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Charge and mass transfer involving hydrogen in MgO crystals thermochemically reduced at high temperatures

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Optical-absorption measurements show that H^- ions are thermally much more stable than anion vacancies when thermochemically reduced MgO samples are annealed in a reducing atmosphere. At 1900 K all anion vacancies are annihilated, but the concentration of H^- ions remains unchanged. Results of electron irradiations on a crystal annealed at 1900 K demonstrate unambiguously that the infrared-absorption peaks previously attributed to H^- ions are indeed due to protons in anion sublattice sites. H^- concentrations can be obtained from the infrared absorbance of the H^- ions. The lifetime of the 2.3-eV *F*-center phosphorescence is shown to be affected by the relative concentrations of H^- ions to anion vacancy. Decreasing the anion-vacancy concentration by thermal annealing, thereby increasing the relative concentration of H^- ions to anion vacancies, leads to an enhancement of the lifetime of the phosphorescence.

I. INTRODUCTION

Recent studies have shown that thermochemical reduction of MgO at high temperatures and pressures produces not only the ultraviolet absorption associated with anion vacancies but also sharp absorption lines in the low-energy infrared spectra which can be attributed to the fundamental vibrations of substitutional H^- ions.[1] At 295 K the peaks occur at 1053, 1032, and 1024 cm^{-1}. The intensity of this three-line spectrum is correlated with the hydrogen content in the crystal and the reduction temperature. An H^- ion in MgO consists of a proton with two electrons occupying an oxygen-vacancy site, which therefore has a net positive charge. As such, it can trap a transient electron. Indeed, it was this expected characteristic of the H^- ion which originally led us to believe that H^- ions were the electron traps responsible for the long-lived phosphorescence of the *F* center (an oxygen vacancy containing two electrons) in MgO and possibly other oxides.[2] The cause of this long-lived phosphorescence has been a subject of discussion for many years.[3–7]

The results of the present work provide (1) unambiguous evidence that the vibrational lines in the infrared are indeed due to protons located at anion sublattice sites, (2) formulations from which H^- concentrations can be deduced from the H^- absorbance, and (3) additional evidence that the lifetime of the *F*-center emission is governed by the H^- ions serving as traps for the excited electron.

II. EXPERIMENTAL PROCEDURES

The MgO crystals used in the present study were grown[8] by the arc-fusion method at the Oak Ridge National Laboratory using high-purity—grade MgO powder from the Kanto Chemical Company, Tokyo, Japan. Typical chemical analyses of the MgO crystals, along with the starting material, have been reported previously.[8,9] Large variations of hydrogen content can be obtained. MgO powder presoaked with H_2O or D_2O resulted in crystals that are very cloudy, due to the presence of cavities containing high-pressure H_2 or D_2 gas.[10] At the other extreme, MgO crystals with a very low OH^- concentration can be produced when grown in a special way.[8]

The method used for reduction at high temperatures involves a process aptly called "subtractive coloration," or thermochemical reduction. The crystals were heated to $\sim$2400 K under a high pressure of magnesium vapor ($\sim$7 atm) in a tantalum bomb, followed by rapid cooling. This process produces anion (oxygen) vacancies, due to a stoichiometric excess of cations. If hydrogen impurities are present in the crystals, they can be trapped at these vacancies, forming H^- ions.[1] The more hydrogen the crystals contain, the more H^- ions that are formed. Thus the balance between the H^- and the *F*-center concentration depends on the concentration of hydrogen in the crystal.

Infrared-absorption measurements were made with a Perkin-Elmer Model 580 spectrophotometer. Oxygen-vacancy concentrations were determined from optical-absorption measurements with a Cary 17D spectrophotometer.

Luminescence was induced by a 60-W deuterium lamp used in conjunction with a 230-nm interference filter. The emitted light was detected with an EMI 9813B photomultiplier tube, and the signal was displayed on a recorder. Stray light from the luminescing crystals was removed using a Corning CS-3-71 filter.

Irradiations were carried out using electrons from a 2.0-MeV Van de Graaff accelerator (High Voltage Engineering). The irradiations were performed on specimens enclosed in a specially designed irradiation chamber using tap water as a coolant. The temperature of the running water was typically at 283 K, and we estimate that during irradiation the temperature of the crystals was raised to 290 K. The flux of electrons on the samples was typically 5 μA/cm^2.

