

Low Temperature Diffusion of Hydrogenic Species in Oxide Crystals: Radiation Induced Diffusion

Y. Chen^a and R. Gonzalez^b

^a Solid State Division, Oak Ridge National Laboratory, P. O. Box 2008,
Oak Ridge, TN 37831-6031, U. S. A.

^b Departamento de Ingenieria, Escuela Politecnica Superior, Universidad Carlos III
Avda. del Mediterraneo, 20, 28913 Leganes, Madrid, Spain.

Normally stable configurations of substitutional protons or deuterons in oxide crystals become highly unstable during ionizing radiation at room temperature, resulting in the displacements of these species. The cross section for radiation-induced-displacements of protons is exceedingly large and is a strong function of temperature. The displacement cross section of protons from cation sites is twice that of deuterons. Diffusion of these species can be induced at temperatures not otherwise possible by thermal means. For example, using electron irradiation near room temperature the O-H bond is readily broken and the hydrogenic species can be channeled along the c-axis in TiO₂ by an applied electric field. Radiation induced displacements of protons from anion sites (hydride ions) at room temperature are also discussed.

1. INTRODUCTION

Hydrogenic species (protons, deuterons, and tritons) normally occupy stable configurations in oxide crystals and do not diffuse except at high temperatures.¹ However, under ionizing radiation, such as electron irradiation, hydrogenic species are displaced readily from cation and anion sites and become highly mobile (referred to as radiation induced diffusion - RID).¹⁻⁴ Therefore, the usual diffusion constants for these species cannot be used to predict the behavior of these isotopes in insulators under ionizing radiation. Because of their mobility, they can be swept in and out of a crystalline material⁵⁻⁹ using an applied electric field near room temperature and possibly even at lower temperatures. We shall first address H⁺, D⁺, and T⁺ ions primarily in substitutional cation sites, concerning (1) thermal diffusion of hydrogenic species in oxides and the associated

isotopic effect, (2) the spectroscopic evidence for RID under ionizing radiation, (3) out-diffusion of protons and deuterons: environmental dependence, and (4) low-temperature diffusion: channeling effects. Finally we discuss (5) room-temperature radiation-induced-displacements of protons from anion sites containing hydride ions.

2. MATERIALS, TECHNIQUES, AND PROCEDURES

Diffusion studies of hydrogenic species were carried out in crystals of MgO, LiNbO₃, and TiO₂ rutile.^{1,2,3,7,8,10} Infrared transmission (or absorption) is used to monitor the presence of the hydrogenic species which are present in the form of OH⁻, OD⁻, and OT⁻ ions, with supporting roles from optical absorption, which monitors electronic transitions, and electron paramagnetic resonance, which detects point defects with unpaired spins. In

most experiments, deuterons were used as the diffusing species in order to distinguish from proton contaminations from the atmosphere or electrical contacts. The irradiating source was a 2.0 MeV Van de Graaff electron generator. Room temperature irradiations were carried out in sample holder using tap water as a coolant, and the low-temperature irradiations were performed in a cryostat cooled by liquid nitrogen. The temperature of sample during irradiation was estimated to be about 290 and 85 K respectively.

3. MATHEMATICAL FORMALISM

The diffusion characteristics for a classical system with a low concentration of defects or impurities such that they do not interact with each other can be described by Ficks's second law; in an isotropic medium the rate of transfer of the diffusing species through a unit area of a section is proportional to the concentration gradient measured perpendicular to the section.¹¹ In one-dimension, Ficks's second law can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (1)$$

where C 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 C . At time t the total concentration of the diffusing species in a sample of thickness $2d$ and area S ($d \ll S$) is given by

$$C(t) = \frac{1}{2d} \int_{-d}^d C(x, t) dx. \quad (2)$$

where $C(x, t)$ is the concentration of the diffusing species at annealing time t .

General solutions of the diffusion equation can be obtained for a variety of initial and

boundary conditions, provided the diffusion coefficient is constant. Here we are dealing with the *out*- and *in*- diffusion of hydrogen isotopes. $C(t)$ is proportional to the optical absorbance of the OH^- , OD^- , and OT^- bands in the sample.

(a) In-diffusion

The solution of Eqs. 1 and 2 can be approximated to be

$$\frac{C(t) - C_0}{C_s - C_0} = \frac{2}{d\sqrt{\pi}} \sqrt{Dt} \quad (3)$$

where C_0 and C_s are the concentrations of the diffusing species at $t=0$ and at saturation respectively. Hence the in-diffusion coefficient can be obtained from the formula

$$D_{\text{in}} = \left(\frac{d}{2}\right)^2 \frac{\pi m^2}{(A_\infty - A_0)^2}, \quad (4)$$

where m is the initial slope for a plot of absorbance versus \sqrt{t} , and A_0 and A_∞ are the absorbance at $t=0$ and at saturation.

(b) Out-diffusion

The diffusion equation is as follows¹¹

$$C(x, t) = \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \quad (5)$$

$$\times \exp\left(-\frac{D_{\text{out}}(2n+1)^2\pi^2 t}{4d^2}\right)$$

$$\times \sin\left(\frac{2n+1}{2d}\pi x\right).$$

Integration of Eq. 2 yields

$$C(t) = \frac{8C_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left(-\frac{D_{\text{out}}(2n+1)^2\pi^2 t}{4d^2}\right) \quad (6)$$

Thus, the out-diffusion coefficient can be obtained from the formula

$$D_{\text{out}} = \frac{4Md^2}{\pi^2} \quad (7)$$

where M is the slope of a semilogarithmic plot of the absorbance $A(t)$, versus isothermal annealing time.

