On the Interpretation of Lattice
Diffusion in Magnesium Oxide

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Abstract

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Magnesium oxide single crystals of greatly improved quality have recently become available, and techniques which permit preparation of diffusion specimens to temperatures as high as 2500°C have been developed. Data are available for cation and anion self-diffusion and tracer diffusion of 14 different impurity cations. Very different interpretations have been given these data.

Magnitudes of experimental diffusion coefficients are in fairly good agreement in the few cases in which ^{different} ~~several~~ investigators have examined a given system. In so far as examined, cation tracer diffusion coefficients appear to be independent of atmosphere. Recent theoretical estimates put the enthalpy for Schottky defect formation at 7 to 8 eV while the best MgO crystals of which present growth techniques are capable cannot display intrinsic behavior at any temperature below their melting point unless H_f is less than 6 eV. Interdiffusion coefficients known to be controlled by cation vacancies extrapolate smoothly to tracer values at zero concentration. It is therefore felt that there is strong evidence that the tracer-type diffusion data obtained to date represent extrinsic

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diffusion controlled by chemically-created vacancies, with energies of motion of the order of 2 eV. Alternative interpretations hinge on hints of structure in Arrhenius plots which may or may not be significant.

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1. Introduction

Diffusion has been more extensively studied in MgO than in any other oxide. Data have been reported for both anion and cation self-diffusion, for tracer-type diffusion of at least 14 different impurity cations, and for interdiffusion between MgO and another oxide in 8 different systems. The possibility of enhanced diffusion along grain boundaries and dislocations has also been examined.

A problem associated with the interpretation of ^{much} ~~the early~~ data for diffusion in MgO has been the lack of a definitive transition from extrinsic, impurity-controlled diffusion at low temperatures, to a range of high temperatures within which one could observe intrinsic transport (controlled by equilibrium defect concentrations rather than those created chemically through impurities). This prevented unambiguous identification of experimental activation energies for diffusion as either an enthalpy for ion migration, H_m , or as a combination of migration and defect-formation enthalpies ($H_m + \frac{1}{2}H_f$ for the case of Schottky defects). A similar dilemma exists for most oxides which display very narrow ranges of stoichiometry.

One would ordinarily conduct measurements at temperatures as close as possible to the melting point of the host material in any attempt to reveal a transition to intrinsic behavior. Magnesium oxide, however, has a high melting temperature (2800°C) and vaporizes rapidly at elevated temperatures. "High" temperatures for this material are accessible only with great difficulty and experiments are extremely difficult to perform. No measurement of diffusion in MgO had been performed at a temperature greater than 1850°C (only $0.69 T_m$ in degrees Kelvin) prior to 1967. Techniques which permit diffusion measurements in MgO at elevated temperatures have now been perfected and experiments have been extended to within

300°C of T_m . A further development has been the availability of magnesium oxide crystals of improved purity and perfection. The quality of the specimens which have been recently studied might, in principle, be close to that required for intrinsic mass transport. Independent measurements of diffusion in several systems have become available for comparison -- often having employed different techniques, and often having proposed very different interpretations.

Much of the data obtained for diffusion in MgO is quite recent. Nearly half of the available literature has appeared within the last three years. A review of the data available for mass transport in MgO would therefore appear to be timely. The present work will contrast the interpretations which have been given to the available data for diffusion in single crystal material. A more extensive review is presented elsewhere.⁽¹⁾

2. The Theoretical Situation

Since magnesium oxide has the rocksalt structure type, one might reasonably expect Schottky defects to predominate in this material. Difficulty has been experienced in extending theoretical calculations from simple ionic materials to oxides. An early attempt⁽²⁾ to apply the Mott-Littleton method to MgO failed* unless the polarizability of the oxygen atoms about a cation vacancy was assumed to be less than half of the normal value. An estimate of $H_f = 4$ to 6 eV was proposed. A later calculation⁽³⁾ provided values of 2.1 - 2.9 eV when only nearest-neighbor interactions about the defect were included, but failed* when second-nearest neighbor oxygen-oxygen interactions were included; a value of $H_f = 3.97$ eV was obtained when interaction parameters were derived from elastic

* "Failure" indicates a negative enthalpy of formation was obtained!

constants. Later refinements⁽⁴⁾ provided values of 9 to 10 eV, while the most recent theoretical estimates of H_f for MgO, using a generalized Mott-Littleton approach and computer calculation⁽⁵⁾, provide $H_f = 7$ to 8 eV.

