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## THE MECHANISMS FOR SELF-DIFFUSION IN MAGNESIUM OXIDE

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### ABSTRACT

Measurements of ionic electrical conductivity and cation self-diffusion, as well as theoretical evaluation of energies for defect formation and migration, suggest that cation transport in MgO occurs by an extrinsic vacancy mechanism. The activation energy measured for anion self-diffusion, however, is incompatible with the theoretically-estimated values for any likely mechanism. In attempts to identify the mechanism for anion transport we have shown that oxygen self-diffusion is essentially independent of  $P_{O_2}$  between  $3 \cdot 10^{-11}$  and 20 kPa. Measurement of the isotope effect for  $^{17}O$ ,  $^{18}O$  diffusion provides a correlation coefficient close to unity, and anion self-diffusion coefficients increase with  $Sc^{3+}$  concentration in doped single crystals. The results are consistent with an interstitial mechanism for anion diffusion.

### INTRODUCTION

Diffusion has likely been studied more extensively in MgO than in any other stoichiometric oxide. Single crystals prepared by arc fusion have long been available. They are, however, of marginal purity, typically containing at least several hundred ppm impurity. As MgO is isostructural with the majority of the alkali halides, it would seem to be a model oxide to which understanding of these simpler ionic solids might be extended. Anion and cation self-diffusion rates have thus been measured by a number of investigators, and, as summarized elsewhere (1), diffusion rates for 14 different impurity cations have been measured.

Measurements by early workers were not in good agreement. Experience in the preparation of specimens, as well as new analytical probes for the measurement of

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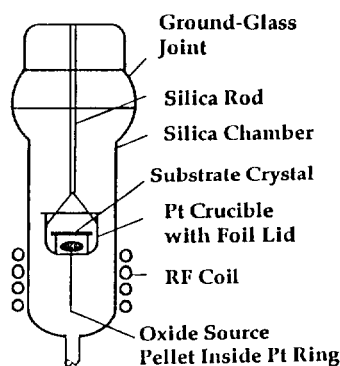
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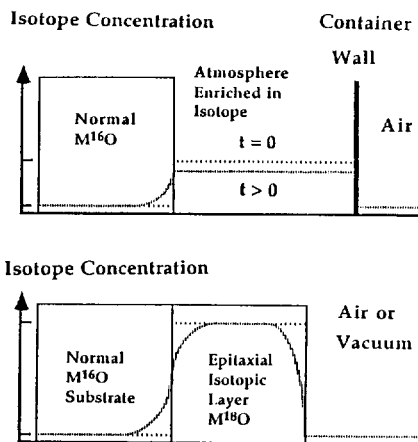
concentration gradients, have led to the convergence of both theory (2-4) and experiment to similar activation energies for cation transport in recent years. Cation transport, as will be briefly summarized below, appears to proceed via an extrinsic vacancy mechanism at temperatures up to the melting point of 2800°C. Anion self-diffusion measurements are in less good agreement, and even more recent reliable measurements performed over a much wider range of temperatures lead to diffusion parameters that do not satisfactorily agree with those provided by theory for any obvious mechanism. The present paper summarizes recent unpublished experiments on oxygen transport in MgO that are consistent with an interstitial mechanism rather than the vacancy process that one would intuitively anticipate for a material with the close-packed rocksalt structure type.

## EXPERIMENTAL

The anion self-diffusion experiments performed in the present studies were facilitated by a unique type of specimen prepared with the aid of chemical vapor transport. The procedure, originally developed by Gruber (5), was adapted for the present work by Yoo (6). A more permanent apparatus was subsequently constructed by Semken (7). In the device, Fig. 1a, a pellet of source oxide in a Pt crucible is surrounded by a Pt ring that supports an MgO host crystal a millimeter or two above the surface of the source pellet.



(a)



(b)

Figure 1. Growth of single-crystal diffusion specimens and the nature of the concentration gradients produced by subsequent annealing. (a) CVT chamber for growth of epitaxial layers of isotopic MgO through transport with HCl carrier. (b) Comparison of gradient produced in the conventional exchange experiment (in which isotopic  $^{18}\text{O}_2$  in a closed vessel is diffused into a crystal of normal  $\text{Mg}^{16}\text{O}$ ) with, below, the present experiments in which  $^{18}\text{O}$  is diffused out of an epitaxial single-crystal layer of  $\text{Mg}^{18}\text{O}$  into air or an atmosphere of reduced  $\text{PO}_2$ . Note, also, the presence of a second gradient for solid-solid interdiffusion between the epitaxial layer and substrate crystal.

The assembly is suspended in a silicic acid atmosphere of gaseous HCl. The platinum component is supported by a generator. A small temperature gradient is created, in part, by asymmetric placement of the Pt crucible and, likely in part, because the Pt ring is a crystal that forms one side of the specimen. The rate is proportional to the source-substrate distance. Rates up to 100  $\mu\text{m}$  per hour are achieved with the single-crystal substrate and has characteristic features of the material. Mechanical perfection is maintained, and dislocations present in the substrate grow

Isotopically-labeled source pellets may be obtained by oxidizing high-purity magnesium metal (0.204% natural abundance),  $^{17}\text{O}$  (0.038% natural abundance). Such pellets may be used for efficient growth of isotopically-labeled single-crystal layers. The substrate crystal is maintained at 1000°C during the 20 minutes required for growth of the specimen. The unique aspects of such a specimen were investigated by measurement of oxygen self diffusion rates maintained at a constant concentration by an annealing of duration  $t$  is given by