III. RESULTS AND DISCUSSION

Defects resulting from thermochemical reduction of MgO at high temperature are primarily anion vacancies and H^- ions. Anion vacancies occur in two charge states: F^+ and F centers, corresponding to vacancies with one and two electrons, respectively. Both of these defects absorb at about 5.0 eV,[11] and when a sample is excited with light of this energy, luminescence bands occur at 3.2 and 2.3 eV. The 3.2-eV band is due to F^+ centers,[11] and the 2.3-eV band to F centers.[12] The anion-vacancy concentration can be determined by the absorption coefficient of the 5.0-eV band, the concentration of the H^- ions can be monitored by the absorption coefficient at 1053 cm^{-1}.

A. Thermal stability of H^- ions and anion vacancies

The thermal stability of H^- ions and anion vacancies was determined by subjecting two samples to isochronal anneals of 10-min duration in a graphite crucible surrounded by flowing nitrogen gas. The results are plotted in Fig. 1. These two samples were those referred to as samples MgO I and MgO II in Ref. 2. The anion-vacancy and H^- concentrations[13] were 1.6×10^{18} cm^{-3} and 2.9×10^{18} cm^{-3}, respectively, for sample MgO I, and 4.1×10^{18} cm^{-3} and 1.3×10^{17} cm^{-3}, respectively, for sample MgO II. Anion vacancies were annihilated at a lower temperature in the crystal in which they were present at a lower concentration (curve I) than in the crystal in which they were present at a higher concentration (curve II). The temperatures at which half of the vacancies disappeared were 1600 and 1800 K for the two samples, respectively. After heating at 1900 K, all the oxygen vacancies in both samples were annihilated, whereas the H^- concentration remained unchanged. Thus, H^- ions in MgO are much more stable than anion vacancies. Since the samples were in an atmosphere in which the oxygen partial pressure was negligible, vacancies are probably lost by diffusing toward the sample surfaces.

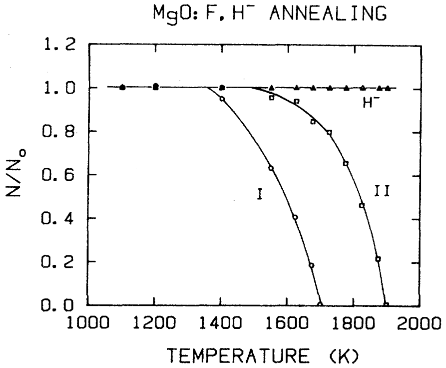

FIG. 1. Normalized concentration of H^- ions and anion vacancies vs isochronal annealing temperature of two thermochemically reduced MgO samples. The two curves labeled I and II referred to anion-vacancy concentrations of samples MgO I and MgO II, respectively. The horizontal line at the top refers to the H^- concentrations for both samples.

Following the anneal at 1900 K, there was no optical-absorption band in the range 0.5–6.0 eV (4000–50000 cm^{-1}). This indicates that the electronic transitions of the H^- ions do not occur in this spectral region, or that the oscillator strength for such transitions is low ($<10^{-3}$). There is no obvious reason why the oscillator strength of H^- ions should be so small. A recent theoretical calculation predicts that the main electronic transition of the H^- ion may be as large as $\sim$9.6 eV, which would place it above the band edge of the host material.[14]

B. Displacement of protons by ionization radiation

Electron irradiations were performed on sample MgO I after it had been heated at 1900 K and therefore contained a large H^- concentration but no anion vacancies. Three irradiations were carried out, corresponding to cumulative doses of 4×10^{15}, 5×10^{16}, and 2×10^{17} e/cm^2. The irradiations pro-

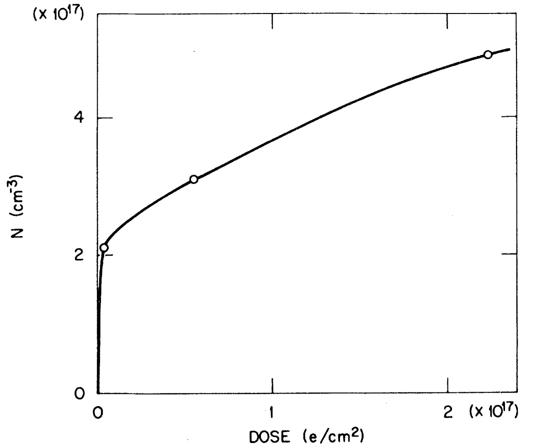

FIG. 2. Concentration of anion vacancies produced, as monitored by the 5.0-eV band, versus three cumulative doses of electron irradiations.