4. THERMAL DIFFUSION

Hydrogenic species forming OH^- , OD^- , and OT^- ions are stable at room temperature and do not diffuse until several hundred degrees above room temperature.¹ In this section we demonstrate that protons in TiO_2 rutile^{10,12} are not mobile until 600 K, and in MgO not until 800 K.¹ We also show that the isotopic effect on thermal diffusion of hydrogenic species are exceedingly small (at least for protons and deuterons), and for all practical purpose they are the same.⁴

The in-diffusion and out-diffusion of hydrogenic species can be illustrated in TiO_2 rutile. We use deuterons as the diffusion species. In TiO_2 the OH^- and OD^- vibrational modes occur at 3277 and 2437 cm^{-1} respectively.¹² The ratio of the frequencies is 1.34, which corresponds well to the theoretical expectation of $[\mu(\text{OD})/\mu(\text{OH})]^{1/2} = 1.37$ for the two isotopes; here μ is the reduced mass of

the radicals. Fig. 1 shows the in-diffusion and subsequent out-diffusion of deuterons. In curve (a), a sample was deuterated isochronally (30 min each) at increasing temperatures. The OD^- absorbance increased with increasing temperatures. After the final D^+ in-diffusion at $T=1173$ K, out-diffusion of the deuterons was performed, also isochronally at increasing temperatures, but in flowing oxygen. It is clear from the figure that no in-diffusion and out-diffusion takes place below 600 K.

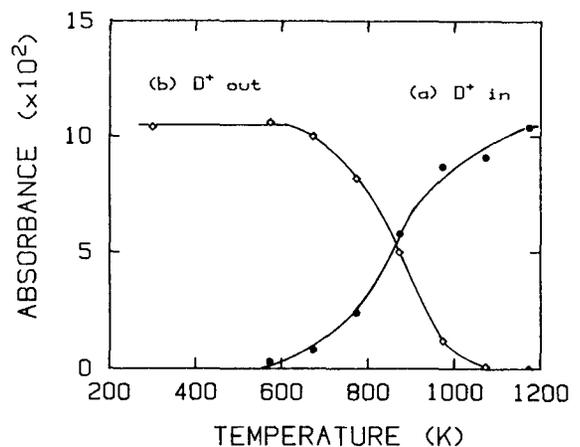


Fig. 1. Absorbance vs. annealing temperature for isochronal in-diffusion of deuterons in TiO_2 rutile from D_2O vapor (curve a) and isochronal out-diffusion of deuterons in O_2 vapor.

A substitutional proton in a normal Mg site forms covalent bonding with one of its six neighboring O^{2-} ions; the lattice distortion results in the following configuration: $\text{Mg}^{2+} - \text{OH}^- - [\text{Mg vacancy}] - \text{O}^{2-} - \text{Mg}^{2+}$. The O-H stretching frequency at this site is 3296 cm^{-1} .¹³ Hence the amplitude of this infrared band provides a measure of the concentration of these substitutional protons. Copious amounts of these protons are produced when a crystal containing H is quenched from high temperatures. The protons are randomly distributed throughout the crystal at high temperatures and are frozen in their substitutional sites by the quenching.

However, if the crystal is slow-cooled, the protons will move around and have ample opportunities to aggregate. Precipitates are found by electron microscopy, and the electron diffraction patterns suggest that the domains are caused by $\text{Mg}(\text{OH})_2$.¹⁴ Furthermore, an infrared band at 3700 cm^{-1} , which corresponds to the O-H vibrational frequency in $\text{Mg}(\text{OH})_2$ powder, confirms the presence of $\text{Mg}(\text{OH})_2$ precipitates in MgO .¹³

Fig. 2(A) illustrates the infrared transmission spectrum of a H-containing crystal

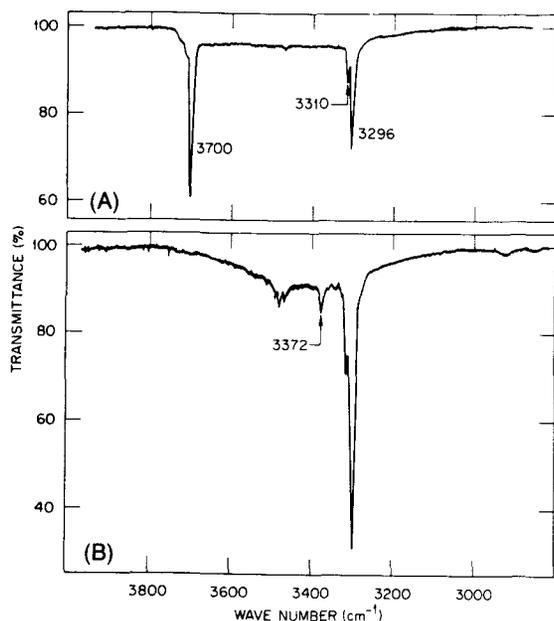


Fig. 2. Infrared spectra of MgO containing hydrogen after (A) slow-cooling from 1400 K and (B) fast-quenching from 1450 K.

after it was slow-cooled from 1400 K to room temperature over a 24 h period. After heating to 1450 K and quenched into a bath of liquid nitrogen, the crystal exhibits the spectrum shown in Fig. 2(B). The behavior of the spectra is reversible indefinitely by alternately show-cooling and quenching, indicating that there exists an inexhaustible

supply of hydrogen in the crystal (in the form of high-pressure hydrogen gas bubbles).¹⁴ As expected, slow-cooling resulted in an increased absorption for the 3700 cm^{-1} band and a decrease in the 3296 cm^{-1} signal. The converse is true for quenching.

Fig. 3 illustrates the thermal behavior of the 3296 cm^{-1} band at intermediate annealing

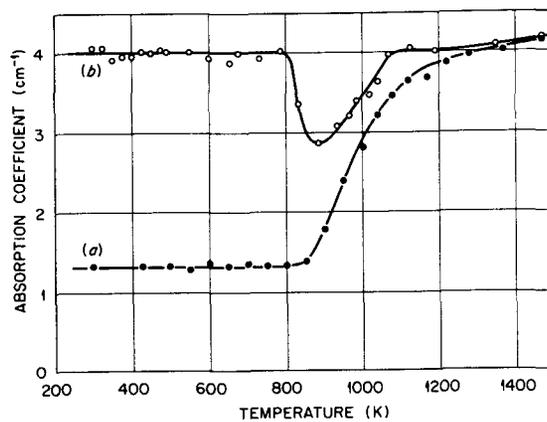


Fig. 3. Absorption coefficient of 3296 cm^{-1} band as a function of isochronal annealing temperature for a hydrogen-containing MgO crystal (a) initially slow-cooled and (b) fast quenched from 1450 K.

