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HYDROGEN IN MgO CRYSTALS THERMOCHEMICALLY REDUCED
AT VERY HIGH TEMPERATURES

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HYDROGEN IN MgO CRYSTALS THERMOCHEMICALLY REDUCED AT VERY HIGH TEMPERATURES*

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Abstract Evidence is presented that H⁻ ions are the main electron traps responsible for the long-lived luminescence of the F centers observed at 2.3 eV in thermochemically reduced MgO crystals.

I. INTRODUCTION

Soluble protons are present in the MgO lattice, primarily as cations, forming covalent OH⁻ ions.¹ The presence of these ions give rise to infrared absorptions in the 3000-4000 cm⁻¹ region. However, when MgO crystals are thermochemically reduced at very high temperatures (>2000 K), protons in the anion sublattice can be formed, giving rise to vibrational modes at frequencies of ~1000 cm⁻¹. These modes have been attributed to H⁻ ions (protons with two electrons each) at oxygen-ion sites.² These studies have important technological implications in that the conditions which prevail in the operation of energy-efficient devices such as the Stirling engine are the same as those which produce H⁻ ions, namely, high temperatures and high pressures of a reducing gas.

By serendipity, the study of protons in the anion sublattice sheds light on another problem: The long-lived

phosphorescence of the F center (anion vacancy with two electrons) in thermochemically reduced (TCR) MgO crystals, also to be referred to as MgO:Mg. After more than a decade of experimental and theoretical investigations, the understanding of the F center in MgO:Mg continues to be a subject of debate. In CaO:Ca experimental results and theoretical calculations on electronic transitions are generally in good agreement, but the situation seems less satisfactory in the case of MgO:Mg. Nevertheless, the key question which has stimulated debate is: What is the cause of long-lived luminescence of the F center in MgO:Mg crystals, or what is the trapping site for the excited electron from an F center?

In MgO both the F\(^+\) (anion vacancy with one electron) and F center absorptions occur at 5.0 eV (250 nm). Upon excitation of a MgO:Mg crystal with light at this wavelength, two emission bands are possible. The 3.2 eV emission has been identified as due to the F\(^+\) center and the 2.3 eV band to the F center. The former decays rapidly once the exciting light is removed, the transition being \(2T_{1u} + 2A_{1g}\). The lifetime of the latter is material dependent and has been observed to vary from a fraction of a second to minutes. It is this long-lived luminescence which is addressed in this article. There has been some excellent work in this area using the highly sensitive ODMR technique to investigate the electronic transitions of this luminescence and to identify trapping sites. Recently a different candidate for the electron trap was proposed: H\(^-\) ion. The proposed process is

\[
\begin{align*}
F + h\nu (5.0 \text{ eV}) &\rightarrow F^+ + e^- \quad (1) \\
H^- + e^- &\rightarrow H^= + H^- + e^- \quad (2) \\
F^+ + e^- &\rightarrow F + h\nu (2.3 \text{ eV}) \quad (3)
\end{align*}
\]
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where the $\text{H}^=$ ion is a $\text{H}^-$ ion with a captured electron. The purpose of this article is to review evidence for the existence of the $\text{H}^-$ ion and present our interpretation of the role it plays in the long-lived phosphorescence of the $\text{F}$ center in MgO:Mg crystals.

II. FORMATION OF $\text{H}^-$ IONS

In general, almost all MgO crystals contain hydrogen to a greater or lesser extent. The crystals are usually grown by the arc-fusion technique using MgO powder as the starting material.\(^9\) These powders invariably contain a certain amount of Mg(OH)$_2$ from which the hydrogen impurities are derived. Large variations of hydrogen content can be obtained. For example, MgO powder presoaked with water produces crystals which are very cloudy, due to the presence of cavities containing high-pressure $\text{H}_2$ gas.\(^{10}\) These cavities can be a perpetual source of hydrogen during high-temperature treatments. At the other extreme, crystals with undetectable or barely detectable OH$^-$ concentrations can be produced when grown in a special way.\(^9\)

Under usual conditions, soluble protons are in substitutional cation sites. However, at very high temperatures ($\sim$2000K) in a reducing atmosphere, they can be present in the anion sublattice, forming $\text{H}^-$ ions.\(^2\) The method used to produce $\text{H}^-$ ions involves a process traditionally referred to in the alkali halides as "additive coloration", but more aptly the process in alkaline earth oxides is a "subtractive coloration"; experimental evidence indicates that the stoichiometric imbalance is due to the removal of oxygen from the crystal rather than absorption of cations from the vapor. This process produces oxygen vacancies. If hydrogen impurities are present, hydrogen can be trapped at oxygen
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vacancies and form H\textsuperscript{-} ions. In practice, the crystals are heated at high temperatures (2000-2500K) and high pressures of magnesium or calcium vapor (4-7 atmospheres) in a tantalum bomb, followed by rapid cooling. Such thermochemical reduction results in the presence of H\textsuperscript{-} ions and F centers; their concentrations depend on the hydrogen content and the temperature of reduction.