duced three prominent effects: (1) creation of new anion vacancies, as monitored by the appearance of an intense absorption band at 5.0 eV, (2) a decrease in the absorbance in the H^- spectrum, and (3) appearance of new OH^- bands. These effects are aspects of the same radiation-induced diffusion process[15] which involves the displacement of protons in the H^- configuration and their relocation elsewhere in the crystal as OH^- ions. The net result is that anion vacancies are left behind. Using the formula[16]

$$n(F)=5\times10^{15}\alpha(F) , \qquad (1)$$

where $n(F)$ denotes the concentration of anion vacancies and $\alpha(F)$ is the absorption coefficient of the 5.0-eV band, the concentration of anion vacancies (F and F^+ centers) produced by the three electron irradiations were calculated to be 2×10^{17}, 3×10^{17}, and 5×10^{17} cm^{-3}, respectively (see Fig. 2). The fact that 2×10^{17} anion vacancies/cm^3 were created by a dose of only 4×10^{15} e/cm^2 indicates that an ionization process, as distinguished from an elastic collision mechanism, is operative. Assuming that the displacement of one proton from an H^--ion site results in the formation of one anion vacancy, the cross section for displacement of protons can be calculated using the relationship

$$\sigma=N^{-1}\Delta N/\Delta\phi . \qquad (2)$$

In this formula, N is the concentration of H^- ions and $\Delta N/\Delta\phi$ is the number of displacement events per cubic centimeter for a given radiation dose in electrons/cm^2. Using the values obtained from the lowest irradiation dose, a cross section of $\sim1\times10^8$ b is obtained, corresponding to a factor of 10^9 greater than that for the elastic collision displacement of oxygen.[16] A cross section of this magnitude is uniquely characteristic of a radiation-induced displacement process of protons (or deuterons),[15] albeit in this case from anion sublattice sites.

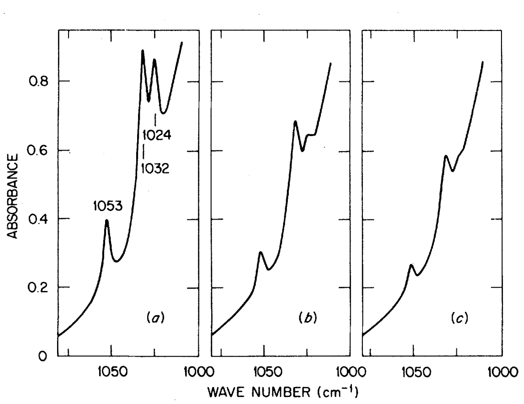

FIG. 3. Infrared spectra for H^- ions prior to electron irradiation (curve a) and after electron irradiations with cumulative doses of 5×10^{16} cm^{-2} (curve b), and 2×10^{17} cm^{-2} (curve c).

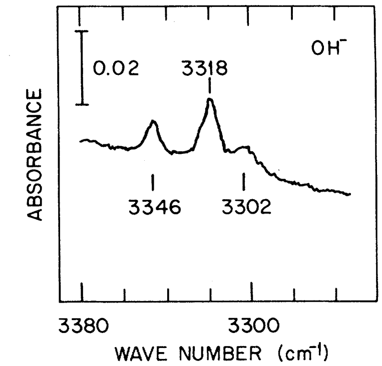

FIG. 4. New OH^- spectrum observed after electron irradiation with a dose of 2×10^{17} cm^{-2}.

We give now more details of the changes in the infrared spectra caused by the electron irradiations. The infrared spectrum corresponding to H^--ion vibrations before irradiation is shown in Fig. 3(a). It was noted previously that the relative intensities of the three bands at 1053, 1032, and 1024 cm^{-1} in different samples appear to be the same.[1] The changes brought about by the two longer irradiations are shown in Figs. 3(b) and 3(c). All three bands decreased in intensity with increasing electron dose, but the 1024-cm^{-1} band decreases disproportionally faster. This indicates that at least one of the three bands is not in fact intensity correlated with the other two and that different charge-compensation and site symmetries may be involved, as suggested previously.[1]

The electron irradiation also produced new OH^- vibrational modes, which increased in intensity as the irradiation progressed. The peaks occurred at

3346, 3318, and 3302 cm^{-1}, as shown in Fig. 4. Prior to the irradiation, there were no bands observable in the 3000–4000-cm^{-1} region. These bands have not been observed in MgO crystals before.