Semi-empirical means have also been employed to estimate H_f and H_m for MgO. A close correlation (to within 10%) between melting temperature and H_f was observed^(6,7) for alkali and heavy-metal halides, and a similar but less exact correlation was noted with the enthalpy for cation migration. Extension of this relation to alkaline earth oxides provided estimates⁽⁷⁾ of $H_f \approx 5.9$ eV and $H_m = 2.6$ eV for MgO. Harding⁽⁸⁾, by combining estimates of energies for solid-state reactions, proposed 4.0 and 6.6 eV for formation enthalpies of doubly - and singly - ionized Schottky defects, respectively.

3. Materials

All single crystal of magnesium oxide which have been employed in diffusion experiments have been produced by submerged-arc fusion. Most crystals have been obtained from the Norton Company, Chippewa, Ontario, Canada. Crystals of improved quality have become available more recently from W. & C. Spicer Ltd., Winchcomb, Cheltenham, England. The Spicer process has been adapted at the Oak Ridge National Laboratory in an extensive program for the production and characterization of MgO crystals⁽⁹⁾. Although the purest and best characterized crystals yet produced, this material, to the writer's knowledge, has not yet been employed in diffusion experiments.

Despite the critical importance of impurity concentration in the interpretation of diffusion data, little is known about the purity of specimens which have actually been employed in experiments. A manufacturer's analysis or reference

to the literature is often all that is reported, in spite of the fact that the purity of crystals supplied by a given vendor may vary greatly from batch-to-batch or even within a given melt. This has been amply demonstrated by the Oak Ridge study⁽⁹⁾.

It is necessary to make several assumptions in order to convert bulk chemical analyses into concentrations of chemically-created point defects. The impurities reported will here be assumed to be in solid solution. Concentrations of monovalent ions will be neglected: OH^- is a serious impurity in crystals of all alkaline earth oxides and the extent of charge compensation is unknown. Only impurities of valence 3 and 4 will be here considered. Two estimates may then be made of the level of chemically-created vacancies: A worst estimate obtained upon taking the highest concentration observed for each element and assuming the variable-valence impurity ions (notably the transition metals) to be in their highest oxidation state, and a best estimate, obtained upon taking the lowest level of impurity of each type reported, and assuming the iron-group impurities to be divalent (probable, for example, in vacuum or in an argon atmosphere). Under these assumptions, and using analyses reported for Norton^(10,11), Spicer⁽⁹⁻¹¹⁾ and ORNL⁽⁹⁾ crystals, the range of anticipated concentrations for cation vacancies may be expected to be 68-221, 27-110, and 14-103 10^{-6} , respectively.* For the best crystals potentially available from these sources, the enthalpy for Schottky-pair formation must be less than 4.8, 5.5 or 6.0 eV, respectively, if intrinsic mass transport is to be observed at any temperature less than 2800°C, the melting temperature of MgO .

*A number of diffusion studies have employed crystals obtained from Ventron Electronics Corporation, Bradford, Pennsylvania, and Monocrystals, Incorporated, Cleveland, Ohio. A single reported analysis of these materials⁽¹³⁾ indicated the presence of 453 and 541 ppmw cation impurity of which the most significant were Ca and Fe (ca. 200 ppmw) and Al (ca. 25).

Arc-fused crystals of MgO display large subgrains which typically range from 500 μ up to several mm in diameter⁽⁹⁻¹²⁾, with mosaic spreads of the order of several minutes of arc^(9,12). Dislocation densities of 1.1 to 2.5×10^5 , and 0.7 to $1.0 \times 10^5 \text{ cm}^{-2}$ have been reported for Norton and Spicer crystal⁽¹⁰⁾, and comparable values of 1 to 10×10^5 for ORNL crystals⁽⁹⁾.