temperatures. The lower curve (a) represents the absorption coefficient of the band when the sample was initially slow-cooled and subjected to isochronal annealing for 10 min at each increasing temperature. After each anneal, the crystal was quenched into liquid nitrogen. Up to 800 K, the absorption coefficient remained unchanged. At higher temperatures the protons were sufficiently energetic that they could diffuse and occupy substitutional sites, thereby enhancing the intensity of the 3296 cm^{-1} band. At $T > 1200\text{ K}$, saturation effect emerged. On the other hand, when the crystal was initially quenched from 1450 K and isochronal annealed in the same manner, the absorption coefficient assume the curve shown in (b). Again at $T < 800\text{ K}$ no change in

absorption was noted, indicating a lack of mobility of the substitutional protons. At 800 K substitutional protons escape and find other preferred sites such as $\text{Mg}(\text{OH})_2$. An inversion of the curve occurred at 900 K. At higher temperatures, the protons become energetic enough to occupy more and more substitutional sites. The curves in Fig. 3 indicate that at $T < 800$ K, protons are not sufficiently energetic to incur a redistribution of substitutional protons.

4.1. Isotopic Effect: Deuterons

Since our diffusion studies were performed with deuterons in order to distinguish them from environmental contaminations, it is important to establish experimentally the ratio of the diffusion coefficients, $D(\text{H}^+)/D(\text{D}^+)$. Classically, a larger value can be expected for protons because of the smaller mass. However, there are systems in which the opposite, $D(\text{H}^+)/D(\text{D}^+) < 1$ is true: fcc metals in certain temperature range.¹⁵⁻¹⁷ The reasons were attributed to quantum effects. Whereas the diffusion coefficients from our experiments⁷ are accurate to $\pm 40\%$, this ratio involves only relative errors and therefore should be better than $\pm 10\%$.

We chose experimental conditions which are *exactly identical* for both proton and deuteron in-diffusion: one sample was used *simultaneously* for both H^+ and D^+ diffusion. An undoped MgO 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 but constant portions of D_2O and H_2O . Equal portions are not necessary because a difference in partial pressures changes both the slope and the saturation value in such a way that the diffusion coefficient obtained is independent of the partial pressure. The absorbance at 3296 and 2445 cm^{-1} were measured after each anneal. The results are plotted against \sqrt{t} in Fig. 4.

While the slope of the OH^- curve was higher than that of the OD^- , the saturation value was also higher. From the absorbance at saturation and the slopes, the ratio $D(\text{H}^+)/D(\text{D}^+)$ was determined to be 1.1 ± 0.1 . Experimental factors which affect the OD^- absorbance affect the OH^- absorbance in exactly the same manner. The departure from the straight lines for each anneal is comparable. Hence, there is little uncertainty in determining the ratio.

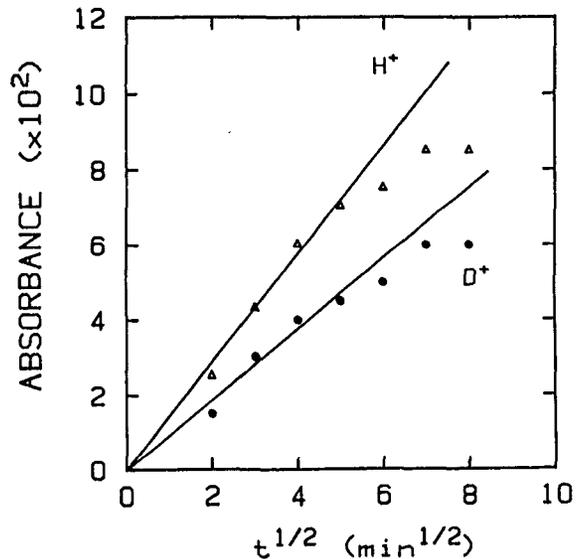


Fig. 4. Absorbance of OH^- and OD^- band vs. \sqrt{t} for an initially hydrogen-free MgO crystal heated in a vapor composed of comparable mixture of D_2O and H_2O at 1873 K. From the slopes the diffusion coefficients were determined to be $D(\text{H}^+) = 1.2 \pm 0.4 \times 10^{-6}$ cm^2/sec and $D(\text{D}^+) = 1.1 \pm 0.4 \times 10^{-6}$ cm^2/sec .

4.2. Isotopic Effect: Tritons

In spite of the importance of tritium in advanced energy devices, very little data are available concerning the diffusion properties of tritium in oxides. The reasons are probably that experiments with tritium are hazardous and expensive. One way to overcome these problems is to produce tritons in samples with very high lithium concentrations. For

example, tritium can be produced in LiNbO_3 crystals by transmutation of ${}^6\text{Li}$ ions according to the following nuclear reaction



with a production cross section of 910 b. The half life of tritium is 12.4 years. The thermal neutron dose used for our irradiation was $7.5 \times 10^{17} \text{ n/cm}^2$.

As-grown crystals of LiNbO_3 exhibit an OH^- vibrational band at 3480 cm^{-1} .¹⁸ After the neutron irradiation this band was absent and two new bands at 3500 and 3550 cm^{-1} appeared in the OH^- region.¹⁹⁻²⁰ In addition, two very weak bands at 2180 and 2211 cm^{-1} were observed (Fig. 5, bottom). Following an anneal at 625 K for 1 h, the band at 3500 cm^{-1} was replaced by one at 3480 cm^{-1} and the band at 2211 cm^{-1} became better resolved (Fig. 5, center). A subsequent anneal for 1 h at 775 K greatly increased the intensity of 3480 cm^{-1} band. The band at 2211 cm^{-1} disappeared and the band at 2180 cm^{-1} became more pronounced (Fig. 5, top). The frequency ratios between the OH^- bands and their OT^- analogs at 2211 and 2180 cm^{-1} are both 1.61 which corresponds well to the theoretical expectation of $[\mu(\text{OH}^-)/\mu(\text{OD}^-)]^{1/2} = 1.64$. Here μ is the reduced mass of the radicals. The two bands are unambiguously attributed to OT^- stretching vibrations.

