EPR detection of the substitutional H^{2-} ion in magnesium oxide

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EPR measurements and theoretical calculations are presented that show that stable, $S = \frac{1}{2}$, substitutional H^{2-} ions (a proton and three electrons trapped at an anion-vacancy site) are formed in MgO when a substitutional H^- ion traps an electron. Irradiation with blue (400 nm) light is found to be very effective in forming H^{2-} ions in MgO.

Recent infrared absorption measurements[1] have shown hydrogen to be present in additively colored MgO, CaO, and SrO crystals in the form of substitutional H^- ions. The defect, which consists of a proton and two electrons trapped at an anion-vacancy site, is referred to as the U center in the alkali halides. The vibrations, which are associated with the substitutional H^- ion in MgO, give rise to infrared absorption bands at 1053, 1032, and 1024 cm^{-1}. Subsequent optical studies[2-6] have further shown that the lifetimes and intensities of the phosphorescence of the F center at 2.3 and 2.1 eV in thermochemically reduced MgO and CaO, respectively, are directly linked to the concentration of H^- ions.

From the results of these studies, together with the results of theoretical calculations of the electronic states of the F center, a model was proposed for the long-lived luminescence of the F center in MgO (see Fig. 10 of Ref. 4). Absorption of a 5.0-eV photon by an F center excites an electron from the $^1A_{1g}$ ground state to a diffuse $^1T_{1u}$ excited state which lies just beneath (< 0.01 eV) the bottom of the conduction band. The excited electron has a very high probability of being trapped elsewhere in the crystal and, in particular, it can be trapped by an H^- ion forming a substitutional H^{2-} ion.

Despite the fact that there now exists a wealth of experimental data confirming that the concentration of H^- ions play a very important role in determining the optical properties of F centers in thermochemically reduced MgO and CaO, the existence of the H^{2-} ion has not been directly verified experimentally. A substitutional H^- ion with two electrons would have an electron spin of zero; a H^{2-} ion, however, in analogy to the $(1s^2 2s)$, ^2S state of atomic lithium, would be expected to be paramagnetic and, therefore, detectable through standard electron paramagnetic resonance (EPR) techniques. In this paper we report the first theoretical calculations of the ground state of a substitutional H^{2-} ion impurity in MgO, and the results of EPR measurements of a hydrogen center in MgO that exhibit the properties consistent with those expected of a substitutional H^{2-} ion impurity.

The three samples of MgO used in this work originated from different melts but had all been reduced at high temperatures and pressures in vapors of magnesium. Prior to being mounted in the spectrometer, all samples were heated to 380 °C to reduce the initial concentrations of Fe^+ ions and F^+ centers.[7] During any subsequent handling, they were shielded from stray ultraviolet and fluorescent light.

The samples were mounted on the copper tip of an Air Products "Displex" closed cycle refrigerator capable of cooling the samples to 13.5 K. The cold finger, shrouded by a quartz tube, could be moved along the axis of a TE_{013} mode cavity. Optical illumination of the sample was done through slits in the walls of the cavity with a combination of a 500-W high-pressure mercury arc lamp and an Oriel 7210 grating monochromator. The EPR spectrometer operated at 16 GHz and employed 100 kHz magnetic field modulation and homodyne detection. Magnetic fields were measured with a proton resonance probe inside the cavity. Figure 1 displays the EPR spectrum in the neighborhood of $g = 2$ after 5 min of blue (400-nm) light irradiation at 20 K. This particular sample had been intentionally doped with deuterium during crystal growth. Since hydrogen is an ubiquitous impurity in MgO, lines from both H^{2-} and D^{2-} ions are present in the spectrum. The twofold hyperfine splitting by the spin-$\frac{1}{2}$ hydrogen nucleus is very clear, while the middle line of the threefold split deuterium $(I = 1)$ resonance, is partially obscured by the F^+ absorption. In Fig. 1, the microwave power level had been increased to the point of partial saturation of the F^+ lines. At higher power levels, the F^+ transitions could be saturated sufficiently to reveal the m_I, $0 \rightarrow 0$ transition of the D^{2-} spectrum fully. The intensity ratio of the deuterium and hydrogen lines is roughly three, which is the same as the infrared intensity ratio for OH^- and OD^- ions prior to thermochemical reduction. In addition to the lines in Fig. 1, lines from Cr^+ and Fe^+ were also detected.

