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Diffusion of deuterium and hydrogen in doped and undoped MgO crystals

R. Gonzalez* and Y. Chen
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

K. L. Tsang
Physics Department, University of Alabama, Birmingham, Alabama 35294
and Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Infrared absorption of OD^- and OH^- ions is used to study diffusion rates of D^+ and H^+ in doped and undoped MgO crystals heated at high temperatures in D_2O and H_2O vapors. Crystals doped with H, Li, Na, Al, V, Cr, Fe, Co, Ni, Cu, Ga, Ag, and Yb are studied. With the exception of the H- and Li-doped crystals, the diffusion characteristics of the doped and undoped MgO crystals are essentially the same. The minimum temperature observed for D^+ diffusion is 1750 K, and the diffusion coefficient is $\sim 1\times 10^{-6}$ cm^2/sec at 1873 K. The ratio of the diffusion coefficients of H^+ and D^+ at 1873 K is $D(H^+)/D(D^+)=1.1\pm 0.1$. Complete removal of soluble H^+ can be accomplished by application of an electric field at 1300 K. In H-doped crystals an exchange of H^+ for D^+ results in large concentrations of OD^- ions. In Li-doped crystals, deuterons diffuse much more readily; the threshold temperature for D^+ diffusion is only 800 K. The higher diffusivity is attributed to a catalytic behavior of Li_2O precipitates.

I. INTRODUCTION

Hydrogen and its isotopes, deuterium and tritium, diffuse much more readily into metals than into ceramics. On one hand, some metals are suitable for hydrogen-storage purposes. On the other hand, the usefulness of ceramics lies precisely in low-hydrogen permeation. For example, in Stirling engines,[1] hydrogen is the preferred working fluid and materials must be available which can withstand high-temperature, high-pressure cycling in hydrogeneous environments with minimal hydrogen losses. Thin oxide films normally are coated on suitable metal-alloy components. It therefore is useful to have quantitative information on diffusion coefficients of hydrogen in oxides.

In the past decade, some concerted efforts have been made to study the diffusion of hydrogen in insulators such as rutile, aluminum oxide, tantalates, and beryllium oxide.[2–9] The present study focuses on the diffusion of deuterium and hydrogen ions in crystalline MgO, both in nominally pure form and doped with various impurities. Because these crystals almost always contain hydrogen, the study was performed primarily with D_2O. The ratio of the diffusion coefficients of H^+ to D^+ is determined. Finally, we show that protons and deuterons can be swept out of these crystals by low electric field applied at moderately high temperatures.

II. EXPERIMENTAL PROCEDURES

The MgO crystals used in the present study, both doped and undoped, were grown by the arc-fusion method[10] at the Oak Ridge National Laboratory. The starting material was high-purity grade MgO powder from the Kanto Chemical Company, Tokyo, Japan. Typical chemical analyses have been reported previously.[10,11] A typical sample had dimensions of 1.0×1.0 cm^2 in area, and 0.10–0.15 cm in thickness. Most MgO crystals contain hydrogen to a greater or lesser extent. MgO powder presoaked with water produces crystals that are very cloudy, due to the presence of cavities containing high-pressure H_2 gas.[12] At the other extreme, crystals with undetectable or barely detectable OH^- concentrations can be produced when grown in a special way.[10]

Infrared absorption measurements were made with a Perkin-Elmer Model 580 Spectrophotometer. High-temperature heat treatments were performed in an Astro furnace (Model No. 1000-2560FP) with a graphite heating element. When used in conjunction with an alumina tube, heat treatments up to 1925 K could be performed. For annealing at $T < 1500$ K, a Marshall furnace with Kanthal heating elements was used. Following thermal annealing, the samples were cooled rapidly in order to maximize the concentration of OH^- (OD^-) ions in the solute and minimize the amount of these ions in brucite form.

Infrared absorption measurements were made on MgO crystals doped with the following impurities: H, Li, Na, Al, V, Cr, Fe, Co, Ni, Cu, Ga, Ag, Au, and Yb. These samples were heated first in D_2O vapor at 1873 K for 30 min, followed by fast cooling in the cooler part of the furnace. Subsequent treatment under identical conditions were performed in H_2O vapor. The exception was a lithium-doped crystal which was treated in the same manner but at 1173 K. The reason for this lower-temperature treatment will be discussed later.