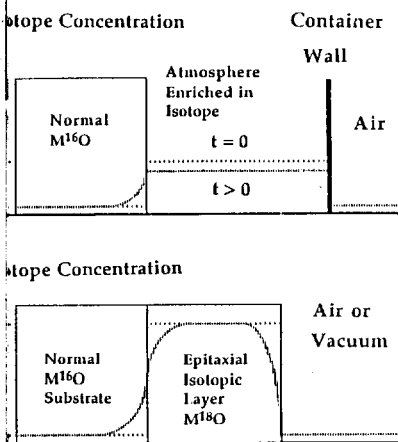
$$[C(18) - C_0(18)] = [C_s(18) - C_0(18)] \text{erfc} \left( \frac{x}{\sqrt{Dt}} \right)$$

where  $C_0(18)$  is the uniform atomic fraction of  $^{18}\text{O}$  in the substrate crystal,  $C(18)$  is the concentration at a distance  $x$  from the surface;  $\text{erfc}$  is the complementary error function. Measurement of diffusion rates as a function of time and reduction of the oxygen pressure reduce the concentration to unmeasurable levels. In contrast, the concentration of  $^{18}\text{O}$  in the atmosphere is reduced to heat the isotopically-labeled epitaxial layer to the desired partial pressure. The concentration of  $^{18}\text{O}$  in the atmosphere at any partial pressure of normal  $^{16}\text{O}_2$  is given by  $C(18) \approx [1 - C(16)]$  to an expression in which  $\text{erf}$  replaces  $\text{erfc}$  in the above gradient for measurement upon conclusion of the experiment. The gradient between the epitaxial isotopic layer and substrate crystal is the solid-state interdiffusion that occurs between the substrate crystal. Comparison of the concentration profiles of the distinct gradients provided a basis for the measurement of surface gradient was free from the possibility of surface flaws.

Concentration gradients of the isotopic oxygen were measured in the present studies by a Model IX705 ion microprobe. A 10 keV

vergence of both theory (2-4) and on transport in recent years. Cation appears to proceed via an extrinsic melting point of 2800°C. Anion self-ment, and even more recent reliable nge of temperatures lead to diffusion n those provided by theory for any es recent unpublished experiments on ith an interstitial mechanism rather rely anticipate for a material with the

in the present studies were facilitated aid of chemical vapor transport. The s adapted for the present work by Yoo tly constructed by Semken (7). In the ucible is surrounded by a Pt ring that above the surface of the source pellet.



(b)

n specimens and the nature of the annealing. (a) CVT chamber for growth n transport with HCl carrier. (b) ational exchange experiment (in which crystal of normal Mg<sup>16</sup>O) with, below, sed out of an epitaxial single-crystal aced PO<sub>2</sub>. Note, also, the presence of a between the epitaxial layer and substrate

The assembly is suspended in a silica chamber, which encloses the transport agent, gaseous HCl. The platinum components are heated by external coils connected to an RF generator. A small temperature gradient exists between source pellet and host crystal, created, in part, by asymmetric placement of the RF heating coils relative to the Pt crucible and, likely in part, because thermal radiation is transmitted through the MgO crystal that forms one side of the cavity. As the transport rate is inversely proportional to the source-substrate distance, rapid deposition of material occurs. Rates up to 100 μm per hour are achieved. The deposited material grows epitaxially on the single-crystal substrate and has chemical purity equal to, or superior to, the source material. Mechanical perfection is also improved as it has been found (5) that dislocations present in the substrate grow out during the first few μm of growth.

Isotopically-labeled source pellets may be prepared by cold-pressing the powder obtained by oxidizing high-purity magnesium ribbon in an atmosphere consisting of <sup>18</sup>O (0.204% natural abundance), <sup>17</sup>O (0.037% natural abundance) or a mixture of the two. Such pellets may be used for efficient and repeated deposition of an epitaxial isotopically-labeled single-crystal layer on the surface of the host crystal. The substrate crystal is maintained at 1000°C so that negligible interdiffusion occurs during the 20 minutes required for growth of a 30 μm isotopic layer. Figure 1b compares the unique aspects of such a specimen with the conventional exchange experiment for measurement of oxygen self diffusion. In the latter, the surface of the specimen is maintained at a constant concentration of <sup>18</sup>O, C<sub>S</sub>(18). The distribution of solute after an annealing of duration t is given by

$$[C(18) - C_0(18)] = [C_S(18) - C_0(18)] \operatorname{erfc} [x(4Dt)^{-1/2}] \quad (1)$$

where C<sub>0</sub>(18) is the uniform atomic fraction of Mg<sup>18</sup>O naturally present in the sample, C(18) is the concentration at a distance x into the sample, and D is the diffusion coefficient; erfc is the complementary Gaussian error function, equal to (1-erf). Measurement of diffusion rates as a function of oxygen partial pressure is difficult as reduction of the oxygen pressure reduces the surface concentration C<sub>S</sub>(18) to small, unmeasurable levels. In contrast, the configuration of the present specimen permits one to heat the isotopically-labeled epitaxial layer in air, vacuum, or an ambient of any desired partial pressure. The concentration of <sup>18</sup>O at the surface remains essentially 0 at any partial pressure of normal <sup>16</sup>O. As <sup>18</sup>O rather than <sup>16</sup>O diffuses out of the specimen, and because C(18) ≈ [1 - C(16)], the distribution of tracer changes from Eq.(1) to an expression in which erf replaces erfc. The specimen provides two concentration gradients for measurement upon conclusion of a diffusion annealing. The first is the gradient between the expitaxial isotopic layer and the ambient atmosphere; the second is the solid-state interdiffusion that occurs between the epitaxial deposit and the substrate crystal. Comparison of the diffusion coefficients obtained from the two distinct gradients provided a basis for establishing that the more easily measured surface gradient was free from the possible influence of a surface reaction or exchange with surface flaws.