We have measured the diffusion coefficients based on out-diffusion of protons, deuterons, and tritons. Between 900 and 975 K , the diffusion coefficients are of the order of $10^{-7} \text{ cm}^2/\text{s}$. An accurate out-diffusion coefficient for tritons relative to protons was not determined, because the triton concentration was too small. However, we have been able to determine that for all practical purpose, the diffusion coefficients for all three isotopes are not vastly different; there was only a 10% difference between protons and deuterons. The charge and the ionic radii are the same for the three isotopes. However, the masses are different.

Therefore we conclude that the charge and/or the ionic size is much more important than the mass in affecting the diffusion behavior for the hydrogenic species in oxides.

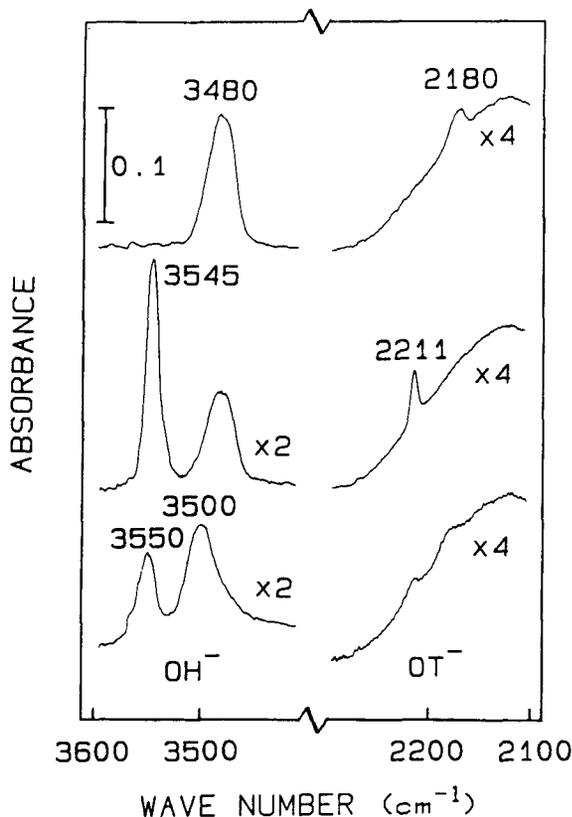


Fig. 5: Absorption spectra of a LiNbO_3 crystal: bottom, as irradiated with thermal neutrons ($7.5 \times 10^{17} \text{ n/cm}^2$); center, after subsequent annealing for 1 h at 625 K in air; top, after additional annealing for 1 h at 775 K in air. The thickness of the sample was 1.0 mm .

5: RADIATION INDUCED DIFFUSION

In MgO protons find themselves mostly distributed between substitutional sites and $\text{Mg}(\text{OH})_2$ precipitates, depending on the previous thermal history of the crystal, as discussed in § 4. Isochronal treatment studies of quenched and slow-cooled crystals indicate

that substitutional protons, as monitored by the O-H stretching frequency at 3296 cm^{-1} , are not mobile below 800 K. However, under the influence of electron irradiation, the proton is mobile even at 85 K.²

5.1. Spectroscopic Evidence

The effect of electron irradiation at $T \sim 290\text{ K}$ is shown in Fig. 6. This crystal was

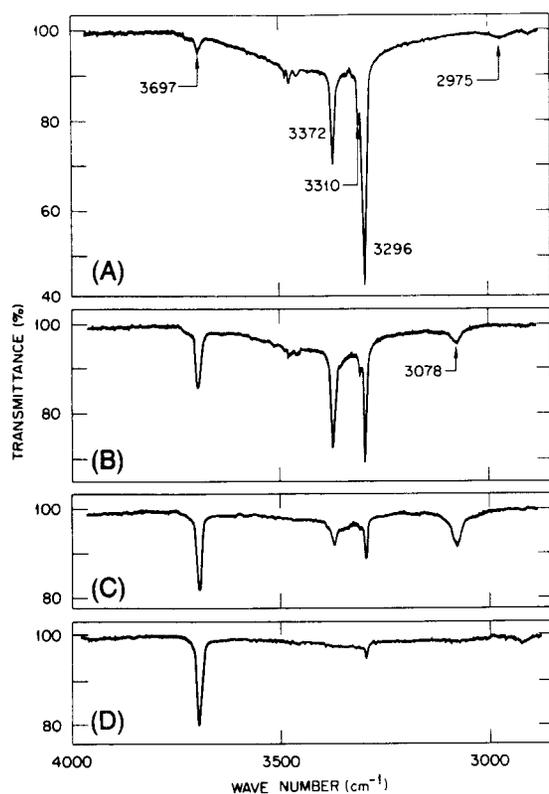


Fig. 6. Infrared spectra of fast-quenched MgO:H crystal after electron irradiation to doses of (A) 3.1×10^{15} , (B) 2.9×10^{16} , (C) 4.4×10^{17} , and (D) $2.6 \times 10^{18}\text{ e/cm}^2$.

initially quenched from 1450 K and exhibited the spectrum shown in Fig. 6(B). Subsequently, it was irradiated with electrons up to doses of $2.6 \times 10^{18}\text{ e/cm}^2$. The intensity of the 3296 cm^{-1} band decreased with irradiation, with most of the decrease occurring during the initial dose of $1 \times 10^{16}\text{ e/cm}^2$. The decay of this band was

attended primarily by the increase in the amplitude of a band at 3697 cm^{-1} . The electron irradiation causes the proton to relocate from its substitutional site to the $\text{Mg}(\text{OH})_2$ precipitate site. The latter varied between 3696 and 3700 cm^{-1} . Since it appeared to be broader than the other bands, it is probably the result of either a size effect of the precipitate, or a combination of $\text{Mg}(\text{OH})_2$ and those which were perturbed by a nearby impurity or defect. The decay of the 3296 cm^{-1} band at 290 K, illustrated in Fig. 6, is plotted in Fig. 7 (bottom). A similar experiment was performed at $T \sim 85\text{ K}$, but measured at room temperature. The decay is plotted at the top of Fig. 7. It is clear that the decrease in absorption at the higher temperature was much more rapid.