C. Determination of H^- concentration

The fact that displacement of protons from anion sublattice sites results in oxygen vacancies permits a direct determination of H^- concentration. The irradiated crystal was isochronally annealed in a graphite crucible surrounded by flowing nitrogen gas for intervals of 10 min each. The results are shown in Fig. 5. Decrease of the 5.0-eV absorbance was attended by an increase in the H^- absorbance; the changes began to take place at about 800 K. The annihilation of the anion vacancies is attributed to the recapture of protons, thereby increasing the H^- concentration. After annealing at 1100 K, almost all the anion vacancies had been annihilated, and the H^- absorbance had been restored to 90–95 % of its preirradiation value. Therefore, it is possible to deduce relationships from which H^- concentrations can be obtained from the H^- infrared absorbance.

The absorbance of the anion vacancies after each anneal is plotted against that of the H^- ions in Fig. 6. The concentration of F and/or F^+ centers can be determined from Eq. (1). The coefficient in this equation is valid for both F and F^+ centers since the ratio of the half-width to the oscillator strength is comparable for both centers. The absorbance of the H^- ions can be determined two ways: with the use of the absorbance at 1053 cm^{-1}, and the use of the sum of the absorbance of the three peaks (1053, 1032, and 1024 cm^{-1}). The former results in curve (a) and the latter in curve (b) in Fig. 6. If we assume that the loss of one F center results in a gain of one H^- ion, then using the slope from curve (a) and Eq. (1), the concentration of H^- ions can be determined from the equation

$$n(H^-)=2.7\times10^{17}\alpha(1053)\ , \qquad (3)$$

where $\alpha(1053\ \mathrm{cm}^{-1})$ is the absorption coefficient of the 1053-cm^{-1} peak. Using slope (b) and Eq. (1), the H^- concentration can be derived from the relationship

$$n(H^-)=5.5\times10^{16}\sum\alpha(H^-)\ , \qquad (4)$$

where $\sum\alpha(H^-)$ is the sum of the absorption coefficients for the three peaks. The error involved is probably within 30%. In general, it is much simpler to use Eq. (3), since the peaks at 1032 and 1024 cm^{-1} occur at the band edge and are relatively more cumbersome to measure.

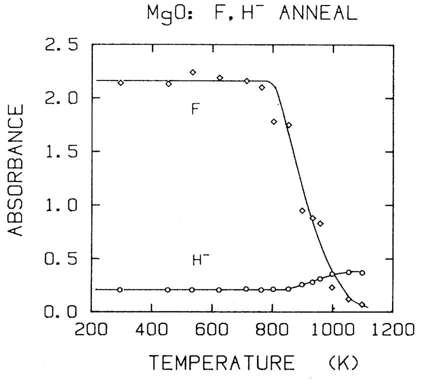

FIG. 5. Absorbance of anion vacancies (F centers) and H^- ions vs isochronal annealing temperature in a reducing atmosphere. The absorbance of the H^- ions were taken to be the sum of the three peaks at 1053, 1032, and 1024 cm^{-1}.

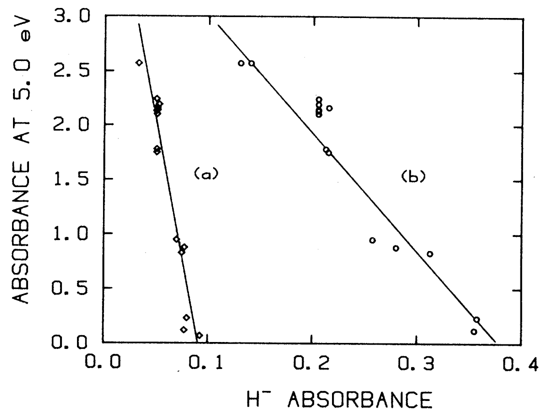

FIG. 6. Absorbance of anion vacancies, as monitored by the 5.0-eV absorption band vs that of H^- ions, as measured from the 1053-cm^{-1} peak [slope (a)] and from the sum of the three peaks [slope (b)].