Concentration gradients of the isotopic oxygen in the annealed single-crystal specimens were measured in the present studies by secondary-ion mass spectrometry using a VG Model IX70S ion microprobe. A 10 keV <sup>133</sup>Cs<sup>+</sup> primary ion beam with total current of

1.0 nA was used in the majority of the analyses. The primary beam was rastered over a 56 x 56 micron square on the sample surface. The secondary ion signal was electronically gated to the central 10% of the rastered area in order to eliminate signals from the walls of the sputtered crater. Plots of the inverse error function of  $[C(18) - C_0(18)]/[C_s(18) - C_0(18)]$  varied linearly with sputtering time and with slopes that provided a relative value of D to within 1%. An uncertainty of  $\pm 25\%$  was introduced in converting from sputtering time to depth as the ease with which MgO hydrates made measurement of pit depths difficult.

### CATION SELF-DIFFUSION AND IONIC CONDUCTIVITY

The first studies of cation self-diffusion in magnesium oxide (8-10) employed  $^{28}\text{Mg}$  as tracer. Although it is the longest-lived radioisotope of magnesium, its half-life is only 21.3 hours (decaying to  $^{28}\text{Al}$  which, in turn, decays with a half-life of 2.3 minutes to stable  $^{28}\text{Si}$ ). These results appeared to have been influenced by impurity carried by the tracer, by virtue of the fact that dilution of the tracer (10) reduced the magnitude of the observed diffusion coefficient. Wuensch, Steele, and Vasilos (11) avoided the problems associated with the use of short-lived  $^{28}\text{Mg}$  through use of the stable isotope  $^{26}\text{Mg}$  (11.17% natural abundance) as a tracer. The results are compared in Figure 2a. Hints of structure in the plot of the radiotracer data suggest regions representing intrinsic diffusion, extrinsic diffusion, and impurity precipitation. The results obtained with the stable isotope may be fit satisfactorily by a single Arrhenius plot over a

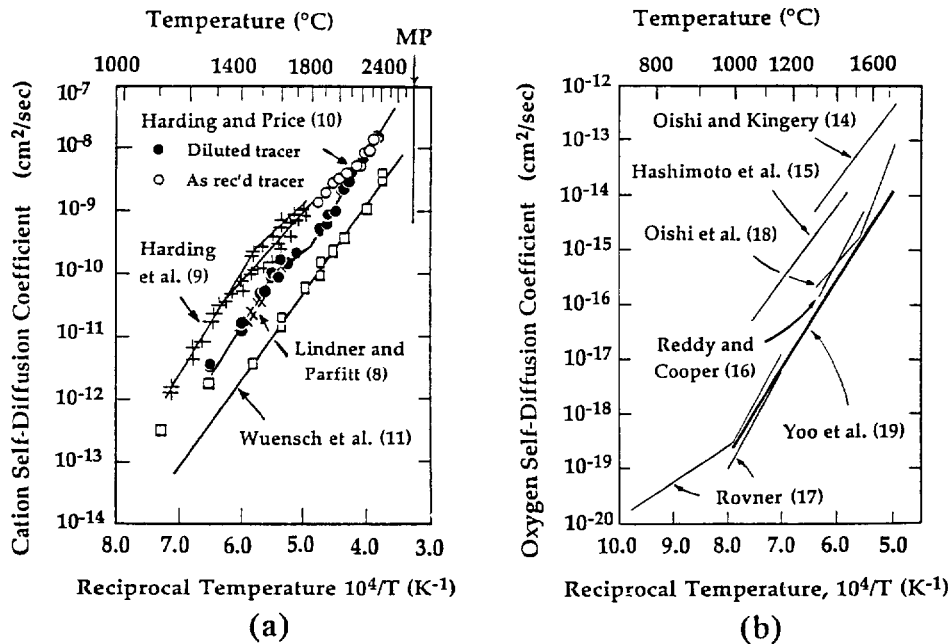


Figure 2. Self-diffusion coefficients in single-crystal MgO as a function of reciprocal temperature. (a) Cation self-diffusion. (b) Anion self-diffusion.

Table 1. Measured and Theoretical Energies

Process	Theoretical	
	Enthalpy (eV)	Ref. (2)
Frenkel Pair Formation	15.2	
Schottky Pair Formation, $H_s$	7.5	7.5
Cation Vacancy Migration, $H_m^+$	2.16	2.16
Anion Vacancy Migration, $H_m^-$	2.38	2.38
Cation-Anion Divacancy Formation, $H_a$	-2.55	
Divacancy Migration(20), $H_m^+ = H_m^-$		
Extrinsic Anion Vacancy Migration (Cation Impurity Dominant), $H_m + H_s$	9.88	9.88
Migration of Divacancy (Cation Impurity Dominant) $H_a + H_m^+ + H_s$	7.33	

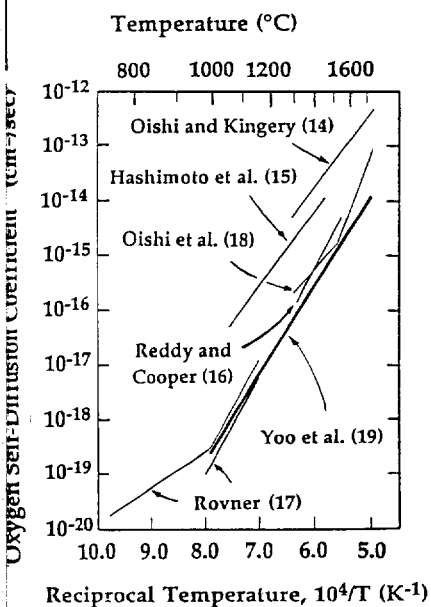
temperature range 1400-2400°C. The data can be fit with a single line, providing a comparison with the theoretical values.