III. FORMALISM

In a classical system consisting of a low concentration of defects or impurities such that they do not interact with each other, diffusion is rigorously described by Fick's law; the rate of transfer of the diffusing substance through a unit area of a section in an isotropic substance is proportional to the concentration gradient measured perpendicular to the section.[13] The fundamental differential equation of diffusion in one dimension is

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2} , \tag{1}$$

where n is the concentration of the diffusing species, x is the coordinate, and D is the diffusion coefficient. For dilute systems, D can be considered independent of n.

The solutions of the diffusion equation have been widely discussed in the literature.[13] Recently, Sonder *et al.*[14] studied the kinetics of iron-redox reactions in MgO by determining the rate of change of Fe^{3+} concentrations. The formalism we shall use for analyzing our diffusion data is analogous to that used by these authors.

Let n_0 be the initial concentration (at $t=0$) of the diffusing species in the sample and $n(x,t)$ be that at annealing time t. For a sample of thickness $2l$ and area S, the total amount of the diffusing species, N_0, at $t=0$ is given by

$$N_0=Vn_0 , \tag{2}$$

where $V=2lS$ is the volume of the sample. At time t the total diffusing species in the sample is given by

$$N(t)=S\int_{x=-l}^{x=l} n(x,t)\,dx . \tag{3}$$

In writing Eq. (3), we neglected the diffusion through the edges of the sample and treated the problem as one dimensional. This is justified because the samples used in our experiment were thin ($l \ll S$). Under our experimental conditions, $Dt \ll l^2$. The solution of Eqs. (1)–(3) can be approximated to be[13]

$$\frac{N(t)-N_0}{N_s-N_0}=\frac{S}{V}\frac{4}{\sqrt{\pi}}\sqrt{Dt} , \tag{4}$$

where N_s is the total amount of diffusing species in the sample at saturation (after a long period of annealing). $N(t)$ in Eq. (4) is proportional to the optical absorbance of the OH^- or OD^- in the sample. Thus, diffusion coefficients can be obtained from the absorbance A of the bands. To do so, it is necessary to obtain the absorbance: Before treatment ($t=0$), as a function of annealing time t, and after long annealing such that the absorbance is saturated. These values are denoted by A_0, $A(t)$, and A_s, respectively. The diffusion coefficient can be calculated from the initial slope M of a plot of the absorbance versus $\sqrt{t}$ and the absorbance at saturation using the expression

$$D=\left[\frac{V}{4S}\right]^2\frac{\pi M^2}{(A_S-A_0)^2} . \tag{5}$$

IV. RESULTS AND DISCUSSION

A. OH^- and OD^- ions in doped and undoped crystals

Past studies[12,15–21] have established unambiguously the origin of three OH^- absorption bands: 3700, 3296, and 3323 cm^{-1}. (Their OD^- analogs occur at 2723, 2445, and 2465 cm^{-1}, respectively.) The 3700-cm^{-1} band is due to OH^- ions in $Mg(OH)_2$ precipitates. The 3296-cm^{-1} band originates from the defect with a linear configuration of $OH^-[++]O^{2-}$, where $[++]$ refers to a Mg^{2+} vacancy; this defect is commonly referred to as the V_{OH^-} center. The 3323-cm^{-1} band has been attributed to the V_{OH} center (V_{OH^-} center with a trapped hole) with configuration $OH^-[++]O^-$, where the O^- ion refers to an O^{2-} ion with a trapped hole.

The observed frequencies corresponding to the isotopically analogous OH^- and OD^- stretching frequencies in crystals with different dopant are tabulated in Table I. The ratio of the frequencies for a given defect is 1.35 ± 0.01, which corresponds well to the theoretical expectation of $[\mu(OD)/\mu(OH)]^{1/2} = 1.37$ for the two isotopes; here μ is the reduced mass of the radicals. There exists a very clear one-to-one correspondence in

TABLE I. OD^- and OH^- absorption bands in undoped and doped MgO crystals, after annealing for 30 min first in D_2O, and then in H_2O vapor at 1873 K, followed by fast cooling. MgO:Li was annealed at 1173 K. Numerals in parentheses are relative intensities for a given crystal, with unity assigned to the band with the highest absorption.