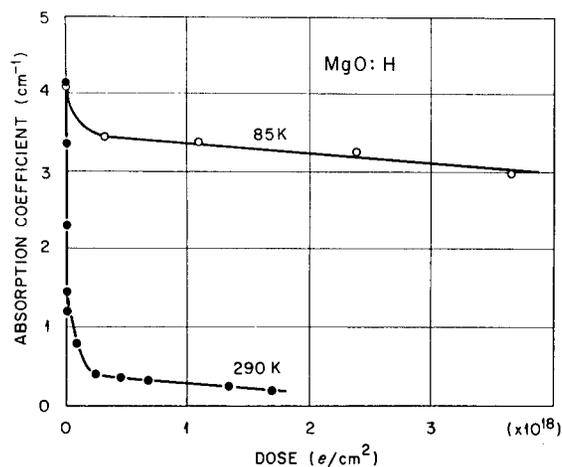


Fig. 7. Decay of the 3296 cm^{-1} absorption band in a hydrogen-containing MgO crystal as a function of electron dose for two irradiating temperatures.

While diffusion constants are meaningless during electron irradiation, we can determine the cross section for the displacement of protons from their substitutional sites.² This displacement initiates the diffusion process. The displacement cross sections of the substitutional protons can be determined by the use of the relationship $\sigma = (\Delta C/C) / \Delta\phi$, where

C is the initial concentration of the substitutional protons in the crystal and $\Delta C/\Delta\phi$ is the number of displaced events per cubic centimeter for a given irradiation dose. Since $\Delta C/C$ is equal to the fractional loss of the 3296 cm^{-1} absorption band, the cross sections can be determined from the initial slopes of the two decay curves. From the slope of the 290 K irradiation shown in Fig. 7 (not fully expanded in order that the decay curves for the two temperatures can be compared on a common abscissa), a cross section of $>3 \times 10^8$ bs was obtained ($1 \text{ b} = 10^{-24} \text{ cm}^2$). For the 85-K irradiation, a value of $\sim 10^6$ bs was determined.

Ionizing radiation has the effect of breaking the O-H bond with phenomenal efficiency. The enormous cross section for the RID appears to have no precedent. The mechanism by which the protons or deuterons are displaced from their sites unmistakably involves ionization (sometimes also referred to as photochemical or radiolysis) rather than elastic collisions. First, the cross section of 10^8 bs, and for that matter also 10^6 bs at 85 K, is far too large to be associated with elastic collisions. The theoretical cross sections for displacements by elastic collisions are of the order of a few bs for ~ 2.0 MeV electrons, and experimental cross sections are almost always much lower, because of annihilation by interstitial-vacancy recombinations. Secondly, subthreshold-energy x rays (20 kV peak) were also found capable of displacing the protons from their sites. Thirdly, irradiation with both low- and high-energy photons showed that there was no energy dependence in the decay of the 3296- cm^{-1} band. A cross section of 10^8 bs requires a displacement mechanism involving capture of secondary electrons or holes created by the incident electrons. (On the average, one electron-hole pair per 100 nm is created by each irradiating electron.). The strong temperature dependence of proton displacement is indicative of a thermally activated process of escape, probably involving a neutral hydrogen atom rather than a H^+

which would have to overcome a large Coulombic barrier. The availability of an abundance of electrons and holes makes it easy for the protons to frequently change their valence and thus avail them the opportunity to become hydrogen atoms. The subsequent migration to form precipitates is more likely in the form of protons than the neutral H atom.

5.2. Isotopic Effect

To compare the displacement probabilities, a MgO crystal containing both protons and deuterons was used.² The procedure involved heating a sample in a vapor containing D_2O and H_2O at 1450 K. The advantage of using one crystal is that the experimental conditions for displacement are *exactly identical* for protons and deuterons: irradiating temperature, beam intensity, and dose. For all intent purposes, the essential difference lies in the mass and the resulting mobility. Fig. 8(a) illustrates the infrared

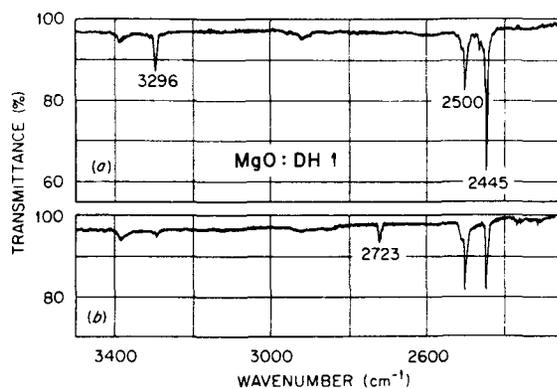


Fig. 8. Infrared absorption spectra of a quenched MgO crystal containing both protons and deuterons (a) before electron irradiation and (b) after electron irradiation to a dose of $4.4 \times 10^{16} \text{ e/cm}^2$.

absorption spectra after thermal quenching from 1450 K. Subsequent measurements were made after electron irradiations with different doses. Fig 8(b) shows the spectra after a cumulative dose of $1.8 \times 10^{17} \text{ e/cm}^2$. The normalized absorption coefficient for both the

3296 cm^{-1} band and its OD^- analogue at 2445 cm^{-1} is plotted against electron dose in Fig. 9. The decay of the OH^- is more rapid than the OD^- curve. Hence we conclude that the proton, because of its lower mass, is displaced more readily than the deuteron. Whereas the isotopic effect is minimal for thermal diffusion, for radiation induced diffusion, it is substantial.

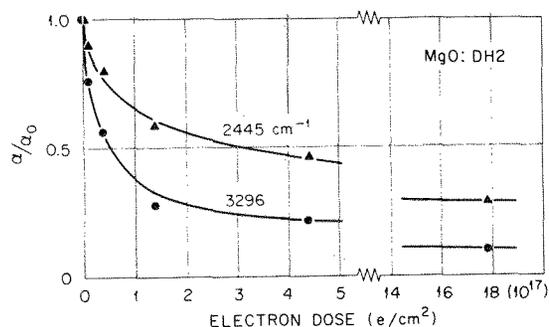


Fig. 9. Normalized decay of the 3296- and 2445-cm^{-1} bands in MgO under electron irradiation.

