the 1027-cm^{-1} local mode, is present to the exclusion of *F* centers, no $[H_x{}^-]^0$ could be created. Similarly, *F* centers without $[H_x{}^-]^+$ prohibit the production of $[H_x{}^-]^0$.

B. Electron paramagnetic resonance (EPR)

In order to monitor the photoconversion process, we have performed EPR studies in the same crystal and under the same bleaching conditions as described in the preceding section. In Fig. 4 we show the EPR spectra of a MgO:Mg crystal at 77 K measured with the external field $\mathbf{H}\|[100]$ before (a) and during optical excitation [(b) and (c)]. Three sets of lines, near $g \sim 2$, corresponding to F^+ centers, Cr^+, and H^{2-} ions, have been followed. The H^{2-} ion here refers to the EPR signal reported by Tombrello *et al.*[12] and shall henceforth be referred to as H^{2-}(EPR), in order to distinguish it from the $[H_x{}^-]^0$ monitored by optical measurements.

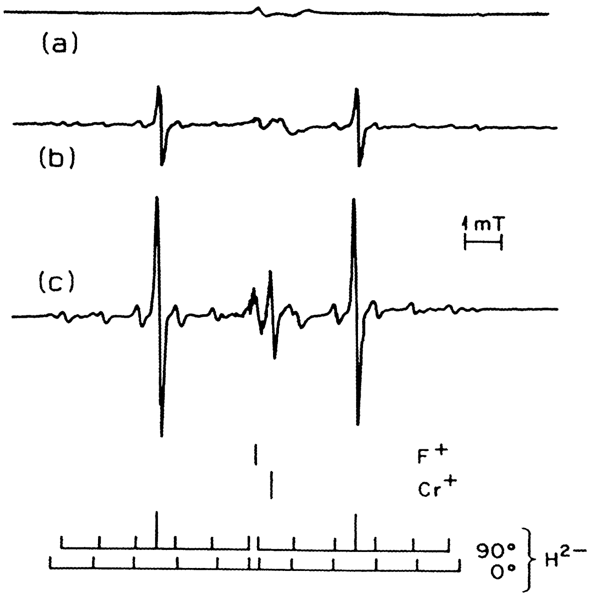

FIG. 4. EPR spectra of a thermochemically reduced MgO taken at 77 K with $\mathbf{H}\|[110]$: (a) before bleaching, (b) after bleaching with blue light (430 nm), and (c) after bleaching with *F* light (250 nm). The stick diagram at the bottom refers to the positions of the lines corresponding to each defect.

The spectra given in Fig. 4 were measured with a high modulation frequency (100 kHz) and relatively high microwave power levels (5 mW). Since the F^+ signal is saturated and is nearly 90° out of phase with the field modulation at these frequencies, the F^+ concentration is not reflected accurately under these conditions. We have used low modulation frequencies and power levels (0.05 mW) to obtain precise measurements of the F^+ signal. The increase of the F^+ signal when measured at low microwave powers overwhelms that of Cr^+ and H^{2-} signals. The Cr^+ signal is best identified under conditions in which the H^{2-}(EPR) ions have been thermally destroyed ($T > 150$ K). In that case, the fine structure described by Barklie *et al.*[15] is clearly seen. In Fig. 4(a) we show the spectrum before bleaching. There exists a residual F^+ concentration. Bleaching with 430-nm light at 77 K produced H^{2-}(EPR) ions and no changes in the F^+ signal [Fig. 4(b)]. Bleaching with *F* light produced Cr^+ signal and an enhancement of both the H^{2-}(EPR) and F^+ signals [Fig. 4(c)]. In all the samples containing both *F* centers and H^- ions that we examined, we observed this same trend—enhancement of F^+, Cr^+, and H^{2-}(EPR) signals when bleached into the 250-nm band. The same effect, but with less efficiency, was achieved when bleaching was performed at 295 K followed by fast quenching into liquid nitrogen.

C. Thermal stability

Isochronal annealing of the defects involved in the photoconversion process described above, viz. F^+, Cr^+, and H^{2-}(EPR), have been studied between 77 and 295 K. All measurements were made at 77 K. The same sample used to obtain the TL glow shown in Fig. 3 was bleached with F light at 77 K. It was then isochronally heated at a given temperature for about 3 min and then cooled down to 77 K. The cycle approximately simulates the TL heating rate. The results are presented in Fig. 3. The H^{2-}(EPR) decays even at 77 K and is destroyed at about 100 K. However, it rejuvenates in the dark at 77 K as shown by the residual concentration above 150 K. On the other hand, the F^+ and Cr^+ readily anneals above 200 K. The decay of the F^+ and Cr^+ is attended by the F thermoluminescence. It is clear from Fig. 3 that the thermal annihilation of Cr^+ is not governed by the decrease of F^+ centers on a one-to-one basis, in agreement with the results of Barklie *et al.*[15] The concentration of F^+ centers in our crystal is 1 to 2 orders of magnitude higher than that of the Cr^+ ion. The thermal conversion of Cr^+ to Cr^{2+} does not scale with that of the F^+ to F conversion, indicating that the latter is governed predominantly by another electron trap. The optically detected $[H_x{}^-]^0$ defect has the correct concentration; its annealing, together with the TL glow curve, matches the F^+ decay shown in Fig. 3.