Sample	OD^- absorption (cm^{-1})	OH^- absorption (cm^{-1})
MgO	2445(1) 2455(0.1)	3296(1) 3310(0.1)
MgO:H	2445(1) 2500(2) 2723(0.2)	3296(1) 3372(2) 3700(0.2)
MgO:Li	2553 (broad band)	3430 (broad band)
MgO:Na	2445(0.2) 2465(1)	3296(0.2) 3323(1)
MgO:Al	2445(0.2) 2465(1)	3296(0.2) 3323(1)
MgO:V	2445(1) 2455(1)	3296(1) 3310(1)
MgO:Cr	2445(1) 2455(0.7)	3296(1) 3310(0.7)
MgO:Fe	2445(1) 2455(0.8)	3296(1) 3310(0.8)
MgO:Co	2445(1) 2455(<0.1)	3296(1) 3310(<0.1)
MgO:Ni	2445(1) 2455(0.2)	3296(1) 3310(0.4)
MgO:Cu	2445(0.4) 2465(1)	3296(<0.1) 3323(1)
MgO:Ga	2445(1) 2455(0.1)	3296(1) 3310(0.2)
MgO:Ag	2445(1) 2465(0.9)	3296(1) 3323(0.9)
MgO:Au	2445(1) 2455(0.1)	3296(1) 3310(0.1)
MgO:Yb	2445(0.3) 2465(1)	3296(0.3) 3323(1)

relative intensities between the OH^- and OD^- analogs, as shown in Table I. The numbers in parenthesis are relative band intensities within a given crystal, with unity assigned to the band with the highest intensity. The 3296- (2445-) cm^{-1} line, due to V_{OH^-} (V_{OD^-}) defects, was present in all crystals except MgO:Li. It has also been found to be the most intense band except in those doped with Na, Cu, Al, and Yb.

It is appropriate to comment on the defect responsible for the 3310- (2455-) cm^{-1} band. Glass and Searle[16] attributed this band to the defect $OH^-[++]O^{2-}M^{3+}$, where M refers to a cation, on the basis of their calculation of the frequency shift due to the trivalent cation. Their experimental findings suggested that the trivalent ion was Fe^{3+} of Cr^{3+}. In subsequent studies, Henderson and Sibley[19] rejected both as the responsible ions because of a noncorrelation of Fe^{3+} concentrations with the 3310-cm^{-1} signals in their samples. Instead they proposed Al^{3+} or Ca^{2+}, the latter because of its larger ionic size. We found no evidence of the 3310-cm^{-1} band in a crystal doped with aluminum. The presence of Al^{3+} ions as substitutional charge compensators for cation vacancies, namely in the V_{Al} center, has been established unequivocally by electron-nuclear double resonance (ENDOR) measurements[22]; it would appear plausible that protons can be trapped at these vacancies. Furthermore, if Al^{3+} is the responsible ion, one would expect to observe the 3310-cm^{-1} band in all MgO crystals, since aluminum is an omnipresent impurity with concentrations of the order of 10^{-5} with respect to the host ions. We conclude that it is highly improbable that Al^{3+} is responsible for the OH^- (OD^-) stretching frequency at 3310 (2455) cm^{-1}. The same argument holds for Ca^{2+}. The 3310-cm^{-1} band is one of two predominant bands in crystals doped with Fe, Cr, V, and Ni. All the crystals used in this study were grown by the same method, in the same arc furnace, and with materials from the same source. Therefore, it is unlikely that an impurity other than these transition-metal ions can give rise to the 3310-cm^{-1} band. Furthermore, we examined Fe-, Cr-, and V-doped crystals from Tateho Chemical Company, Hyogo-ken, Japan, and found that they also exhibited a strong 3310-cm^{-1} band. Hence, the optical spectra of Fe- and Cr-doped crystals from three sources, Oak Ridge, Tateho, and Bristol,[16] are consistent in this respect.

The band observed at 3323 (2465) cm^{-1} in the present work is not associated with the V_{OH} (V_{OD}) defect. We recall that the V_{OH} defect is produced by an ionizing radiation, such as with γ rays, x rays, or electrons, and it decays at room temperature with a half-life of a few hours[23]; it disappears almost instantly at $T=400$ K. The new 3323-cm^{-1} band was produced in the Na-, Al-, Cu-, Ag-, and Yb-doped crystals without irradiation. In fact, it was observed even after heat treatment. Furthermore, the presence of the V_{OH} defect would have exhibited a characteristic optical-absorption band in the visible region at 2.3 eV. No such coloration was observed. We conclude that the V_{OH} defect is not responsible for the 3323-cm^{-1} band observed in these crystals, and that there exists another defect whose OH^- vibration occurs at the same frequency.