The electrical conductivity of MgO has been measured with considerable disagreement. The measured values and electronic transport numbers depend on oxygen partial pressure. The separate measurement of the ionic portion of the conductivity was almost simultaneously by Duclot and Dreyfus. In the latter study, crystals were intentionally doped with valence in concentrations sufficient for the formation of a vacancy to be the dominant point defect. The relationship with the Nernst-Einstein relation was used to determine the cation self-diffusion coefficients if an assumption that the concentration of oxygen vacancies is assumed. Concentrations of oxygen vacancies were 1000 ppm (11); 1000 ppm (10). The activation energies for cation self-diffusion are 2.29 eV (13), in excellent agreement with the theoretical value for vacancy migration (Table 1). The activation energy is comparable, but somewhat higher by a factor of 1.5, by experimental uncertainty. It is interesting to note that adjacent to an impurity cation, theory predicts an activation energy of 2.16 eV, essentially independent of the nature of the impurity.

The primary beam was rastered over a secondary ion signal was electronically in order to eliminate signals from the inverse error function of [C(18) - sputtering time and with slopes that uncertainty of  $\pm 25\%$  was introduced in ease with which MgO hydrates made

## DUCTIVITY

esium oxide (8-10) employed  $^{28}\text{Mg}$  as isotope of magnesium, its half-life is only decays with a half-life of 2.3 minutes to n influenced by impurity carried by the tracer (10) reduced the magnitude of the and Vasilos (11) avoided the problems through use of the stable isotope  $^{26}\text{Mg}$  lts are compared in Figure 2a. Hints of suggest regions representing intrinsic precipitation. The results obtained with by a single Arrhenius plot over a



(b)

ystal MgO as a function of reciprocal Anion self-diffusion.

Table 1. Measured and Theoretical Energies for Diffusion and Defect Formation in MgO

Theoretical		Experimental	
Process	Enthalpy (eV) Ref. (2) Ref. (3)	Process	Energy(eV)
Frenkel Pair Formation	15.2		
Schottky Pair Formation, $H_s$	7.5 7.2		
Cation Vacancy Migration, $H_m^+$	2.16 2.07	Cation Self-Diffusion(11)	2.76 $\pm$ 0.08
Anion Vacancy Migration, $H_m^-$	2.38 2.11	Ionic Conductivity(12,13)	2.2, 2.29 $\pm$ 0.21
Cation-Anion Divacancy Formation, $H_a$	-2.55	Anion Self-Diffusion(19)	3.24 $\pm$ 0.13
Divacancy Migration(20), $H_m^+ = H_m^-$			
Extrinsic Anion Vacancy Migration (Cation Impurity Dominant), $H_m^+ + H_s$	9.88 9.83		
Migration of Divacancy (Cation Impurity Dominant) $H_a + H_m^+ + H_s$	7.33		

temperature range 1400-2400°C. The data of Harding and Price may be satisfactorily fit with a single line, providing a comparable activation energy.

The electrical conductivity of MgO has been examined in well over a dozen studies, with considerable disagreement. The material is a mixed conductor in which the ionic and electronic transport numbers depend in a complex way on purity, temperature, and oxygen partial pressure. The separation of the two components, and reliable measurement of the ionic portion of the conductivity was performed independently and almost simultaneously by Duclot and Deportes (12) and Sempolinski and Kingery (13). In the latter study, crystals were intentionally doped with trivalent ions of fixed valence in concentrations sufficient for these species and their charge compensating vacancy to be the dominant point defect. The vacancy diffusion coefficient calculated with the Nernst-Einstein relation was found to predict the magnitudes of the measured cation self-diffusion coefficients if an appropriate concentration of extrinsic cation vacancies is assumed. Concentrations of 100 and 200 ppm provide lines that bracket the results of Wuensch et. al. (11); 1000 ppm provides agreement with the data of Harding and Price (10). The activation energies found for ionic conduction are 2.2 eV (12) and 2.29 eV (13), in excellent agreement with the theoretical values estimated by cation vacancy migration (Table 1). The activation energy for cation self-diffusion (11) is comparable, but somewhat higher by an amount, ca. 0.5 eV, which seems outside experimental uncertainty. It is interesting to note that, for a jump by a cation adjacent to an impurity cation, theory (4) provides an enthalpy of motion of 2.7 to 2.8 eV, essentially independent of the nature of the impurity. Although the agreement

with the measured activation energy for cation self-diffusion is excellent, it may be fortuitous as it is difficult to reconcile the fact that ionic conduction in specimens much more heavily doped with  $\text{Sc}^{3+}$  (13) provides an activation energy that closely corresponds to that calculated for motion of an isolated cation vacancy. Nevertheless, in spite of this remaining higher-order puzzle, the general agreement between the experimental values for the activation energy for cation self-diffusion and ionic conductivity, on the one hand, with the theoretical enthalpies for cation vacancy migration, combined with the agreement between diffusivities directly measured with those calculated from conductivity with the aid of the Nernst-Einstein relation, make a convincing case for the conclusion that cation migration proceeds by a vacancy mechanism and that the vacancy concentration is fixed by accidental impurities. Indeed, the high enthalpy calculated for the formation of Schottky vacancy pairs suggests that on the order of one ppm of aliovalent cation impurity would be sufficient to cause cation transport in MgO to be extrinsic at all temperatures up to its melting temperature of 2800°C.

#### OXYGEN SELF-DIFFUSION

A number of direct measurements of oxygen diffusion in MgO have been performed, the great majority using gas exchange methods. The various activation energies for diffusion that are provided by these experiments are not in especially good agreement with either theory or each other. The magnitude of the diffusion coefficients that have been measured at a particular temperature vary by more than two orders of magnitude. Such variation, however, would not be unexpected if transport occurred by an extrinsic mechanism controlled by impurity.