III. IDENTIFICATION OF H\textsuperscript{-} IONS

The presence of H\textsuperscript{-} ions can be monitored spectroscopically by infrared absorption lines at \(\sim 1000 \text{ cm}^{-1}\).\textsuperscript{2} That these lines are due to substitutional protons in the anion sublattice can be demonstrated unambiguously by experiments involving ionizing radiation. Details are discussed in the following.

a) Infrared Absorption Lines

After TCR in the tantalum bomb at \(\sim 2400\text{K}\), a very cloudy crystal becomes less cloudy. At such high temperatures, the pressure of H\textsubscript{2} in the cavities is about \(10^3\) atmospheres and out-diffusion of hydrogen undoubtedly occurs. OH\textsuperscript{-} absorption lines disappear, and sharp lines at 1024, 1032 and 1053 cm\textsuperscript{-1} emerge. At 80K, these lines sharpen and shift to 1056, 1034 and 1027 cm\textsuperscript{-1}, respectively. The intensity of these lines depends strongly on both the initial hydrogen content, as monitored by the cloudiness of the crystal and the OH\textsuperscript{-} lines, and the temperature of the reduction. The unusually large intensity of these three lines shown in Fig. 1 was obtainable only for a very cloudy crystal reduced at 2400K. The relative intensities of the lines, however, are roughly constant from sample to sample. These lines are attributed to H\textsuperscript{-} ions.
FIGURE 1. Room temperature transmission spectrum of an MgO crystal with high hydrogen content after reduction at 2400K in a tantalum bomb. The sample thickness was 0.6 mm. In the small inset, the band at 2098 cm\(^{-1}\) is magnified 5X in the vertical direction. The large inset is enlarged 2X and 5X in the horizontal and vertical directions, respectively. (After Ref. 2).

A low-intensity signal is observed at 2098 cm\(^{-1}\). This line is observed only for crystals in which the H\(^-\) lines are intense. We attribute this line to the first-harmonic vibration for the 1053 cm\(^{-1}\) absorption. For a detailed discussion on the identification of the three lines as due to H\(^-\) ions and the 2098 cm\(^{-1}\) line as a first harmonic, the reader is referred to Ref. 2.

The intensities of the three sharp, closely spaced lines are comparable, but not necessarily equal or
rationally related. This may indicate a lowering of the point-group symmetry around the H\textsuperscript{−} ion from $O_\text{h}$ to a less symmetric configuration, which in turn may be due to local charge compensation as discussed by Gourley and Vance for "accidentally colored" CaO crystals.\textsuperscript{11} The observation of the first harmonic in MgO is further evidence of reduced symmetry around the H\textsuperscript{−} ion, since the first harmonic is not an optically allowed transition in $O_\text{h}$ symmetry.

b) Thermal Stability of H\textsuperscript{−} Ions

H\textsuperscript{−} ions are thermally much more stable than anion vacancies.\textsuperscript{12} Two crystals, labeled MgO-I and MgO-II, whose H\textsuperscript{−} and F center concentrations are given in Table I, were subjected to isochronal anneals of 10-min duration in a graphite crucible surrounded by flowing nitrogen gas. The normalized concentrations of the two species are plotted in Fig. 2. The temperature at which half of the vacancies disappeared were 1600 and 1800K, respectively. After heating at 1900K, all the oxygen vacancies were annihilated, whereas the H\textsuperscript{−} concentration remained unchanged.

Following the anneal at 1900K, there was no optical absorption band in the range 0.5 to 6.0 eV (4,000-50,000 cm\textsuperscript{−1}). This result indicates that either the electronic transitions of the H\textsuperscript{−} ions do not occur in this spectral region, or that the oscillator strength for such transitions is low (<10\textsuperscript{−3}). There is no obvious reason why the oscillator strength of H\textsuperscript{−} ions should be so small. A recent theoretical calculation predicts that the main electronic transition of the H\textsuperscript{−} ion may be as large as 9.6 eV, a value which would place it close to the band edge.\textsuperscript{13,14}

c) Displacement of Protons by Ionizing Radiation

Electron irradiations (2 MeV) were performed\textsuperscript{12} on the
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![Graph showing normalized concentration of H\textsuperscript{−} ions and anion vacancies versus isochronal annealing temperature of two MgO:Mg samples. The two curves labeled I and II refer to anion vacancy concentrations of MgO-I and MgO-II respectively. The horizontal lines at the top refer to the H\textsuperscript{−} concentration for both samples. (After Ref. 12)]