6. PROTON OUT-DIFFUSION: EFFECTS OF ENVIRONMENT

The hydrogenic species can be extracted efficiently from LiNbO_3 near room temperature by electron irradiation in vacuum.⁴ In contrast, this same effect is not observed when the irradiation is carried out in air. In undoped LiNbO_3 , the presence of hydrogen in the form of OH^- can be monitored by the absorption peak at 3480 cm^{-1} .¹⁸ In deuterated crystals the corresponding OD^- absorption appears at 2570 cm^{-1} . In order to unambiguously distinguish the outdiffusion from the indiffusion species, deuterons were used as the out-diffusing species. Prior to electron irradiation, the samples were

deuterated at 1273 K in flowing D_2O vapor for 30 mins. Electron irradiation at $T \sim 350\text{ K}$ produced a decrease in the OD^- absorption band. In Fig. 10 the logarithm of the OD^- absorbance at 2570 cm^{-1} is plotted against the electron dose. The exponential decrease is consistent with a process involving a constant interaction cross section. From the slope we estimate the effective cross section to be $\sim 10^6\text{ b}$. This enormous cross section indicates that the displacement of the deuterons is again due to an ionization rather than an elastic-collision process.

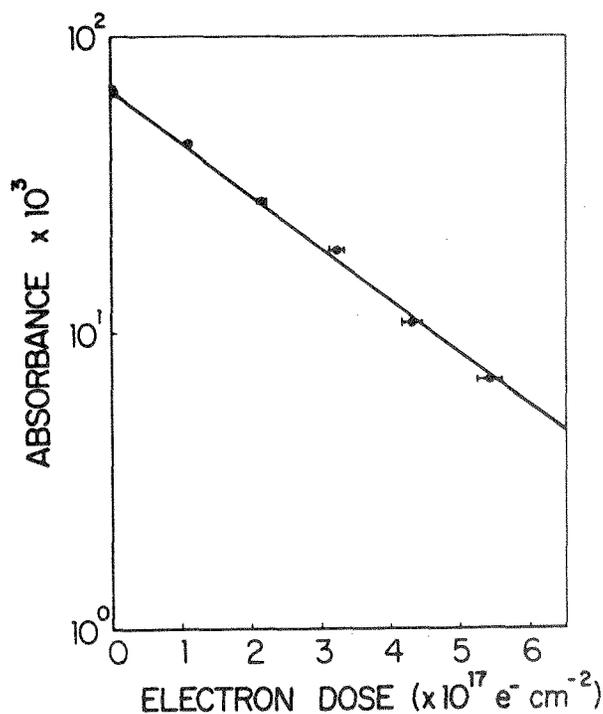


Fig. 10. Absorbance of the OD^- ions at the 2570 cm^{-1} band against electron dose at $T > 350\text{ K}$.

The same experiment was performed in air.⁴ In contrast, the irradiation produced no significant change in the deuteron concentration. These results emphasize the important role played by the surrounding atmosphere.

7. LOW-TEMPERATURE DIFFUSION: CHANNELING EFFECT

The presence of protons in crystalline oxides can sometimes be detrimental or beneficial for certain applications. Because ionizing radiation can break the OH⁻ bond efficiently, a method is devised to enhance diffusion of these species at unusually low temperatures.¹⁰ It has been shown that protons can be swept out of crystalline oxides⁵⁻⁹ at elevated temperature using an electric field. We now demonstrate that diffusion of deuterons and protons can be induced near room temperature by breaking the O-H bond with electron irradiation and sweeping these species by an applied electric field.

7.1. c_{\parallel} Direction

Rutile (TiO₂ crystal) was chosen¹⁰ for demonstration of the feasibility of proton (deuteron) diffusion at low temperatures

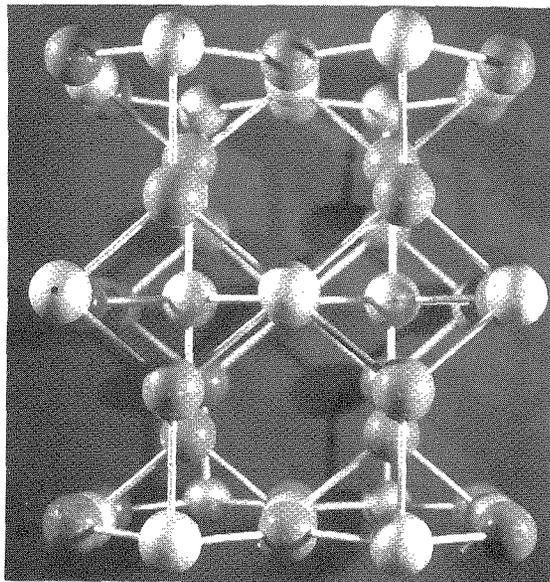


Fig. 11: Model of rutile looking into the c -direction.

enhanced by radiation- and electric-field induced diffusion (REID) because it possess a

large open channel for easy diffusion (see Fig. 11). The low activation energy for proton diffusion along the c axis (c_{\parallel} direction) makes it ideal for such a study. In the Arrhenius equation, $D = D_0 \exp(-E/kT)$, where D is the diffusion coefficient, and the activation energy E is 0.59 eV in the c_{\parallel} direction and 1.28 eV in the c_{\perp} direction.¹² The presence of protons and deuterons in TiO₂ was identified by OH⁻ and OD⁻ infrared absorption bands at 3277 and 2437 cm⁻¹ respectively. Deuterons were used as the diffusing species in order to distinguish them from proton contaminations. Irradiations were carried out with 2.0 MeV electrons with the beam intensity maintained at 8-9 mA/cm². The sample temperature was 340 K, and the electric field was 2000 V/cm. Fig. 12(a) shows the spectrum of a c_{\parallel} crystal prior to REID. The