B. Diffusion measurements

Since hydrogen is present in nearly all MgO crystals to a greater or lesser extent, deuterons were used as the diffusing species. In order to relate the diffusion coefficient of deuterium to that of hydrogen, we studied the isotopic effect of D^+ and H^+ diffusion. These results will be presented in Sec. IV C.

The minimum temperature at which deuterons diffuse into MgO crystals, doped or undoped, was observed to be about 1750 K, with heating times of 1 h. The exception is MgO:Li crystals, for which the minimum temperature is ~ 800 K. It is also noted that for MgO:H (cloudy) crystals which had high-OH^- concentrations, the amount of deuterium that diffused into the crystal was higher than in crystals which had low-OH^- concentrations. We attribute this difference in permeability to $H^+ \leftrightarrow D^+$ exchange. With the exception of MgO:H and MgO:Li, the diffusion characteristics were similar in MgO crystals. For these reasons, the emphasis of the diffusion studies was placed on three types of crystals: undoped MgO, MgO:H, and MgO:Li.

Figure 1 shows the spectra of these three crystals after being annealed in D_2O vapor. In the undoped MgO crystal, the V_{OH^-} signal at 3296 cm^{-1} was completely removed and the deuterium analog of this band at 2445 cm^{-1} emerged. In the MgO:H crystal the intensities of all the OD^- bands were considerably greater, even though the diffusion conditions were the same. The 2445-cm^{-1} band was much larger in the hydrogen-doped crystal. The presence of the 3296-cm^{-1} band may

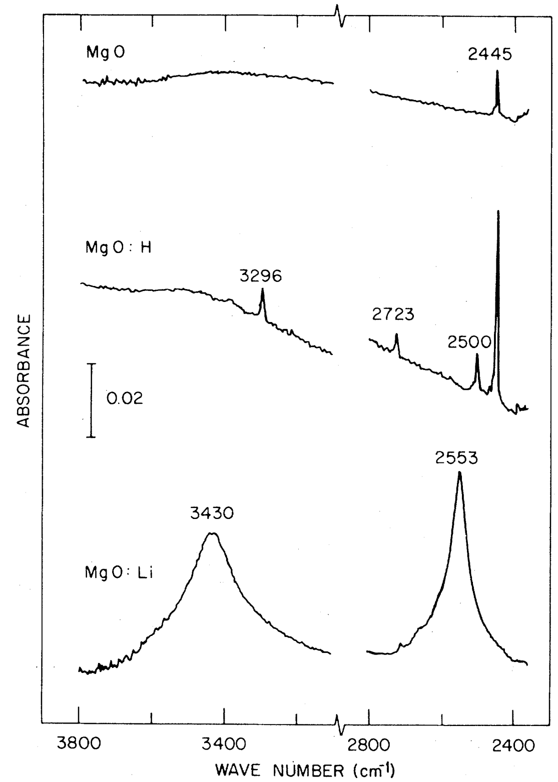

FIG. 1. Absorption spectra of an undoped MgO crystal (top), and a H-doped MgO crystal (center), after both had been heated in D_2O vapor at 1873 K for 30 min. Spectrum at the bottom illustrates the OD^- absorption in a MgO:Li crystal after it had been heated in D_2O vapor at 1173 K for 30 min.

be due to the continuous diffusion of hydrogen from the high-pressure hydrogen-containing cavities in the crystal. Two other bands, at 2500 and 2723 cm^{-1}, also appeared. The latter is due to OD^- ions in $Mg(OD)_2$ precipitates. In the MgO:Li sample, the broad band centering at 3430 cm^{-1} was replaced by a band at 2553 cm^{-1}. These bands are due to OH^- and OD^- ions, respectively.[24]

1. Undoped MgO and MgO:H

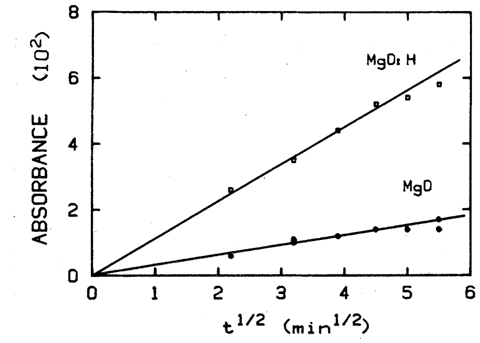

FIG. 2. Absorbance of OD^- ions at 2445 cm^{-1} vs $\sqrt{t}$ for an undoped and a MgO:H crystal following anneals at 1873 K. Thicknesses of the crystals were 1.52 and 1.56 mm, respectively. Solid circles represent data from another crystal.