D. Lifetime of the 2.3-eV phosphorescence

We have shown previously that the lifetime of the 2.3-eV phosphorescence measured near room temperature in different samples was determined by the concentration of H^- ions.[2] This result gave strong evidence that H^- ions, acting as electron traps, were responsible for the lifetime of the 2.3-eV emission. We present here the results of experiments which indicate that in a crystal containing a low H^- concentration, thermal annealing of F centers increases the phosphorescence lifetime. In these experiments the decay of the 2.3-eV emission, following excitation with 5.4-eV light, was measured in sample MgO II after it had been annealed isochronally at successively higher temperatures in a graphite crucible. As Fig. 1 shows, this treatment causes the F centers to anneal out, while the H^--ion concentration remains

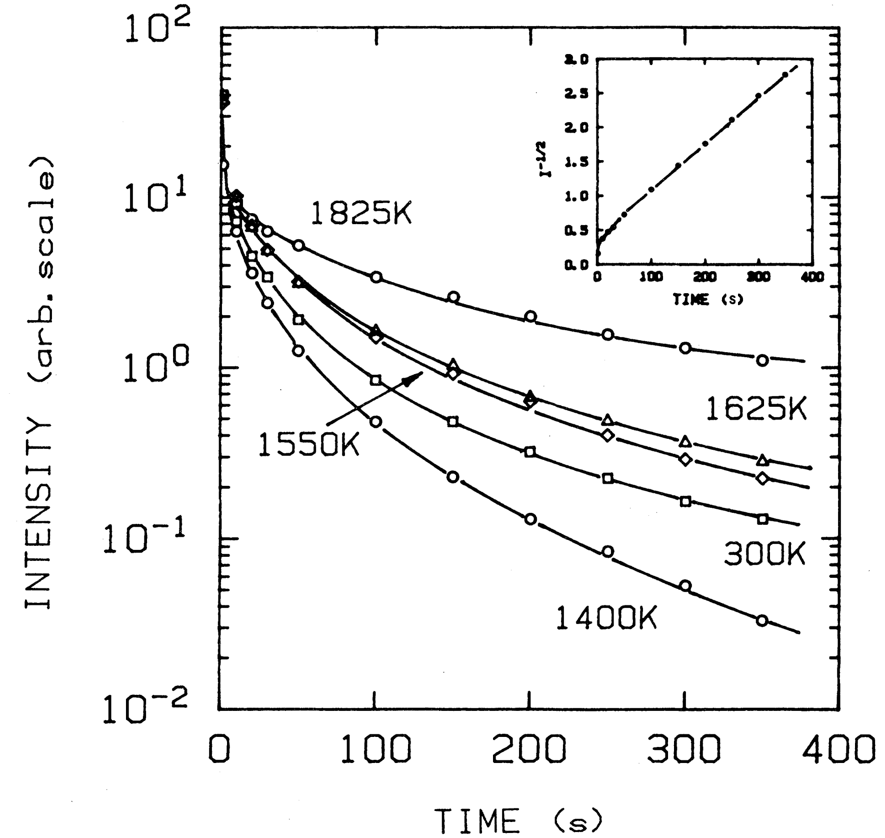

FIG. 7. Decay behavior of the 2.3-eV emission intensity of sample MgO II after annealing at different temperatures.

unchanged. Prior to each measurement the sample was carefully masked so that only light emitted from a clean surface was detected. The sample was illuminated until the 2.3-eV emission reached a maximum, and then the excitation was removed. Figure 7 shows that as the annealing progressed and, therefore, as the concentration ratio of H^- ions to anion vacancies increased, the lifetime of the 2.3-eV emission became increasingly long. There was an initial decrease in the lifetime following the first anneal at 1400 K, but as Fig. 1 shows, this anneal did not measurably decrease the concentration of anion vacancies; therefore, we are not sure what caused the slightly reduced lifetime at this stage. However, for the remaining anneals the trend is clear. Following the procedure used previously,[2] the time over which the emission intensity decays to one-tenth of its initial value is regarded as a reasonable measure of the lifetime. We plot the lifetime against the normalized concentration of anion vacancies in Fig. 8. As the anion-vacancy concentration decreased, the lifetime increased. After annealing at 1825 K, the lifetime increased an order of magnitude. The results for sample MgO I were similar but since the lifetime of the emission was initially much longer, the effect of annealing was not nearly as marked.