At least part of the reason for the difference among the reported activation energies lies in the small temperature range over which exchange experiments may be performed. The range of temperatures does not exceed 450°C in any exchange experiment that has been reported, and the range often is as small as 200°C. Through study of the diffusion of  $^{18}\text{O}$  out of the epitaxial single-crystal layers of  $\text{Mg}^{18}\text{O}$  described above, we were recently able (19) to perform reliable measurements over a temperature range of 1000-1650°C. The results are shown in Fig. 2b as a bold line. There is fair agreement with the more recent of these measurements in terms of the magnitudes of the diffusion coefficients that were measured, and significant difference only with early measurements in which the possibility of enhanced diffusion along the dislocations in crushed powder samples was not appreciated. The activation energy obtained in our recent work,  $3.24 \pm 0.13$  eV is squarely in the middle of the range of values previously reported. It is very difficult to explain this value in terms of the theoretical estimates of energies relevant to the defect structure of MgO. Table 1 shows that the value is clearly incompatible with an intrinsic vacancy diffusion mechanism or with extrinsic diffusion in a crystal whose defect structure is controlled by cation impurity. Mechanisms involving cation-anion vacancy association also lead to energies that differ from the experimental value by amounts that are far outside the range of experimental uncertainty.

It seems well established that cation self-diffusion in MgO proceeds by a vacancy mechanism and that the vacancy concentrations are determined by cation impurities. If

this is the case, and if Schottky concentrations and anion self-diffusion by an amount greater than the three measured anion and cation self-diffusion some defect other than an anion vacancy self-diffusion. The experiments describe the nature of this defect.

#### ANION DIFFUSION AS A FUNCTION

To determine the dependence of anion samples were annealed in air and in the of  $\text{CO}_2/\text{CO}$  mixtures in volume ratios pressures that ranged between approximately depending upon temperature. The anneal to three hours at 1500°C. The distributions established through SIM pressure in Fig. 3a. The data at 1400° measurements are presently being extended Uchikoba. The data provide no evidence oxygen partial pressure at temperatures to the data at 1400° and 1450°C provided respectively.) This would be the case if fixed by impurities. The data, however, defect. At 1500°C, the data suggest a

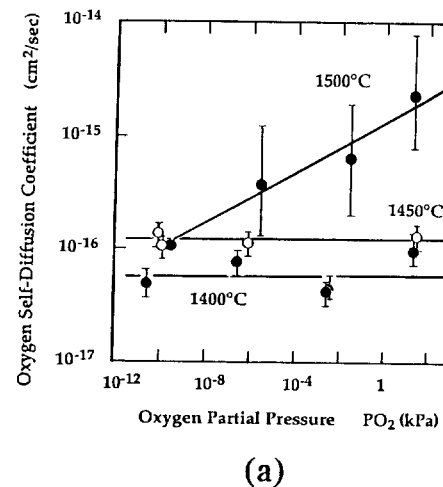


Figure 3. (a) Anion self-diffusion coefficient as a function of oxygen partial pressure. The slope of the line is  $0.11$ . (b) Anion self-diffusion in single-crystal MgO as a function of reciprocal temperature. The data are wt% in the source material from which

self-diffusion is excellent, it may be at ionic conduction in specimens much as an activation energy that closely isolated cation vacancy. Nevertheless, the general agreement between the theory for cation self-diffusion and ionic enthalpies for cation vacancy diffusivities directly measured with the Nernst-Einstein relation, make anion migration proceeds by a vacancy on is fixed by accidental impurities. The formation of Schottky vacancy pairs and cation impurity would be sufficient to account for the observed behavior at all temperatures up to its melting

diffusion in MgO have been performed, the various activation energies for anion diffusion are not in especially good agreement with the theoretical values. The magnitude of the diffusion coefficients that are measured vary by more than two orders of magnitude, which is unexpected if transport occurred by an intrinsic vacancy mechanism.

Among the reported activation energies for anion diffusion, which exchange experiments may be used to determine, none exceed 450°C in any exchange experiment often is as small as 200°C. Through the use of epitaxial single-crystal layers of  $Mg^{18}O$ , we can perform reliable measurements over a wide range of temperatures as shown in Fig. 2b as a bold line. These measurements in terms of the activation energy are shown in Fig. 2c. There is a significant difference between the values measured, and significant difference in the magnitude of the diffusion coefficients. The possibility of enhanced diffusion along the grain boundaries is not appreciated. The activation energy is approximately 1.5 eV, squarely in the middle of the range of values reported. It is difficult to explain this value in terms of the defect structure of MgO. Table 1 shows that the energy for an intrinsic vacancy diffusion mechanism is 1.5 eV. If the defect structure is controlled by cation vacancies, the energy for a vacancy association also lead to energies of activation that are far outside the range of values reported.

Anion diffusion in MgO proceeds by a vacancy mechanism. The activation energies are determined by cation impurities. If

this is the case, and if Schottky equilibrium is maintained, anion vacancy concentrations and anion self-diffusion coefficients should be depressed—and probably by an amount greater than the three orders of magnitude difference between the measured anion and cation self-diffusion coefficients. It seems likely, therefore, that some defect other than an anion vacancy might become the defect responsible for anion self-diffusion. The experiments described below were performed to provide insight into the nature of this defect.