Figure 2 plots the OD^- absorbance $A(t)$, monitored by the 2445-cm^{-1} band, versus $\sqrt{t}$ for an undoped MgO and a MgO:H crystal following anneals in D_2O vapor at 1873 K. The linearity of the two plots indicates the validity of the $\sqrt{t}$ dependence. Portions of the absorbance approaching saturation are not shown. The diffusion coefficients D, were calculated from the slopes M and the absorbance at saturation using Eq. (5). The values obtained are $D(\text{MgO}) = 1.4 \pm 0.5 \times 10^{-6}$ cm^2/sec, and $D(\text{MgO:H}) = 0.9 \pm 0.4 \times 10^{-6}$ cm^2/sec. It is noted that even though the slope is steeper in MgO:H, the absorbance at saturation is also higher. We conclude that these is no substantial difference in the diffusion coefficients between these two crystals.

It is clear from Fig. 2 that hydrogen (or deuterium) can be replaced by a $H^+ \leftrightarrow D^+$ exchange process. Prolonged heating in oxygen in a dry atmosphere at 1873 K also removed hydrogen or deuterium. For MgO:H crystals, removal of the infrared OH^- bands required longer times, probably because there is a continuous diffusion of hydrogen from the high-pressure H_2 gas in the cavities.

We also investigated whether diffusion coefficients are affected by the surface preparation of the samples, viz., cleaved as opposed to chemically polished. In an earlier study,[25] it was found that in cleaved or abraded MgO crystals deformation bands propagate from surface microcracks to a depth of ~1 mm at elevated temperature and that these bands can be eliminated by prior chemical polishing using phosphoric acid at 380 K. It was suggested that the dislocations in these bands may affect high-temperature conductivity of impurities. We did not observe significant differences in the diffusion coefficients between cleaved and chemically polished surfaces, probably because at 1873 K the induced dislocations are expected to anneal out rapidly.[26]

2. *Anomalous MgO:Li*

As indicated earlier, the lowest temperature for deuterium to diffuse into MgO under our experimental conditions is ~ 1750 K. MgO:Li is an anomaly among MgO crystals. The lowest temperature is ~ 800 K, as shown in Fig. 3. A crystal, $t = 1.62$ mm, was annealed isochronally for 5-min intervals at increasing temperatures in D_2O vapor. The crystal initially contained hydrogen, as evidenced by the presence of the broad 3430-cm^{-1} band. After each anneal, the OD^- and the OH^- concentrations were monitored by their respective broad bands. Figure 3 provides clear evidence that the OD^- concentrations increased at the expense of the OH^- concentrations; in fact, the two curves give an appearance of a mirror reflection of one another. Also, the temperature at which OH^- concentration begins to diminish corresponds well to the lowest temperature for deuterium diffusion.

Parameters such as activation energy and a preexponential diffusion factor can be obtained by measuring diffusion coefficients at different temperatures. Since the threshold temperature for deuterium diffusion in most MgO crystals is close to upper limit of our furnace capabilities, it is not feasible to obtain these constants, except in the case of MgO:Li. Isothermal annealing in D_2O vapor at three different temperatures was performed on three MgO:Li crystals with the same thickness and initial hydrogen concentration. After each annealing, the concentrations of deuterium were measured. The results for the three temperatures are plotted in Fig. 4. Using the cross-cut method[27] on these curves, an activation energy $E = 1.9 \pm 0.2$ eV was obtained. Plotting the absorbance versus $\sqrt{t}$ for the 1173-K diffusion, in a manner shown in Fig. 2, the diffusion coefficient was found to be $D = 1.0 \pm 0.4 \times 10^{-6}$ cm^2/sec. Using the values of E and D for 1173 K, the preexponential factor D_0 in the Arrhenius equation

$$D = D_0 e^{-E/kT} \tag{6}$$

was determined to be $D_0 \sim 150$ cm^2/sec, which is an exceptionally large value.

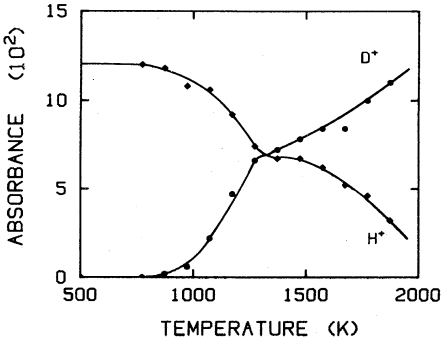

FIG. 3. Absorbance of OD^- and OH^- ions vs isochronal annealing temperature for a MgO:Li crystal. Crystal thickness was 1.62 mm.