Crystal which had been annealed at 1900K (see above). Irradiations up to a dose of 2\times10^{17} e/cm\textsuperscript{2} were carried out. Three prominent effects were produced: (1) Creation of new anion vacancies, (2) a decrease in the absorbance in the H\textsuperscript{−} spectrum, and (3) appearance of new OH\textsuperscript{−} bands. All these effects are aspects of radiation-induced-diffusion processes involving the displacement of protons in the H\textsuperscript{−} configuration and their relocation elsewhere as OH\textsuperscript{−} ions. The net result is that anion vacancies are left behind. A cross
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section of ~1x10^8 barns, which is a factor of 10^9 greater than that for elastic-collision displacement of oxygen, is obtained. A cross section of this magnitude is uniquely characteristic of a radiation-induced-displacement of protons,\textsuperscript{15} albeit in this case from anion sublattice sites. These observations indicate unambiguously that the infrared absorption lines near 1000 cm\textsuperscript{-1} are due to protons in anion sites.

Greater details are presented elsewhere.\textsuperscript{12} However, it is shown in Fig. 3 that the irradiations caused changes in the infrared spectra. All three bands decreased in inten-

![Infrared absorption spectra](image)

FIGURE 3. Infrared absorption spectra for H\textsuperscript{-} ions prior to electron irradiation (curve a) and after electron irradiations with cumulative doses of 5x10\textsuperscript{16} cm\textsuperscript{-2} (curve b), and 2 x 10\textsuperscript{17} cm\textsuperscript{-2} (curve c). (After Ref. 12)
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sity with increasing dose, but the 1024 cm\(^{-1}\) band decreased disproportionately faster. This observation indicates that at least one of three bands is not intensity-correlated with the other two and that different charge compensation and site symmetries may be involved. Concomitant with the decrease in H\(^-\) intensity, new OH\(^-\) vibrational modes appeared. The peaks occurred at 3346, 3316, and 3302 cm\(^{-1}\), as shown in Fig. 4a. Prior to irradiation, there were no bands observable in the 3000-4000 cm\(^{-1}\) region. A deuterated crystal which underwent the same TCR, thermal annealing and electron irradiations exhibited peaks at 2481, 2461, and 2449 cm\(^{-1}\) (Fig. 4b).

![Graph showing absorbance vs. wavenumber with peaks at 3346, 3316, 3302 cm\(^{-1}\) for OH\(^-\) and 2481, 2461, 2449 cm\(^{-1}\) for OD\(^-\).](image)

FIGURE 4. New OH\(^-\) (curve a) and OD\(^-\) (curve b) spectra after electron irradiations.

IV. CAUSE OF THE F-CENTER PHOSPHORESCENCE

In this section evidence is presented that H\(^-\) ions are the major electron traps responsible for the long-lived
phosphorescence at 2.3 eV near room temperature in MgO:Mg. Firstly, we show a correlation between the concentration of H\textsuperscript{-} ions and the lifetime of the luminescence at 2.3 eV. Secondly, the luminescence lifetime of an MgO:Mg crystal can be significantly enhanced by increasing the ratio of the H\textsuperscript{-} concentration to that of the F center.

a) H\textsuperscript{-} Concentration vs Luminescence Lifetime

The period over which the luminescence intensity falls to 1/10 the initial value is regarded as a reasonable measure of phosphorescence lifetime. The F-center and H\textsuperscript{-} concentrations of three crystals, labeled MgO-I, MgO-II, and MgO-III, and their luminescence lifetimes are given in Table I. The luminescence decays at 260K of the F band in these three crystals are plotted in Fig. 5.\textsuperscript{8} MgO-I had the highest H\textsuperscript{-} concentration and its luminescence lifetime was also the greatest. The H\textsuperscript{-} concentration of MgO-III was about two orders of magnitude lower, and its luminescence lifetime