The dislocation density actually present in a diffusion specimen may be higher than the native dislocation density and will depend upon the procedures used to prepare a surface for deposition of isotope or solute. MgO is quite susceptible to deformation on the $(110)[110]$ slip system of the rocksalt structure type. Cleavage on (100) produces 0.5 to 1.0μ cleavage steps and extensive damage on $\{110\}$ slip bands near such steps*. Mechanical polishing is usually used to remove cleavage steps, but this procedure increases dislocations by up to three orders of magnitude⁽¹⁰⁾ to $\text{ca } 10^8 \text{ cm}^{-2}$. Comparable densities have been deduced from decorated dislocations in the diffusion zone under polished surfaces⁽¹⁴⁾. Annealing at elevated temperatures ($>1850^\circ\text{C}$) reduced mechanical damage by factors of two to three⁽¹⁰⁾, but does not restore dislocation densities to the native levels. It is important to note that the damaged layer extends to of the order of 50μ under a polished surface⁽¹⁰⁾. This is comparable to the extent of the diffusion zone in typical samples analyzed by sectioning techniques. The most satisfactory surfaces for diffusion specimens appear to be obtained by a combination of hand lapping and chemical polishing⁽¹⁰⁾.

* See, for example, Fig. 1 in Ref. 10.

4. Distribution of Solute

The distribution of solute concentration, C , after a diffusion annealing of duration t is governed by the partial differential equation known as Fick's second law:

$$\partial C / \partial t = \partial / \partial x (D^* \partial C / \partial x) \quad (1)$$

where D^* is the tracer diffusion coefficient, and x is the penetration of solute into a sample which is assumed to be large (in the two remaining directions) relative to the extent of solute redistribution. The determination of diffusion coefficients usually involves experimental measurement of solute distribution in an annealed sample prepared with boundary or initial conditions such that a simple solution to (1) obtains.

Two options exist for the establishment of the solute gradient: Direct measurement of concentration as a function of penetration, x , through microprobe analysis or through counting of the activity of radiotracer in sections serially ground from a sample or, alternatively, measurement of the residual activity of radiotracer which remains in a sample after removal of a layer of thickness x' . The expected solute distributions are summarized in Fig. 1. The solutions tabulated under the Fractional Residual Activity technique are obtained under the assumption that the absorption of the radiation emitted by the tracer isotope is negligible. A solution for experiments in which this is not the case has been provided by Gruzin⁽¹⁵⁾ for samples to which an initial thin film of radiotracer has been applied. Terms employed in Fig. 1 which have not previously been defined are: S , initial amount of solute per unit area in thin-film samples; h , initial thickness of film in thick-film samples; C_0 surface concentration in vapor-exchange

specimens, initial (uniform) concentration of solute in thick-film or semi-infinite interdiffusion specimen, or limit of solid solubility in thin film specimen with incompletely dissolved layer of solute. Of the functions given, erf is the Gaussian error function; erfc is $1 - \text{erf}$, the complementary error function; and ierfc is the integrated complementary error function.

Oxygen self-diffusion coefficients have been measured through the exchange between a solid sample and an atmosphere enriched with the stable isotope ^{18}O . Although the distribution of isotope in the sample itself could be determined, powders are usually employed to increase surface area, and all experiments with MgO have monitored the depletion of the isotopic content of the vapor. The ratio of the amount of isotope at time t to that at complete equilibration is

$$M(t)/M(\infty) = (1 + \alpha) \{1 - [v_1 / (v_1 + v_2)] e \text{erfc} [(3v_1/\alpha)(D^*t/a^2)^{1/2}] - [v_2 / (v_1 + v_2)] e \text{erfc} [-(3v_2/\alpha)(D^*t/a^2)^{1/2}]\}t + \dots \quad (2)$$

where $e \text{erfc } z = e^{z^2} \text{erfc } z$, α is the ratio of oxygen in the atmosphere to that in the sample, a is the radius of a spherical sample,

$$v_1 = \frac{1}{2} [(1 + 4/3\alpha)^{1/2} + 1] \text{ and } v_2 = v_1 - 1.$$

For small (D^*t) , (2) reduces to $(36 D^*t / \pi \alpha^2 a^2)^{1/2}$. Equation (2) must be applied under the assumptions that diffusion rather than surface reaction controls exchange with the atmosphere, that the powder sample may be described as an assemblage of spheres of appropriate radius a , and that exchange with surface imperfections and the sample chamber is negligible or may be corrected. It has usually been assumed that these conditions are met when values of (D^*t/a^2) obtained from (2), when plotted as a function of time, give a linear relation which extrapolates through the origin.