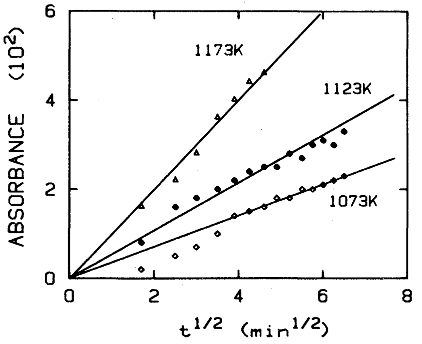

FIG. 4. Absorbance vs $\sqrt{t}$ at three temperatures for MgO:Li crystals.

It is of interest to compare the diffusion coefficient of MgO:Li with other MgO crystals at the same temperature. By an extrapolation using the above E and D_0 values, the diffusion coefficient of MgO:Li at 1873 K is calculated to be $D = 1 \times 10^{-3}$ cm^2/sec. This value is 3 orders of magnitude larger than that of undoped MgO crystals. There is evidence that the higher diffusivity is due to Li_2O precipitates[28,29] in the crystals: First, for samples which had been immersed in HCl to dissolve any exposed Li_2O precipitates, deuterium did not diffuse into the crystal at 1173 K. Secondly, after a prolonged heat treatment in oxygen at 1473 K so that the lithium ions were all in solution form,[28] deuterium did not diffuse into the crystal.

C. Isotopic effect

Since the diffusion work reported in the previous two sections was performed with deuterons, we need to establish experimentally the ratio $D(H^+)/D(D^+)$. Classically, a larger value can be expected for hydrogen because of the smaller mass. However, that need not be a foregone conclusion, since there are systems in which the opposite, $D(H^+)/D(D^+) < 1$, is true: fcc metals in certain temperature ranges.[30] The reasons were attributed to quantum effects.[31,32]

Whereas the values obtained for the diffusion coefficients are accurate to ±40%, the $D(\mathrm{H}^+)/D(\mathrm{D}^+)$ ratio in this study involves only relative errors and should be accurate to better than ±10%. We chose experimental conditions which are *exactly identical* for both hydrogen and deuterium diffusion: One sample was used *simultaneously* for both H and D diffusion. An undoped crystal was initially heated at 1873 K in flowing oxygen for several hours until all traces of OH^- bands disappeared. The crystal was then isothermally annealed at 1873 K in an atmosphere comprised of comparable concentrations of D_2O and H_2O. Equal concentrations are not necessary because a difference in partial pressure changes both the slope and saturation value such that the same diffusion coefficient is obtained. The absorbances at 3296 and 2445 cm^{-1} were measured after each anneal. The results are plotted against $\sqrt{t}$ in Fig. 5. while the slope of the OH^- curve is higher than that of the OD^-, the saturation value is also higher. From the slopes and the absorbance at saturation, the ratio $D(\mathrm{H}^+)/D(\mathrm{D}^+)$ is determined to be 1.1 ± 0.1. Experimental factors which affect the OD^- absorbance affect the OH^- absorbance in the same manner. The departure from the straight lines for each anneal, shown in the figure, is comparable for both OD^- and OH^-. Hence, there is little uncertainty in determining the ratio of the diffusion coefficients. We conclude that there is no appreciable difference between $D(\mathrm{D}^+)$ and $D(\mathrm{H}^+)$ at 1873 K.

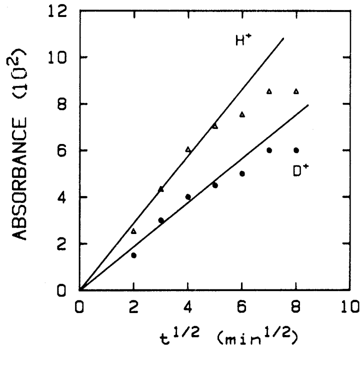

FIG. 5. Absorbance of the 3296- and 2445-cm^{-1} band vs $\sqrt{t}$ for a hydrogen-free crystal heated in a mixture of D_2O and H_2O vapor at 1873 K. From the slopes shown in the figure, the diffusion coefficients were $D(\mathrm{H}^+) = 1.2 \pm 0.4 \times 10^{-6}$ $\mathrm{cm}^2/\mathrm{sec}$ and $D(\mathrm{D}^+) = 1.1 \pm 0.4 \times 10^{-6}$ $\mathrm{cm}^2/\mathrm{sec}$. Sample thickness was 1.46 mm.