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anion Vacancies</th>
<th>H\textsuperscript{-} Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO-I</td>
<td>330</td>
<td>1.6x10\textsuperscript{18}</td>
</tr>
<tr>
<td>MgO-II</td>
<td>820</td>
<td>4.1x10\textsuperscript{18}</td>
</tr>
<tr>
<td>MgO-III</td>
<td>110</td>
<td>5.5x10\textsuperscript{17}</td>
</tr>
</tbody>
</table>

a. Absorption coefficient at 5.0 eV.
b. Calculated from \( n_F = 5.0 \times 10^{15} \alpha_F \) (see Ref. 12).c. Absorption coefficient at 1053 cm\textsuperscript{-1}.
d. Calculated from \( n_H = 2.7 \times 10^{17} \alpha_H \) where \( \alpha_H \) is the absorption coefficient at 1053 cm\textsuperscript{-1} (see Ref. 12).
FIGURE 5. Luminescence decay at 260K of the 2.3 eV band in three MgO:Mg crystals. The concentration of H\(^-\) ions decreases from sample MgO-I through MgO-III. (After Ref. 8)

was also correspondingly lower. Other MgO:Mg crystals also exhibit the same type of correlation. In general, if the value of the ratio of the H\(^-\) ion/F-center concentrations is one or larger, a phosphorescence lifetime in excess of 200 seconds can be expected.

b) Enhancement of Phosphorescence Lifetime

If H\(^-\) ions are indeed the electron trap responsible for the
long-lived luminescence, then the ratio of H⁻ ion to F-center concentrations is a parameter which will have a direct bearing on the luminescence lifetime. This can be demonstrated with sample MgO-II, in which the H⁻ concentration is much less than that of the F center. The sample was annealed isochronally at successively higher temperatures in a graphite crucible. As Fig. 2 shows, this treatment causes the F centers to anneal out while the H⁻ concentration remains unchanged. Fig. 6 shows that as the annealing

![Graphical representation of decay behavior](image)

**FIGURE 6.** Decay behavior of the 2.3 eV emission intensity of MgO-II after annealing at different temperatures. (After Ref. 12)
progressed and, therefore, as the concentration ratio of H\textsuperscript{-} ions to anion vacancies increased, the lifetime of the 2.3 eV luminescence became increasingly longer. There was an initial decrease in the lifetime following the first anneal at 1400K, but for the remaining anneals the trend became clear. The phosphorescence lifetime is plotted against the normalized concentration of anion vacancies in Fig. 7. As the anion-vacancy concentration decreased, the

![Graph](image)

**FIGURE 7.** Lifetime of the 2.3 eV emission vs. the normalized absorption of the 5.0 eV band. The data were obtained by annealing MgO-II at different temperatures, a treatment which resulted in a loss of anion-vacancy concentration but no loss of H\textsuperscript{-} ions. (After Ref. 12)
lifetime increased. After annealing at 1825K, the lifetime increased an order of magnitude. The results for sample MgO-I were similar, but since the lifetime of the luminescence was initially much longer, the effect of annealing was not as pronounced.

It is apparent from Fig. 6 that the decay of the 2.3 eV luminescence does not follow first-order kinetics. When \((\text{intensity})^{-1/2}\) is plotted against time, straight lines are obtained, indicating that the decay follows second-order kinetics\(^ {16}\). Such behavior is consistent with our proposed model that \(\text{H}^-\) 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 \(\text{F}^+\) centers, following thermal release from metastable \(\text{H}^-\) ions.

V. CONCLUDING REMARKS

These results showed that the lifetime of the 2.3 eV luminescence is determined by the \(\text{H}^-\) concentration. A graphic description is shown in the Fig. 8 diagram. Absorption of a photon by an F center excites an electron from the \(^1\text{A}_g\) ground state to a \(^1\text{T}_{1u}\) excited state. There exists a high probability of the electron escaping into the conduction band, from which it can be trapped elsewhere in the crystal. We proposed that it can be trapped at an \(\text{H}^-\) ion, thus forming an \(\text{H}^=\) ion and leaving behind an \(\text{F}^+\) center. Above 240K an \(\text{H}^-\) ion is unstable and the outermost electron is thermally excited into the conduction band with an activation energy of 0.56 eV. It can either return to a positively charged anion vacancy (\(\text{F}^+\) center), resulting in the 2.3 eV emission, or be captured by another positively charged \(\text{H}^-\) ion, thereby further delaying the inevitable
FIGURE 8. Schematic representation of the effect of substitutional H⁻ ions on the 2.3 eV luminescence in MgO:Mg crystals. (a) Schematic MgO lattice containing anion vacancies and hydrogen ions. (b) Schematic energy level diagram for the F center, the H⁻ ion and the conduction band. (After Ref. 14)
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return to an anion vacancy. It is this successive capture by H\(^-\) ions that leads to the long phosphorescence lifetime. A relatively high H\(^-\) concentration implies a high probability for successive capture by H\(^-\) ions, thereby resulting in a long-lived luminescence.

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