IV. DISCUSSION

The experimental results described above permit us to draw several pertinent conclusions concerning the nature of the defects and the physical processes which govern the photoconversions.

We draw our attention to the nature of the H^- ions. The three local modes, at 1056, 1034, and 1027 cm^{-1}, are not intensity correlated, based on observations in different crystals and electron irradiation. For example, the 1027-cm^{-1} mode is destroyed by bleaching into the F band whereas the other two remain unaffected. The 1056-cm^{-1} local mode presents a second harmonic which cannot be attributed to the 1034-cm^{-1} mode. They are due to different species involving the H^- ion in an oxygen site. It is likely that the small differences in frequency arise from small local perturbations. The perturbations are probably due to vacancies or other impurities. These perturbing species produce a lowering of the local symmetry which is evident in the second harmonic associated with the 1056-cm^{-1} local mode. The distortion could be sufficiently small that no splitting of the lines is observed experimentally.

In our present work, only one of the H^- species is activated when bleaching into the F band. The other species are unable to capture electrons. A similar behavior has also been observed in CaO:Ca.[16] Since bleaching into the F band produces a large F^+ concentration, a large amount of electrons is released. These electrons are trapped by one of the perturbed H^- species producing what we designated as a $[H_x{}^-]^0$ complex. It is this defect that is responsible for the TL peak at 260 K (or the long-lived phosphorescence at 295 K) and an absorption peak at 400 nm.

We deduce that the electron trap is a perturbed species, because if it were an unperturbed H^{2-} ion, it would (1) have thermal stability which scales with the thermal annealing of the F^+ center, (2) be paramagnetic, and (3) cause a larger shift from the H^- local mode. Our results show, first, that the thermal stability of our experimentally observed $[H_x{}^-]^0$, as characterized by the 1037-cm^{-1} local mode and the electronic transition at 400 nm, indeed vanish with the F^+ center. Secondly, no EPR signal due to an unpaired electron at a proton was associated with $[H_x{}^-]^0$ defects. Thirdly, the frequency shift is only 10 cm^{-1} (1027 to 1037 cm^{-1}). The second and third observations clearly argue that our optically detected $[H_x{}^-]^0$ is not due to an unperturbed H^{2-} ion. A possible configuration for our $[H_x{}^-]^0$ would be a M^+H^- complex resulting from $M^{2+}H^-$ having trapped an electron at the M^{2+} rather than the H^- site, where M refers to an unidentified cation; in this case, the hydrogen is not paramagnetic and the perturbation on the proton vibrational frequency is small.

The concentrations of the $[H_x{}^-]^0$ and H^{2-} (EPR) are different. The former is about 5×10^{17} cm^{-3}, estimated from Fig. 3 in conjunction with Eq. (4) of Ref. 8; this value is compatible with the F^+ concentration after bleaching with F light. The H^{2-} (EPR) concentration, on the other hand, is about 1 order of magnitude lower (1×10^{16} to 1×10^{17} cm^{-3}). Concentrations of this magnitude are difficult to detect optically in the local modes, and so far we have not been able to detect the local mode due to H^{2-}(EPR) or the H^- species responsible for the H^{2-}(EPR). This magnitude is more compatible with the Fe^+ and F^+ concentration due to blue-light pumping at low temperature.[12]

It is clear that there exist at least two types of electron traps involving hydrogen in thermochemically reduced MgO crystals: the H^{2-}(EPR) as reported by Tombrello *et al.*, and the $[H_x{}^-]^0$ detected optically in the present work. They possess different properties: (1) In one case the electron is trapped at the proton, and in the other it is not; (2) the former can be produced by bleaching with F or blue light, whereas the latter can be produced only with F light; (3) the H^{2-}(EPR) anneals at $\sim$100 K, whereas the $[H_x{}^-]^0$ anneals at $\sim$260 K; and (4) their concentrations are different.

V. SUMMARY AND CONCLUSIONS

We have identified, by optical techniques, a complex containing a H^- ion which has trapped an electron during optical bleaching of the F center. This complex, referred to as $[H_x{}^-]^0$, is clearly the dominant entity involved in the $F \rightarrow F^+$ process, given in Eqs. (1) and (2). This complex is identified by the H^- local mode at 1037 cm^{-1} and an electronic transition characterized by a broad absorption band centered at $\sim$400 nm. It is metastable near room temperature, the process being governed by the reverse of Eqs. (1) and (2), and is responsible for the F thermoluminescence peak observed at 260 K. The magnetic, thermal, and bleaching properties are different from those of the H^{2-} ion identified by

EPR. Consequently, we conclude that the H^{2-}(EPR) ion cannot be responsible for the *F* phosphorescence at room temperature. Furthermore, we have shown that the Cr^+ ion is not the predominant metastable trap responsible for the $F \leftrightarrow F^+$ photoconversion.

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