#### ANION DIFFUSION AS A FUNCTION OF OXYGEN PARTIAL PRESSURE

To determine the dependence of anion self-diffusion rates on oxygen partial pressure, samples were annealed in air and in three increasingly reducing atmospheres consisting of  $CO_2/CO$  mixtures in volume ratios 100, 1, and 0.01. This provided oxygen partial pressures that ranged between approximately 22 and  $10^{-12}$  kPa, the precise limits depending upon temperature. The annealing conditions ranged from 72 hours at 1300°C to three hours at 1500°C. The diffusion coefficients evaluated from the  $^{18}O$  distributions established through SIMS are plotted as a function of oxygen partial pressure in Fig. 3a. The data at 1400° and 1450°C were obtained by Semken (7). The measurements are presently being extended to a broader range of temperatures by Uchikoba. The data provide no evidence for a dependence of diffusion coefficient upon oxygen partial pressure at temperatures below 1500°C. (Specifically, least-squares fit to the data at 1400° and 1450°C provide slopes of  $+0.006 \pm 0.02$  and  $+0.005 \pm 0.02$ , respectively.) This would be the case if point defect concentrations were dominated and fixed by impurities. The data, however, provide no insight into the nature of the point defect. At 1500°C, the data suggest a very slight increase of diffusivity with oxygen

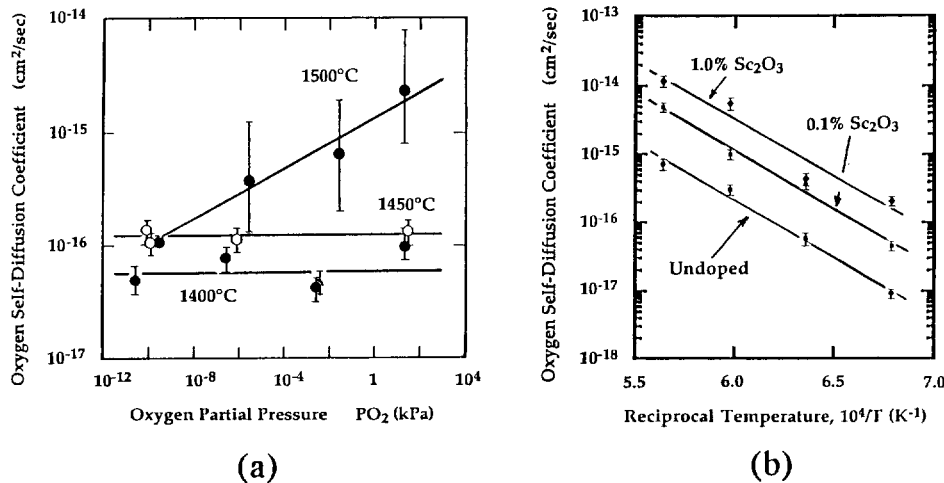


Figure 3. (a) Anion self-diffusion coefficients in single-crystal MgO as a function of oxygen partial pressure. The slope of the line fitted to the 1500°C data corresponds to a pressure dependence  $PO_2^{0.11}$ . (b) Anion self-diffusion coefficients in  $Sc^{3+}$ -doped single-crystal MgO as a function of reciprocal temperature. (The  $Sc_2O_3$  concentrations given are wt% in the source material from which the crystals were grown.)

partial pressure, the pressure dependence being on the order of  $PO_2^{0.1}$ .

### ISOTOPE EFFECT FOR ANION SELF-DIFFUSION

The two minor stable isotopes of oxygen,  $^{17}O$  and  $^{18}O$ , have different masses and, therefore, diffuse at different rates. The ratio of their diffusion coefficients can provide information on the correlation coefficient,  $f$ , according to the relation

$$f\Delta K = [1 - (D_{18}/D_{17})] / [1 - (M_{17}/M_{18})^{1/2}] \quad (2)$$

where  $M$  is the mass of the isotope;  $\Delta K$  is the fraction of the translational kinetic energy possessed by the diffusing atom at the saddle point of its jump and is thus less than unity. The quantity  $f\Delta K$  is therefore equivalent to a lower limit for the correlation factor which, in turn, is the quantity that relates tracer diffusion coefficient and self-diffusion coefficient, according to  $D_{\text{tracer}} = fD_{\text{self}}$ . For diffusion by means of vacancies distributed over a face-centered lattice (21), the value of  $f$  is 0.781. The diffusive jumps are independent of the array of sites for the case of diffusion by an interstitial mechanism and  $f$  therefore is unity. Eq. (2) shows that the isotope effect will be subtle,  $D_{17}/D_{18}$  being on the order of  $(M_{18}/M_{17})^{1/2}$  or, given the isotopic masses, 17.999 and 16.999, respectively, on the order of 1.029.

An attempt was made to measure the isotope effect for oxygen self-diffusion by preparing a single-crystal deposit from a source pellet produced by oxidizing magnesium ribbon in an atmosphere of 48%  $^{17}O_2$  and 42%  $^{18}O_2$  and using SIMS to measure the gradients for diffusion of both  $^{17}O$  and  $^{18}O$  out of the resulting deposit. As has been noted, the uncertainty in the absolute value of the diffusivities obtained in the present work is on the order of  $\pm 25\%$ , the predominant source of error arising from difficulty in correlating sputtering time in the SIMS instrument with the depth of the crater produced by the primary ion beam. This uncertainty cancels in measurement of gradients for two isotopes diffused simultaneously in the same specimen. Error is then predominantly determined by the uncertainty in the slope in the plot of the inverse error function of reduced concentration as a function of penetration (about 1% for each gradient). The  $^{17}O$  gradient is difficult to establish for  $MgO$ , however, because of the ease with which the material hydrates:  $^{16}OH$  thus makes a significant contribution to mass number 17 in the spectrum and creates artifacts, especially near the surface of the specimen. It is necessary, therefore, to work with materials of the greatest possible enrichment in  $^{17}O$ . Semken (7) analysed two different samples that had been prepared at  $1400^\circ C$  and obtained ratios  $D_{17}/D_{18} = 1.040$  and  $1.034$ , both values with an uncertainty of  $\pm 0.010$ . Adopting  $1.037 \pm 0.020$  as the average of the two results, Eq. (2) provides a value of  $f\Delta K$  of  $1.274 \pm 0.491$ . As  $f\Delta K$  cannot exceed unity, our experimental value is thus  $0.783 < f\Delta K < 1.0$ . The value, with its experimental uncertainty, lies just outside the value 0.781 for a vacancy mechanism. We have attempted measurement of the isotope effect at higher and lower temperatures. Unfortunately, isotopic gases with high  $^{17}O_2$  enrichment are not presently available, and the measurements that we have attempted with samples containing lower initial  $^{17}O$  concentration have been subject to higher errors as a result of  $^{16}OH$  interference. We obtain a value of  $f\Delta K$  of  $0.99 \pm 0.25$  at  $1200^\circ C$ , which again is consistent with an interstitial mechanism, but other determinations (e.g.,  $0.63 \pm 1.0$  at  $1300^\circ C$ ) carry standard deviations too large to