D. Sweeping by electric field

Removal of hydrogen from oxides by application of an electric field has been established for materials with open channels, such as quartz.[33–35] In the present work, we find that H^+ or D^+ can also be removed effectively from a tight lattice such as MgO. Five transparent samples with the same thickness (1.58 mm), containing moderate amounts of OH^- ions, were used. Each was heated at a different temperature for 70 min in a dry nitrogen atomosphere. During the heat treatment, a field of 2000 V/cm was applied to part of the crystal, so that the area without electric field could be used as a control. The results are shown in Fig. 6. After the anneal, the samples were fast-cooled and the absorbance at 3296 cm^{-1} for both areas was measured. Out-diffusion of hydrogen is apparent at $T = 1100$ K or higher. Removal of hydrogen is much more effective with an applied field. For example, at 1300 K all the hydrogen was swept out by the field, whereas only 10% was removed in the region where no field was applied.

A study on the hydrogen profiles was performed on the field-induced areas of the samples. It was found that most of the hydrogen concentrated near the negative electrode. This observation is consistent with the expectation that protons are swept toward the negative polarity.

It is of interest to contemplate whether or not hydrogen (or deuterium) can be removed from an oxide near room temperature. We have seen that at elevated temperatures, protons can be swept out of a MgO crystal using an electric field. However, if the temperature is not sufficiently high, another mechanism is needed to break the OH^- bond. Such a mechanism is indeed available: radiation-

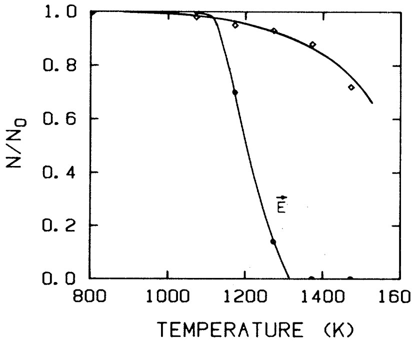

FIG. 6. Normalized concentrations of OH^- ions vs annealing temperature with and without an electric field.

induced diffusion[36] by electron irradiation. The cross section for OH^- dissociation is very large, $\sim 10^8$ barns. Experimentally, an electric field of 4000 V/cm was applied to a deuterated MgO crystal, which was simultaneously irradiated with 2.0-MeV electrons. The temperature of the crystal during the irradiation was estimated to be 400 − 450 K. After irradiation with a dose of $\sim 3\times 10^{17}$ electrons/cm^2, no appreciable loss of deuterons was observed. It is believed that the deuterons drifted only a short distance before they are trapped at other sites. One may speculate that the drifting is more effective along large open channels in certain materials.

V. SUMMARY AND CONCLUSIONS

Undoped MgO and MgO crystals doped with H, Li, Na, Al, V, Cr, Fe, Co, Ni, Cu, Ga, Ag, Au, and Yb were heated in D_2O and/or H_2O vapor at elevated temperatures. The OH^- and OD^- stretching frequencies were measured. Excepting H and Li, there is no evidence that the presence of impurities induces either a higher solubility of D^+ or H^+ ions, or a different diffusion coefficient. The lowest temperature for D^+ diffusion, and presumably also that of H^+, is 1750 K for a 1-h heat treatment. The diffusion coefficient of deuterons is about 1×10^{-6} cm^2/sec at 1873 K. At this temperature the diffusion coefficient of protons is effectively the same as that of deuterons, the ratio being 1.1 ± 0.1. While MgO does not have open channels for protons to diffuse through (as does quartz), nevertheless, removal of soluble protons can be accomplished by electric field sweeping at temperatures above 1100 K.

In translucent crystals containing cavities of high-pressure H_2 gas, the level of deuterons that can be introduced is much higher than that of MgO crystals without such cavities. The large initial OH^- concentrations was replaced by OD^- ions, presumably by an exchange process.

Deuterons diffuse much more readily in MgO:Li crystals. The minimum temperature for D^+ diffusion is much lower, occurring at about 800 K for 1-h diffusion. Evidence is provided that the presence of Li_2O precipitates at the surface enhances the diffusion of deuterons.

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[*] Permanent address: Departmento de Fisica de Estado Solido, Facultad de Ciencias Fisicas, Universidad Complutense, Madrid, Spain.