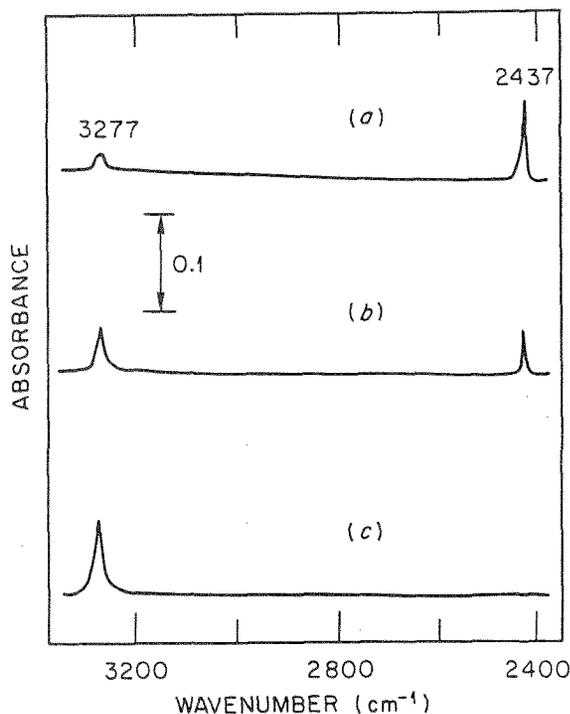


Fig. 12: Infrared absorption spectra of a c_{\parallel} TiO₂ crystal (a) after deuteration in D₂O for 3 h at ~1200 K, and subsequent irradiation with electrons with an applied field of 2000 V/cm for (b) 1 h, and (c) 2 h.

crystal contained primarily OD^- and very little OH^- ions. After REID for 1 h, the crystal exhibited the spectrum shown in Fig. 12(b). Approximately half the deuterons had been swept out and replaced by protons, presumably because of in-diffusion from the electrical contacts and/or atmosphere. After another hour of REID, virtually all the deuterons were removed and replaced by protons, shown in Fig. 12(c). Hence under this condition, out-diffusion of deuterons occurred at the effective rate of about 0.5 mm/h.

7.2. c_{\perp} Direction

The same experiment was carried out in a c_{\perp} direction. Some loss of OD^- absorbance was observed, but the out-diffusion rate was less than 5% of that in the c_{\parallel} direction.¹⁰

7.3. Temperature Dependence

REID of deuterons in another c_{\parallel} sample was performed under identical conditions except the temperature was 50 K higher - at 390 K.¹⁰ The rate of D^+ removal was twice as fast. There was one other notable difference: The deuterons were not replaced by protons. A profile of the OD^- concentrations was performed along the thickness of a crystal after 80% of the deuterons had been removed. Consecutive 0.1-mm increments were removed from the cathode side by polishing. The results showed unambiguously that deuterons were concentrated near the cathode, indicating that the deuterons migrated toward the negative electrode.

7.4. Electric Field Effect

Electric field dependence of REID on D^+ out-diffusion was performed.¹⁰ Several c_{\parallel} samples were irradiated at 360 K for 30 mins each. The results are plotted in Fig. 13. A strong electric field dependence was observed.

Field strength less than 1000 V/cm were not very effective in enhancing D^+ out-diffusion.

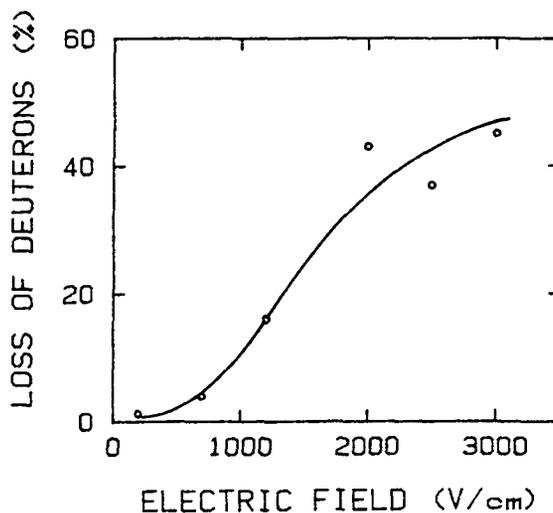


Fig. 13. Loss of OD^- absorbance (in percent) vs electric field strength. Each sample was irradiated for 30 min.

8.0 HYDRIDE IONS

The above discussions address protons substituting for indigenous cations. We shall now discuss hydride ions in MgO and the radiation induced diffusion of hydride ions.³ An H^- ion, or hydride ion, consists of a proton with two electrons occupying an oxygen-vacancy site, which therefore has a net positive charge.²¹ As such, it can trap a transient electron.

8.1 Production and Properties

Hydride ions in MgO are produced by a process, referred to as thermochemical reduction, at high temperatures and high pressure: $T > 2000$ K under ~ 7 atmospheres of magnesium vapor in a tantalum vessel.²¹ This process produces anion (oxygen) vacancies, due to a stoichiometric excess of cations. If

hydrogen impurities are present in the crystals (and they almost always do, to a greater or lesser extent), some are trapped at these vacancies, forming H^- ions. The more hydrogen the crystals contain, the more H^- ions are formed. These ions are identified by sharp absorption lines in the low-energy infrared spectrum which can be attributed to the fundamental vibrations of substitutional H^- ions. At 295 K the peaks occur at 1053, 1032, and 1024 cm^{-1} .²¹ The intensity of this three-line spectrum is correlated with the hydrogen content in the crystal and the thermochemical reduction temperature. The H^- ions are extremely stable: whereas the anion vacancies produced by thermochemical reduction begin to be unstable at 1500 K, the hydride ions do not vanish even at 1900 K.

8.2 Radiation Induced Diffusion

Ionizing radiation displaces protons from H^- sites with a cross section comparable to that from substitutional cation sites.³ Electron irradiations were performed on a thermochemically reduced MgO crystal 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 infrared spectra are shown in Fig. 14. The irradiation produced three prominent effects: (1) creation of new anion vacancies, (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 process which involves the displacement of protons in the H^- configuration and their relocation elsewhere in the crystal as OH^- ions. Using the initial slope of a curve plotting anion vacancy concentration versus electron dose, a cross section of $\sim 1 \times 10^8$ b is obtained. A cross section of this magnitude is uniquely characteristic of a radiation induced displacement of protons (or deuterons), albeit in this case from anion sublattice sites.