provide any information. An isotope effect has definitely been observed, and the results support an interstitial mechanism. Experiments are needed to absolutely exclude a vacancy mechanism.

### A MODEL FOR POINT DEFECT CONCENTRATIONS

The lack of any significant dependence of the diffusion coefficient on oxygen partial pressure suggests that the concentration of point defects is fixed by impurities. The material is heavily doped with such as  $Si^{4+}$  and  $Al^{3+}$ . These impurities are compensated by such as  $SiO_2 \rightarrow Si^{2+}Mg + 2OO + V^{2-}$  or  $Al^{3+}Mg + 3OO + V^{2-}$  vacancies (that clearly seem to control the concentration) in a relation such as

$$[V^{2-}] = [Mg^{2+}] + [Al^{3+}] - [Si^{4+}]$$

If Schottky equilibrium is maintained,

$$[V^{2-}] = [V^{2-}]_{\text{Schottky}}$$

and the elevated concentration  $[V^{2-}]$  of oxygen vacancies below levels that might be expected at equilibrium provides

$$[O^{2-}] = [V^{2-}] + [V^{2-}]_{\text{Schottky}}$$

Upon obtaining  $[V^{2-}]$  from Eq. (4) and substituting into Eq. (3)

$$[O^{2-}] = K_f/[V^{2-}] = K_f/[V^{2-}]_{\text{Schottky}} + [V^{2-}]_{\text{Schottky}}$$

The concentration of oxygen interstitials is  $[O^{2-}] = (H_f - H_s)/RT$  and the activation energy for oxygen diffusion thus be  $(H_f - H_s + H_m)$ . Anion self-diffusion in  $MgO$  that no impurity oxidized to higher valence state, both consistent with experiment. The concentration of oxygen diffusion should be proportional to the concentration of oxygen vacancies, providing a basis for an additional test of the interstitial mechanism.

### ANION SELF-DIFFUSION IN $Sc^{3+}$ -DO

Oxygen diffusion coefficients were determined for  $Sc^{3+}$  to examine the dependence of the diffusion coefficient on the concentration of aliovalent impurity that is the concentration of silicon. The experiments were carried out in the same fashion, except that  $Sc_2O_3$  was added to the source pellet. The results presents plots of oxygen self-diffusion coefficient versus temperature between  $1200^\circ$  and  $1500^\circ C$  for



in the order of  $PO_2^{0.1}$ .

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and  $^{18}O$ , have different masses and, so of their diffusion coefficients can be related, according to the relation

$$D_{18}/D_{16} = (M_{16}/M_{18})^{1/2} \quad (2)$$

The fraction of the translational kinetic energy at the saddle point of its jump and is thus less than equivalent to a lower limit for the factor  $f$  that relates tracer diffusion coefficient  $D_{tr} = fD_{self}$ . For diffusion by means of interstitials (21), the value of  $f$  is 0.781. The number of sites for the case of diffusion by an interstitial (Eq. (2) shows that the isotope effect is  $(M_{18}/M_{16})^{1/2}$  or, given the isotopic ratio of 1.029.

The effect for oxygen self-diffusion by a source pellet produced by oxidizing  $^{16}O_2$  and 42%  $^{18}O_2$  and using SIMS to analyze  $^{18}O$  out of the resulting deposit. As the value of the diffusivities obtained in the dominant source of error arising from the SIMS instrument with the depth of the analysis uncertainty cancels in measurement of the ratio of  $^{18}O$  to  $^{16}O$  in the same specimen. Error is then only in the slope in the plot of the inverse of the fraction of penetration (about 1% for each analysis) for MgO, however, because of the analysis thus makes a significant contribution to the artifacts, especially near the surface of the analysis with materials of the greatest possible analysis different samples that had been prepared with 1.040 and 1.034, both values with an error as the average of the two results, Eq. (2) cannot exceed unity, our experimental error with its experimental uncertainty, lies just in the error. We have attempted measurement of the error. Unfortunately, isotopic gases were not available, and the measurements that were made with initial  $^{17}O$  concentration have been of little reference. We obtain a value of  $fAK$  of about 1.0 with an interstitial mechanism, but the error bars carry standard deviations too large to

provide any information. An isotope effect of the correct magnitude has, however, definitely been observed, and the value of the correlation coefficients so obtained support an interstitial mechanism. Experimental uncertainty, however, does not allow one to absolutely exclude a vacancy mechanism.