5. Results of Self-Diffusion Studies

Four studies of cation self diffusion (10,13,16,17) and three studies of oxygen self-diffusion (18-20) have been performed for MgO. The results, along with data for tracer-type diffusion of 14 different impurity cations, are tabulated in Fig. 2, with an indication of the technique employed, the temperature range over which measurements were conducted and the atmosphere. The data are arranged in order of increasing ionic radius⁽²¹⁾ of the diffusing specie.

The ²⁸Mg tracer measurements of Lindner and Parfitt⁽¹⁷⁾ were the first diffusion data of any sort to be obtained for MgO. These data were an anomaly for many years. The value of D_0 , $0.249 \frac{\text{cm}^2}{\text{sec}}$, was a reasonable one for intrinsic diffusion, and the activation energy, 3.43 eV, could be interpreted as $1/2 H_f$ (ca. 2.5 eV) plus a reasonable energy for ion migration (ca. 1eV). The results were thus generally believed to represent intrinsic diffusion. This interpretation was supported by Lindner and Parfitt's statement⁽¹⁷⁾ that there was evidence for a lower activation energy at lower temperatures. (There is no indication of this, however, in the results which were reported, and additional data were never forthcoming.) In contrast, data later obtained for the diffusion of impurity cations of similar radius clearly were representative of extrinsic diffusion by virtue of small preexponential terms (ca. 10^{-5}) and activation energies (ca. 2 eV) which were less than one-half of most theoretically-estimated energies for Schottky-pair formation. It was inferred that the Infra Red Development Corp. crystals which had been employed were exceptionally pure (10 ppm Ca and 1 ppm Al, Fe and Co were quoted by Lindner and Parfitt⁽¹⁷⁾), but analyses of a number of crystals from this source indicate⁽²²⁾ 10-400 ppm Si, 100 ppm Fe and 1000 ppm Al. Also overlooked is the fact that Lindner and Parfitt employed both Infra Red Development Corp. crystals

and the Norton Co. crystals employed in many subsequent studies. No difference in transport behavior was noted, and the two types of materials were consequently not distinguished.

More extensive data for ^{28}Mg self-diffusion were reported for two grades of crystals by Harding et al⁽¹³⁾. The diffusion coefficients were larger than those of Lindner and Parfitt as shown in Fig. 3. Results were identical for both Monocrystals and Ventron crystals below 1400°C. This region was assumed to be influenced by impurity precipitation ("Region IV", by convention). Above 1400°C, data for the two materials appeared to diverge. The higher-temperature data were assumed to represent extrinsic diffusion (Region II) influenced by the onset of the intrinsic diffusion which Lindner and Parfitt's data were assumed to represent.

The data of Harding et al⁽¹³⁾ were subsequently shown by Harding and Price⁽¹⁶⁾ to have been influenced by Al impurity born by the tracer solution which had been deposited on the crystal. Further, the difference in behavior previously observed between the Monocrystals and Ventron specimens was attributed to differences in the purity of tracer which had been applied. Both grades of crystals were subsequently interpreted as giving comparable results^(16,23) as, indeed, their chemical analyses would suggest.

The revised ^{28}Mg diffusion coefficients are smaller by a factor of roughly 4 and, in a comparable temperature range, agree precisely with the data of Lindner and Parfitt. The results are again interpreted as representing impurity precipitation, extrinsic and intrinsic regions of mass transport as temperature is increased, except that Lindner and Parfitt's data are now included in region IV. Values of H_m of 1.56 ± 0.08 eV and H_f of 3.8 ± 0.3 were thereby inferred.

Wuensch et al.⁽¹⁰⁾ attempted to circumvent the problems associated with use of the short-lived isotope ^{28}Mg (21.3 hr half life) by employing the stable isotope ^{26}Mg (11.17% natural abundance) as tracer. The isotopic content of sections ground from the specimens was determined through mass spectrometry. No difference between the behavior of Spicer and Norton crystals was noted. The data, also included in Fig. 3, may be fit by a single Arrhenius plot over a temperature range of 1400 - 2400°C, and the average departure of the data from this fit is 1.2 standard deviations. Wuensch et al. interpret their data as extrinsic over the entire temperature range. The activation energy, 2.76 ± 0.08 eV is very close to the value of 2.6 eV predicted by the empirical correlation between H_m and melting temperature^(6,7).