It is apparent in Fig. 7 that the decay of the 2.3-eV emission does not follow first-order kinetics. The insert in Fig. 7 shows the data for $T=300$ K

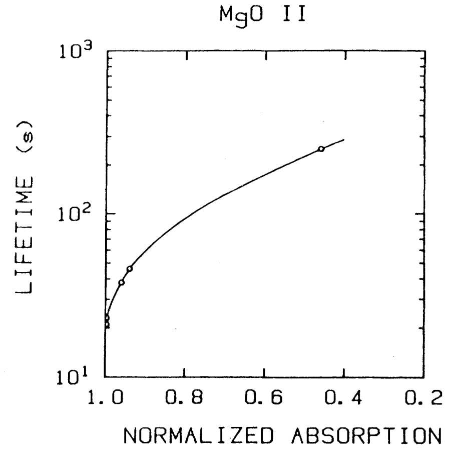

FIG. 8. Lifetime of the 2.3-eV emission vs the normalized absorption of the 5.0-eV band. The data were obtained by annealing sample MgO II at different temperatures resulting in a loss of anion-vacancy concentration but no loss of H^- concentration.

plotted as the inverse square root of the intensity versus time. A straight line on such a plot indicates that the decay follows second-order kinetics.[17] The insert in Fig. 7 shows, therefore, that for the 2.3-eV emission there is an initial relatively fast transient decay which is followed by a long-lived second-order process. Such behavior is consistent with our model that H^- ions act as metastable traps for electrons optically excited from *F* centers, and that the 2.3-eV emission results when these electrons recombine with F^+ centers, following thermal release from metastable H^{2-} ions.

The optical emission from anion vacancies from several thermochemically reduced MgO samples measured between 6 and 300 K has been investigated.[18]

IV. SUMMARY AND CONCLUSIONS

The results of the present investigation on thermochemically reduced MgO lead to the following conclusions: Firstly, H^- ions are thermally more stable than anion vacancies. Whereas, anion vacancies disappear at 1900 K in a reducing atmosphere, H^- ions can survive annealing in a reducing atmosphere at 1900 K without loss in concentration. Secondly, electron irradiation of annealed crystals containing H^- ions and no anion vacancies resulted in a loss of H^- absorbance, the emergence of new OH^- signals, and a large absorbance of the 5.0-eV band. These results indicate that protons in the anion sublattice are displaced and relocated elsewhere in the crystal as OH^- ions, leaving behind anion vacancies. The magnitude of the cross section, $\sim 10^8$ b, is uniquely characteristic of a radiation-induced displacement process of protons in MgO. Thirdly, we demonstrated that in a crystal, in which the H^- concentration is appreciably lower than that of the anion vacancies, annihilation of the latter by thermal annealing markedly enhances the phosphorescence lifetime. On the other hand, for a crystal in which the H^- and anion-vacancy concentrations are comparable, the initial lifetime is already long and the increase in lifetime due to the annealing is therefore not as pronounced. These results are consistent with our model that H^- ions serve as metastable traps for optically excited electrons from *F* centers, thereby forming H^{2-} ions. Electrons released from H^{2-} ions can either return to the positively charged anion vacancies (F^+ centers), resulting in the 2.3-eV emission, or be captured by other positively charged H^- ions, thereby further delaying the inevitable return to the anion vacancies. We propose that it is this successive capture of H^- ions that leads to the long phosphorescence lifetime. A relatively high H^- concentration implies a high probability for successive captures by H^- ions, thereby resulting in a long-lived phosphorescence. Lastly, the second-order decay of the phosphorescence intensity is also compatible with our contention that H^- ions are the main traps for electrons optically excited from *F* centers.

In summary, the infrared lines near 1000 cm^{-1} have been umambiguously demonstrated to be due to protons located at anion sublattice sites (H^- ions), and further evidence is provided that these ions are the main electron traps responsible for the long-lived luminescence of the *F* center. Details of the study of this luminescence are reported in the following paper.[18]

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