Stable H^{2-} lines could be created in all samples with blue light at 20 K. In addition, the blue light decreased the intensity of the Fe^+ lines and increased the intensity of the Cr^+ lines. Apparently, the blue light liberated electrons from Fe^+ ions, with Cr^{2+} and H^- ions acting as traps for
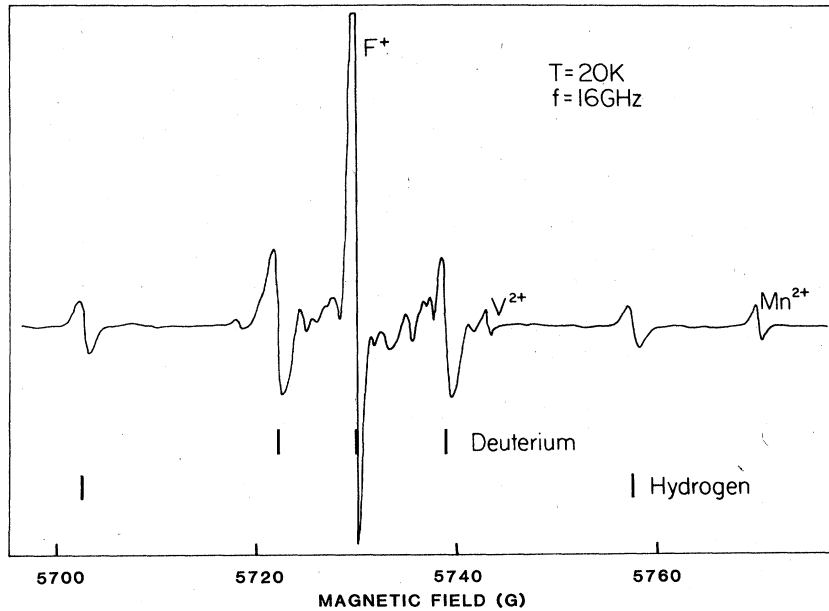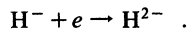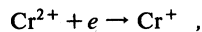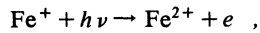
FIG. 1. Experimental EPR spectrum of substitutional H^{2-} and D^{2-} ions in MgO taken at 20 K.

these photoelectrons. The relevant processes are summarized below.

$$Fe^+ + h\nu \rightarrow Fe^{2+} + e \ ,$$

$$Cr^{2+} + e \rightarrow Cr^+ \ ,$$

$$H^- + e \rightarrow H^{2-} \ .$$

The second reaction has also been observed by Barklie, Blount, Henderson, and O'Connell.[8] On the other hand, irradiation with uv light in the range 250–300 nm increased the concentration of F^+, Fe^+, and Cr^+ in all samples. This suggests that the uv light liberates electrons from F centers with Fe^{2+} and Cr^{2+} acting as the principal electron traps as represented below.

$$F + h\nu \rightarrow F^+ + e \ ,$$

$$Fe^{2+} + e \rightarrow Fe^+ \ ,$$

$$Cr^{2+} + e \rightarrow Cr^+ \ .$$
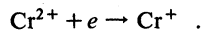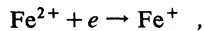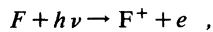
However, with uv, the expected trapping of electrons by H^- ions to form H^{2-} centers could only be observed in one sample. For others, the uv even destroyed H^{2-} centers that had previously been created with blue light. Apparently uv is quite effective in removing electrons from H^{2-} centers. Then, in the presence of strong competition for photoelectrons from other traps such as Fe^{++}, Cr^{++}, and F^+, the steady-state concentration of H^{2-} centers can be small under uv irradiation.

The EPR spectra for the D^{2-} and H^{2-} ions were fitted to the following spin Hamiltonian:

$$H = g\beta\vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S} \ .$$

For D^{2-} ($S = \frac{1}{2}, I = 1$)

$$g_D = 1.9949 \pm 0.0001 \ ,$$

$$A_D = (8.3 \pm 0.5) \times 10^{-4} \ cm^{-1} \ .$$

For H^{2-} ($S = \frac{1}{2}, I = \frac{1}{2}$)

$$g_H = 1.9948 \pm 0.0001 \ ,$$

$$A_H = (52.7 \pm 0.5) \times 10^{-4} \ cm^{-1} \ .$$

No change in these spin-Hamiltonian parameters could be detected in the temperature range 13.5–50 K, nor could we detect anisotropy in the g values or hyperfine coupling constant. The experimental ratio $A_H/A_D = 6.4 \pm 0.4$ is in good agreement with the value of 6.5 expected from the ratio of nuclear magnetic moments of hydrogen and deuterium. The value of A_H of 52.7×10^{-4} cm^{-1} is quite small compared to 400×10^{-4} cm^{-1} which is typical for atomic hydrogen in alkaline-earth oxides.[9]

The model, upon which the present calculation of the electronic structure of the $^2A_{1g}$ ground state of the H^{2-} ion in MgO is based, follows closely that used in earlier studies of the F center in the alkaline-earth oxides.[4, 10] The one-electron orbitals ψ_k for the H^{2-} ion are of the form

$$\psi_k(\vec{r}) = \sum_\alpha c_{k\alpha}\chi_\alpha(\vec{r}) \ . \tag{1}$$

The basis functions χ_α have the form

$$\chi_\alpha(\vec{r}) = N_\alpha\left[f_\alpha(\vec{r}) - \sum_{\nu\neq0}\sum_{i=1}^{n_\nu}\phi_i(\vec{r}-\vec{R}_\nu)S_{\nu i,\alpha}\right] \ , \tag{2}$$

where N_α is an orbital renormalization factor, the index ν runs over the $1nn$ Mg^{2+} ions, and $\phi_i(\vec{r}-\vec{R}_\nu)$ denotes the ith crystal orbital on the νth Mg^{2+} ion. The functions f_α are taken to be Slater-type orbitals (STO's) multiplied by the appropriate cubic harmonic:

$$f_\alpha(\vec{r}) = [(2\beta)^{2n+1}/(2n)!]^{1/2}r^{n-1}e^{-\beta r}K_{\Gamma_p}(\theta, \phi) \ . \tag{3}$$