The data of Wuensch et al. are smaller than those of Harding and Price by a factor of about 7.8 at all temperatures up to the melting temperature. It has been noted⁽¹⁰⁾ that an activation energy of the order 2.6 eV also results if a single Arrhenius plot is fit to the data of Harding et al.⁽¹³⁾ over their entire temperature range. The data obtained by Wuensch et al. at 1100° and 1257°C do not fit the curve which describes their data at higher temperatures. These two data, however, were obtained from crystals prepared in a different manner than the others. Very small diffusion gradients had been anticipated at these temperatures and the requisite of surface flatness was considered more important than removal of the damaged surface layer through chemical polishing. These two specimens therefore possessed dislocation densities in the diffusion zone which were two to three orders of magnitude larger than that in the remaining samples. It is of interest to note that these two data are in good agreement with the results of Harding and Price⁽¹⁶⁾, and that the latter workers measured short gradients into similar mechanically-polished surfaces.

Results obtained in three sets of gas-exchange measurements of oxygen self-diffusion are plotted as a function of reciprocal temperature in Fig. 4. The diffusion coefficients are at least two orders of magnitude smaller than those for magnesium self-diffusion. The data of Hashimoto et al.⁽²⁰⁾ provide interesting evidence for enhanced oxygen diffusion at grain boundaries. Crushed polycrystalline samples with two different particle sizes were studied. When $\bar{d}$ in (2) was taken as the particle size of the powders, diffusion coefficients of differing magnitudes were obtained. If $\bar{d}$ was instead taken to be the size of the grains contained within the particles, data from the two experiments fell on a single curve which was in excellent agreement* with earlier data of Oishi and Kingery⁽¹⁸⁾ with powders obtained from a crushed single crystal.

Data of Rovner⁽¹⁹⁾ at lower temperatures are an order of magnitude smaller and indicate a somewhat larger activation energy. The measurements were complicated, however, by the necessity of having to make large corrections for exchange with the system, possible desorption of isotope from the system during sampling, and the rate plots which did not extrapolate to zero at zero time. Rovner further reported dependences of diffusion on oxygen partial pressure (although based upon measurements at only two pressures) equal to $+0.48 \pm 0.05$ for Cr-doped crystals, -0.7 ± 0.3 for Li-doped crystals and 0.22 ± 0.1 for Semi-Elements crystals. The latter dependence was assumed to represent the $+1/6$ value expected for intrinsic diffusion of doubly-charged interstitials. O'Keeffe and Moore⁽²⁴⁾ have pointed out a similarity between Oishi and Kingery's results for MgO and their measurements

*The data obtained by Hashimoto et al. were obtained at a different partial pressure than those of Oishi and Kingery. If a $1/6$ power dependence on oxygen partial pressure is assumed⁽¹⁹⁾, scaling the data brings the results in even closer accord.

of oxygen self-diffusion in NiO, for which an interstitial mechanism is also suggested.

6. Results for Impurity Cation Diffusion

Figure 2 summarizes the experimental conditions and results obtained for tracer-like diffusion of 14 different impurity cations. Much of the data is characterized by small values of D_0 , typically 10^{-5} cm²/sec. Many activation energies are of the order of 2 eV, which is close to one-half of even the lower theoretical estimates of H_f . These data presumably represent extrinsic diffusion.

A few systems have been studied by several investigators who often have used different experimental techniques. A comparison of these results reveals a general qualitative agreement, but illustrates some problems of interpretation. Calcium diffusion has been studied by Rungis and Mortlock⁽²⁶⁾ through autoradiography of ⁴⁵Ca gradients, by Wuensch and Vasilos⁽³⁶⁾ with the aid of electron microprobe analysis, and by Harding⁽³⁰⁾ through application of the Gruzin technique to measurements of ⁴⁵Ca residual activity. Figure 5 shows the three sets of results* to be in reasonably good agreement, although the data of Harding provide a somewhat higher activation energy.