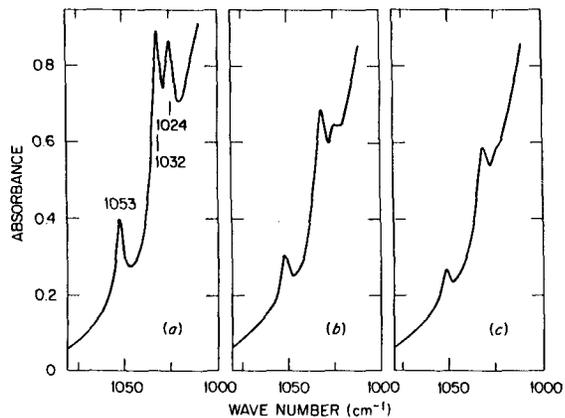


Fig. 14. Infrared spectra for H^- ions prior to electron irradiation (curve a) and after electron irradiation with cumulative doses of 5×10^{16} (curve b) and 2×10^{17} e/cm^2 (curve c).

9.0 CONCLUDING REMARKS

Protons and deuterons normally form thermally stable configurations in oxide crystals near room temperature and diffuse out of the crystals only at high temperatures; these temperatures are usually several hundred degrees above room temperature. However, under electron irradiation they become highly unstable at temperatures as low as 85 K; even at this low temperature they are quite mobile. The mechanism by which the hydrogenic species are displaced from their sites unmistakably involves ionization rather than elastic collisions. The cross section of 10^8 b is far too large (by several orders of magnitude) to be associated with a knock-on mechanism. Furthermore, a cross section of this magnitude requires a displacement (or diffusion) mechanism involving capture of secondary electrons or holes created by the primary electrons. On the average, one electron-hole pair per 100 nm is created by each primary electron. The strong temperature

dependence of hydrogen displacement indicates a thermally activated process of escape, probably involving a neutral hydrogen atom rather than a H^+ which would have to overcome a large Coulomb barrier. The subsequent migration to aggregate at precipitates is more likely in the form of protons rather than the neutral H atom.

Out-diffusion can be achieved efficiently in rutile (TiO_2) near room temperature by breaking the O-H (or O-D) bond during electron irradiation and subsequently sweeping out the protons or deuterons along the c axis by means of an applied electric field. On the basis of the present work, it is proposed that diffusion of protons (and perhaps even other light impurity ions) can be induced in other oxides with the use of radiation and electric-field induced diffusion. This method can have the important advantage of controlling such diffusion in materials which cannot be exposed to elevated temperatures without structural complications, such as phase change, dislocations, grain boundaries, precipitation of impurities, or change of stoichiometry. Furthermore, radiation induced diffusion of deuterons and tritons has important implications in advanced energy systems.

ACKNOWLEDGEMENTS

Research sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract no. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. One of us (RG) gratefully acknowledges the support of the Comision Interministerial de Ciencia y Tecnologia (CICYT) of Spain.

REFERENCES

1. Y. Chen, M. M. Abraham, and L. C. Templeton, *J. of Am. Ceram. Soc.* **60**, 101 (1977).
2. Y. Chen, M. M. Abraham, and H. T. Tohver, *Phys. Rev. Lett.* **26**, 1757 (1976).
3. Y. Chen, R. Gonzalez, O. E. Schow, and G. P. Summers, *Phys. Rev.* **B 27**, 1276 (1983).
4. R. Gonzalez, E. R. Hodgson, C. Ballesteros, and Y. Chen, *Phys. Rev. Lett.* **67**, 2057 (1991).
5. J. C. King and H. H. Sander, *IEEE Trans. Nucl. Sci.* **19**, 23 (1972).
6. S. P. Doherty, J. J. Martin, A. F. Armington, and R.N.Brown, *J. Appl. Phys.* **51**, 4164 (1980).
7. R. Gonzalez, Y. Chen, and K. L. Tsang, *Phys. Rev.* **B 26**, 4637 (1982).
8. R. Gonzalez, Y. Chen, and K. L. Tsang, and G. P. Summers, *Appl. Phys. Lett.* **41**, 739 (1982).
9. R. Gonzalez, R. Hantehzadeh, C. Y. Chen, L. E. Halliburton, and Y. Chen, *Phys. Rev. B* **39**, 1302 (1989).
10. Y. Chen, R. Gonzalez, and K. L. Tsang, *Phys. Rev. Lett.* **53**, 1077 (1984).
11. J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford 1956).
12. O. W. Johnson, S. H. Paek, and J. W. deFord, *J. Appl. Phys.* **46**, 1026 (1975).
13. B. Henderson and W. A. Sibley, *J. Chem. Phys.* **55**, 1276 (1971).
14. A. Briggs, Ph.D. theses, University of Bradford, 1970 (unpublished); A. Briggs, *J. Mater. Sci.* **10**, 729 (1975).
15. J. Volkl and G. Alefeld, in *Hydrogen in Metals I*, edited by J. Volkl and G. Alefeld (Springer, Berlin, 1978).
16. E. Gorham-Bergeron, *Phys. Rev. Lett.* **37**, 146 (1976).
17. A. M. Stoneham, *J. Nucl. Mat.* **69-70**, 109 (1978).
18. R. G. Smith, D. B. Fraser, R. T. Denton, and T. C. Rich, *J. Appl. Phys.* **39**, 4600 (1968).
19. R. Gonzalez, Y. Chen, and M. M. Abraham, *Phys. Rev.* **B 37**, 6433 (1988).
20. R. Gonzalez, C. Ballesteros, Y. Chen and M. M. Abraham, *Phys. Rev.* **B 39**, 11085 (1989).
21. R. Gonzalez, Y. Chen, and M. M. Mostoller, *Phys. Rev.* **B 24**, 6862 (1981).

Yok Chen, a research scientist in the Solid State Division at the Oak Ridge National Laboratory since 1965, also serves as a program manager in the Office of Basic Energy Sciences at the U.S. Department of Energy in Washington D. C. on a half-time basis. He has a bachelor's degree in chemistry from the University of Wisconsin-Madison, and a Ph.D. degree in physics from Purdue University in 1965. He is a member of the MRS, ASMI, TMS, and a fellow of the APS, and A Cer S. He was a co-winner of an I.R.-100 award for one of the most important inventions for 1972, and again in 1985. His interests are in the areas of optical, electrical, and mechanical properties of oxides, with particular emphasis on fusion and laser materials.