[1] W. D. Klopp and D. O. Welch, U. S. Department of Energy Report No. ER-151 (unpublished).

[2] J. W. De Ford and O. W. Johnson, J. Appl. Phys. 44, 3001 (1973).

[3] O. W. Johnson, J. W. De Ford, and J. W. Shaner, J. Appl. Phys. 44, 3008 (1973).

[4] J. D. Fowler, D. Chandra, T. S. Elleman, A. W. Payne, and K. Verghese, J. Am. Ceram. Soc. 60, 155 (1977).

[5] J. B. Bates and R. A. Perkins, Phys. Rev. B 16, 3713 (1977).

[6] J. B. Bates, J. C. Wang, and R. A. Perkins, Phys. Rev. B 19, 4130 (1979).

[7] J. V. Cathcart, R. A. Perkins, J. B. Bates, and L. C. Manley, J. Appl. Phys. 50, 4110 (1979).

[8] H. Engstrom, J. B. Bates, J. C. Wang, and M. M. Abraham, Phys. Rev. B 21, 1520 (1980).

[9] H. Engstrom, J. B. Bates, and L. A. Boatner, J. Chem. Phys. 73, 1073 (1980).

[10] M. M. Abraham, C. T. Butler, and Y. Chen, J. Chem. Phys. 55, 3752 (1971).

[11] Y. Chen, D. L. Truesblood, O. E. Schow, and H. T. Tohver, J. Phys. C 3, 2501 (1970).

[12] A. Briggs, Ph.D. thesis, University of Bradford, 1970 (unpublished); A. Briggs, J. Mater. Sci. 10, 729 (1975).

[13] J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, 1956).

[14] E. Sonder, T. G. Stratton, and R. A. Weeks, J. Chem. Phys. 70, 4603 (1979).

[15] P. W. Kirklin, P. Auzins, and J. E. Wertz, J. Phys. Chem. Solids 26, 1067 (1965).

[16] A. M. Glass and T. M. Searle, J. Chem. Phys. 46, 2092 (1967).

[17] W. A. Sibley, C. M. Nelson, and Y. Chen, J. Chem. Phys. 48, 4582 (1968).

[18] T. M. Searle, J. Phys. Chem. Solids 30, 2143 (1969).

[19] B. Henderson and W. A. Sibley, J. Chem. Phys. 55, 1276 (1971).

[20] B. Henderson, J. L. Kolopus, and W. P. Unruh, J. Chem. Phys. 55, 3519 (1971).

[21] Y. Chen, M. M. Abraham, L. C. Templeton, and W. P. Unruh, Phys. Rev. B 11, 881 (1975).

[22] W. P. Unruh, Y. Chen, and M. M. Abraham, Phys. Rev. Lett. 30, 446 (1973).

[23] M. M. Abraham, Y. Chen, and W. P. Unruh, Phys. Rev. B 9, 1842 (1974).

[24] Y. Chen, E. Montesa, J. L. Boldu, and M. M. Abraham, Phys. Rev. B 24, 5 (1981).

[25] Y. Chen, N. Dudney, J. Narayan, and V. M. Orera, Philos. Mag. 44, 63 (1981).

[26] J. Narayan and J. Washburn, Philos. Mag. 26, 1179 (1972); Cryst. Lattice Defects 3, 91 (1972).

[27] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1963).

[28] Y. Chen, H. T. Tohver, J. Narayan, and M. M. Abraham, Phys. Rev. B 16, 5535 (1977).

[29] J. Narayan, M. M. Abraham, Y. Chen, and H. T. Tohver, Philos. Mag. A 38, 247 (1978).

[30] J. Volkl and G. Alefeld, in *Hydrogen in Metals I*, edited by G. Alefeld and J. Volkl (Springer, Berlin, 1978).

[31] E. Gorham-Bergeron, Phys. Rev. Lett. 37, 146 (1976).

[32] A. M. Stoneham, J. Nucl. Mater. 69-70, 109 (1978).

[33] A. Kats, Philips Res. Rep. 17, 133 (1962).

[34] J. C. King and H. H. Sander, IEEE Trans. Nucl. Sci. NS-19, 23 (1972).

[35] S. P. Doherty, J. J. Martin, A. F. Armington, and R. N. Brown, J. Appl. Phys. 51, 4164 (1980).

[36] Y. Chen, M. M. Abraham, and H. T. Tohver, Phys. Rev. Lett. 37, 1757 (1976).