*Wuensch and Vasilos⁽³⁶⁾ prepared samples at temperatures as low as 790°C but found that measurement of shallow gradients was broadened by fluorescence. A procedure for correcting this effect was proposed⁽³⁶⁾, but this has not yet been carried out. Fig. 5 shows only high-temperature diffusion coefficients which, having been determined from gradients in excess of 50μ, are not influenced by fluorescence.

Figure 6 compares diffusion coefficients for Ni^{2+} obtained over a temperature range of $1000^\circ - 2460^\circ\text{C}$ by Wuensch and Vasilos^(11,33,34) through electron microprobe analysis of thin-film and vapor exchange samples, and data obtained by Harding⁽²³⁾ through measurement of the residual activity of ^{63}Ni after sectioning. Also included in Fig. 6 are the values of chemical diffusion coefficients obtained by Blank and Pask⁽³⁹⁾ and Appel and Pask⁽⁴⁰⁾ in interdiffusion experiments; the values plotted are those obtained when $\tilde{D}$ is extrapolated to zero Ni concentration where $\tilde{D}$ reduces to the tracer diffusion coefficient. The data are in extraordinarily good agreement over the entire temperature range. The interpretation afforded the results has been quite different. Wuensch and Vasilos⁽¹¹⁾ describe the data by a single activation energy which is taken to represent H_m . The departure of the data from the relation at the highest temperatures was not considered significant and was felt to be due to the difficulty in preparing such samples. (The temperature of 2460°C is 370° above the melting temperature of NiO , and two-thirds of the NiO-MgO solid solution series is above the solidus of the system). The data of Harding⁽²³⁾ however, replicate the deviation. It is thus real, but whether it merely indicates similar experimental difficulties is uncertain. Harding interprets his data as displaying a high temperature ($1900^\circ - 2500^\circ\text{C}$) intrinsic region, an intermediate region ($1600^\circ - 1900^\circ$) of extrinsic diffusion with $H_m = 1.6 \text{ eV}$, and a low temperature ($1100^\circ - 1600^\circ$) region influenced by impurity precipitation and dislocation-enhanced diffusion. A value of $H_f = 3.4 \pm 0.3 \text{ eV}$ is provided by this interpretation.

These two sets of measurement are in agreement on two other points. No difference is again observed between the diffusion rates of Ni^{2+} in Norton Co. and Spicer Ltd., or Ventron and Monocrystals specimens, respectively. Further,

both studies conducted measurements in argon and also in air. No effect of atmosphere was observed in either case. A similar result is also found for ^{28}Mg self-diffusion⁽¹⁶⁾ and for ^{133}Ba ⁽²³⁾ and ^7Be ⁽²⁹⁾ diffusion.

Anomalies in concentration gradients have been encountered in the diffusion of Sr^{2+} ⁽²⁸⁾ and Ba^{2+} ^(14,23) in MgO . Two or even three⁽⁴¹⁾ slopes are found in the profile. The slope at low solute penetration in MgO has been assumed to represent lattice diffusion, while that at large penetrations has been assumed to be due to dislocation-enhanced diffusion. The latter interpretation would seem supported by the observation that results in this region are dependent upon history of the sample and the duration of a preanneal⁽⁴¹⁾. Such anomalies appear to be unique to the heavy alkaline earth cations and have indeed been also observed in studies of cation self-diffusion in the respective oxides CaO ⁽⁴²⁾, SrO ⁽⁴³⁾ and BaO ^(44,45). In the self-diffusion studies, however, the near surface slope was considered to be an anomaly, and the large-penetration slope was considered to represent lattice diffusion. (The near-surface diffusion coefficients in one study⁽⁴⁴⁾ of cation self-diffusion in BaO yield an activation energy of 12 eV - several eV higher than the energy of formation of BaO). Murarka and Swalin found that the depth of the near-surface zone increased with time of exposure of a specimen to atmosphere⁽⁴³⁾ and interpret the effect as being due to formation of an hydroxide layer. An additional observation may be made concerning the anomaly as observed in MgO . The near-surface gradient extends to a depth of 25-40 μ , which is of the same order of magnitude observed by Wuensch et al.⁽¹⁰⁾ for the extent of the layer of damage under a ground surface. While the correspondance may be fortuitous, it still holds that the data interpreted as representing lattice diffusion of Sr^{2+} and Ba^{2+} in MgO were obtained from a zone which may have had dislocation densities two or three orders of magnitude higher than in the layer which was interpreted as representing dislocation-enhanced diffusion.