The linear coefficients in Eq. (1) were determined by the open-shell Hartree-Fock-Roothaan procedure.[11] The approximations involved in constructing the Hamiltonian ma-

trix elements follow those of one of the authors' earlier works.[10] The effects of lattice distortion and off-center relaxation of the H^{2-} ion in the oxygen vacancy were neglected in the present calculation. The results of the calculation predict a stable $^2A_{1g}$ ground state for the H^{2-} ion. The $2a_{1g}$ ("$2s$") electron orbital is diffuse and has an average radius of 3.9 Å, which places it just beyond the $3nn$ shell of ions. This corresponds to roughly twice the average radius of the $2s$ electron in the ^2S ground state of the Li atom. The non-linear parameters and linear coefficients for the $2a_{1g}$ orbital are given in Table I.

The isotropic hyperfine interaction at the hydrogen nucleus, A_H, is related to the square of the unpaired electron in the $2a_{1g}$ orbital by

$$A_H = \frac{2}{3}\mu_0 g_e \mu_e g_p \mu_p |\psi_{2a_{1g}}(0)|^2 , \qquad (4)$$

where

$$|\psi_{2a_{1g}}(0)|^2 = |\sum_\alpha C_{2a_{1g}, \alpha} \chi_\alpha(0)|^2 .$$

Our calculations give $|\psi_{2a_{1g}}(0)|^2 = 0.095$ Å^{-3}. From the experimental value for A_H we obtain $|\psi_{H^{2-}}(0)|^2_{expt} = 0.238$ Å^{-3}. This is to be compared to the free H-atom value of $|\psi_H(0)|^2 = 2.148$ Å^{-3}.

We observe that the calculated value of $|\psi(0)|^2$ is roughly one-half the measured value. This factor of 2 discrepancy is attributable to several aspects of the present calculation.

(i) In the calculation of $|\psi(0)|^2$, overlap contributions from the second nearest-neighbor oxygen ions and beyond were neglected. The inclusion of these contributions tend to increase the value of $|\psi(0)|^2$.

(ii) The effects of lattice relaxation have not been incorporated into the present calculations. Our earlier work has shown that lattice relaxation can have a pronounced effect on the wave functions of defects in crystals.[10]

(iii) The present calculations are based upon the open-shell Hartree-Fock-Roothaan procedure. It is well known that the unrestricted Hartree-Fock results for the Li atom give a spin density at the origin that is 35% larger than that predicted by a RHF calculation.[12]

For these reasons, we regard the agreement between the calculated and measured values of $|\psi(0)|^2$ to be reasonably good.

The EPR spectrum and the ratio of A_H/A_D for the sample doped with deuterium clearly indicates that the EPR signal is associated with a hydrogen impurity. Furthermore, the

TABLE I. $2a_{1g}$ orbital for the H^{2-} ion in MgO.

α	n_α	C_α	β_α
1	1	0.084 013	2.474 72
2	1	−0.012 035	4.692 09
3	2	−0.509 481	0.267 63
4	2	−0.846 660	0.533 99
5	2	0.558 377	1.001 13
6	2	−0.017 158	1.662 85

absence of anisotropy in the present measurements apparently rules out the possibility of this center being an OH^{2-} ion.[13,14] This conclusion is further reinforced by the fact that the OH concentration in these crystals is undetectable as monitored by infrared absorption measurements. EPR measurements of interstitial and substitutional atomic hydrogen in alkaline-earth oxides,[9] alkali halides, alkaline-earth halides, and quartz[15] show no significant reduction in A_H from the free-atom value. This is in sharp contrast with the value of A_H measured for this defect, which is roughly one order of magnitude smaller than that of a free hydrogen atom. Infrared absorption measurements indicate a high concentration of substitutional H^- ions present prior to irradiation with blue light. This combined with the good agreement between the experiment value of A_H with that obtained using the calculated spin density at the proton for a substitutional H^{2-} ion lead us to conclude that the observed EPR signals are those of substitutional H^{2-} and D^{2-} ion impurities.

In summary, we have presented the results of experimental and theoretical studies of the H^{2-} ion in MgO. These studies have shown that (i) an observed EPR spectrum is that of a hydrogen center exhibiting the properties expected of a substitutional H^{2-} ion, (ii) substitutional H^- ions are effective, low-temperature electron traps in MgO, forming stable H^{2-} ions, and (iii) irradiation with blue (400-nm) light is very effective in forming H^{2-} ions in additively colored MgO.

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