#### A MODEL FOR POINT DEFECT CONCENTRATIONS

The lack of any significant dependence of anion self-diffusion in MgO on oxygen partial pressure suggests that the concentration of the defect that is responsible for transport is fixed by impurities. The material is known to be heavily doped with donor cations, such as  $Si^{4+}$  and  $Al^{3+}$ . These impurities must be charge-compensated by a mechanism such as  $SiO_2 \rightarrow Si^{''}Mg + 2O_O + V''Mg$ . This will fix the concentration of the cation vacancies (that clearly seem to control ionic conductivity and cation diffusion) by a relation such as

$$[V''Mg] = [Si^{''}Mg] \quad (3)$$

If Schottky equilibrium is maintained, then

$$[V''Mg][V''O] = K_s = \exp(-H_s/RT), \quad (4)$$

and the elevated concentration  $[V''Mg]$  will suppress the population of oxygen vacancies below levels that might contribute effectively to anion transport. Frenkel equilibrium provides

$$[O''_i][V''O] = K_f = \exp(-H_f/RT) \quad (5)$$

Upon obtaining  $[V''O]$  from Eq. (4) and substitution of Eq. (3), Eq. (5) provides

$$[O''_i] = K_f/[V''O] = K_f[V''Mg]/K_s = [Si^{''}Mg] K_f/K_s \quad (6)$$

The concentration of oxygen interstitials would thus vary with temperature as  $\exp(-(H_f - H_s)/RT)$  and the activation energy for diffusion via an interstitial mechanism would thus be  $(H_f - H_s + H_m)$ . Anion self-diffusion would be independent of  $PO_2$  (provided that no impurity oxidized to higher valence) and would have a correlation factor of unity, both consistent with experiment. Equation (6) further predicts that oxygen self-diffusion should be proportional to the concentration of aliovalent cation impurity, providing a basis for an additional test of the model.

#### ANION SELF-DIFFUSION IN $Sc^{3+}$ -DOPED MgO

Oxygen diffusion coefficients were determined for epitaxial layers of  $Mg^{18}O$  doped with  $Sc^{3+}$  to examine the dependence of anion self-diffusion coefficients on the concentration of aliovalent impurity that is analogous to Eq. (6),  $1/2 [ScMg^{3+}]$  replacing the concentration of silicon. The epitaxial layers were deposited in the normal fashion, except that  $Sc_2O_3$  was added to the isotopically-labeled source pellet. Fig. 3b presents plots of oxygen self-diffusion coefficients as a function of reciprocal temperature between 1200° and 1500°C for crystals grown from an undoped source pellet

and crystals grown from source material that contained 0.1 and 1.0 wt%  $\text{Sc}_2\text{O}_3$ . The anion self-diffusion coefficient was indeed found to increase as the amount of  $\text{Sc}^{3+}$  in the source material increases. We have yet to determine a precise value for the corresponding amount of  $\text{Sc}^{3+}$  contained in the epitaxial layers. The concentration is undoubtedly much smaller than that in the source pellet, but is difficult to measure given the low level of the dopant and the fact that the  $\text{Sc}^{3+}$  is confined to an epitaxial layer of but a few microns thickness. If one assumes that the concentration of dopant in the crystal is proportional to that contained in the deposit, the ratio of the magnitude of the diffusion coefficients in Fig. 3b at a given temperature is on the order of what would be predicted by Eq. (6). The activation energies of the fits to the data of Fig. 3b are 3.34, 3.38, and 3.28 eV, respectively, in order of increasing  $\text{Sc}^{3+}$  concentration. Given the narrower range of temperatures over which the data were obtained, the agreement with the value  $3.24 \pm 0.13$  eV of Yoo et al. (19) is excellent.

Thus, while cation self-diffusion and ionic electrical conductivity seem controlled by aliovalent cation vacancies, the absence of significant dependence of anion self-diffusivity on oxygen partial pressure, a correlation coefficient on the order of unity, and the fact that oxygen self-diffusion coefficients increase with increasing level of aliovalent cation dopant, are all consistent with anion self-diffusion proceeding via an interstitial-type mechanism. The activation energy for this process, namely  $(H_f - H_s + H_m)$  does not lead to very close agreement between experiment and values predicted by theoretical values for  $H_f$  and  $H_s$  in Table 1. These suggest a migration energy for the defect on the order of 7.7 eV, which is unacceptably large. Relatively little effort has been expended, however, on estimation of the enthalpy for Frenkel pair formation in MgO as the large magnitude of the estimate would seem to make this defect an unlikely candidate for a role in mass transport. A 30% reduction in the theoretical value for  $H_f$  would result in a more reasonable agreement between theory and experiment. Alternatively, an interstitialcy mechanism may be involved. A possible defect might be a peroxy center consisting of a pair of charged oxygen ion interstitials associated with an oxygen vacancy,  $(\text{O}_i^- - \text{V}_\text{O}^{2+} - \text{O}_i^-)^x$ . In this connection, the ability of the alkaline earth elements to form  $\text{MO}_2$  peroxides as stable compounds at low temperatures is worth noting.

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contained 0.1 and 1.0 wt% Sc<sub>2</sub>O<sub>3</sub>. The  $D$  is found to increase as the amount of Sc<sup>3+</sup> in the deposit increases. The concentration is difficult to measure in the surface pellet, but is difficult to measure at the Sc<sup>3+</sup> is confined to an epitaxial layer. It seems that the concentration of dopant in the deposit, the ratio of the magnitude of  $D$  at different temperatures is on the order of what would be expected from the energies of the fits to the data of Fig. 3b of increasing Sc<sup>3+</sup> concentration. Given the agreement of the data were obtained, the agreement is excellent.

Electrical conductivity seem controlled by the significant dependence of anion self-diffusion coefficient on the order of unity,  $D$  values increase with increasing level of Sc<sup>3+</sup>. Anion self-diffusion proceeding via an interstitial mechanism for this process, namely (H<sub>f</sub> - H<sub>s</sub>) between experiment and values predicted by these suggest a migration energy for the defect is probably large. Relatively little effort has been made to determine the enthalpy for Frenkel pair formation in MgO. It would seem to make this defect an unlikely mechanism for reduction in the theoretical value for H<sub>f</sub> - H<sub>s</sub> between theory and experiment. A possible defect might be oxygen ion interstitials associated with Sc<sup>3+</sup>. In this connection, the ability of the oxides as stable compounds at low

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