7. Critique and Discussion

With the availability of improved single-crystals of MgO in recent years, much more attention has been paid to the characterization of host crystals, preservation of their integrity during the preparation of diffusion couples, and the extension of the range of temperatures over which samples might be prepared. Many criticisms of experiments performed ten or fifteen years ago may be made in light of these advances.

Impurity-cation diffusion specimens of the sort prepared with thin-film boundary conditions by Wuensch and Vasilos for subsequent microprobe analysis present several problems. The amount of solute which is applied as an initial layer is large in comparison to that employed in radio tracer diffusion experiments. There is therefore potential for the introduction of impurities into the specimen - carried either in the deposit itself, or in the form of anions retained upon calcination of a chloride or nitrate deposit. The stable isotope studies of Wuensch et al.⁽¹⁰⁾ also employed thick deposits, but an attempt was made to purify the isotopic oxide. Even so, potential for contamination exists relative to a conventional radiotracer experiment. The discrepancy between the cation self-diffusion results of Harding and Price⁽¹⁶⁾ and Wuensch et al.⁽¹⁰⁾ would therefore cast suspicion on the latter study were it not for the fact that the stable isotope diffusion coefficients were smaller over the entire temperature range which has been explored.

The microprobe studies of Wuensch and Vasilos also present an ambiguity in that they are a curious hybrid between measurement of a chemical interdiffusion coefficient and a tracer diffusion coefficient. Interdiffusion between MgO and

a second oxide is clearly involved in early stages of the diffusion annealing. In final stages of such experiments the solute oxide is present in lower concentrations (ca. 10 to 0.02 molc%), but these are hardly tracer levels. It has been established that the tracer diffusion coefficient for divalent transition metal cations in MgO in air increases exponentially with solute concentration⁽⁴⁶⁾. It is thus somewhat surprising that the former concentration gradients usually display perfect linearity over a concentration range spanning two and one-half orders of magnitude. The ambiguity in this type of experiment appears not to be serious by virtue of the excellent agreement between radiotracer and microprobe values displayed in Fig. 6.

It has been generally known that polishing or cleaving a crystal introduces surface damage. This has not been a source of concern in diffusion couple preparation until recently, not has it been fully appreciated that, in MgO, such damage may involve an increase in dislocation density by two to three orders of magnitude to a depth of 50 μ . In systems where cation sizes are similar, and complete solid solubility exists (eg, NiO-MgO), it has been directly demonstrated^(47,48) that the excess dislocations cause no enhancement of mass transport. Also, in most interdiffusion experiments and in tracer-like samples prepared for microprobe analysis, the solute penetration has extended to depths of several hundred microns (ie, two to seven times the depth of the damaged layer) and the effect was probably not of importance. In the radiotracer experiments of Harding, Mortlock and coworkers, however, isotope penetrations were limited to depths of the order of 50 μ in order to permit residual activity analysis without the necessity of absorption corrections. Sample surfaces had been mechanically polished. The isotope gradient was thus confined entirely to the damaged layer.

A disadvantage of the thin-film type of tracer impurity experiment (as opposed to vapor-exchange) at ultra-high temperatures is that the host crystal is in contact with a layer of solute which may be liquid in the initial stages of the experiment. The observation of Harding⁽²³⁾ that Ni^{2+} appeared to be very much less soluble in MgO at temperatures of 1800° to 2500°C therefore seems suspicious: NiO forms a complete series of solid solutions with MgO at much lower temperatures; also, pure NiO melts at 2090°C . These points may be important since much of the basis for the different interpretations which have been given to the existing data hinge on hints of structure above 1900°C in Arrhenius plots.

There appears to be no real difference in the mass transport behavior in MgO crystal obtained from different sources - at least on the basis of the evidence in the few experiments for which such comparisons have been made. This seems at first surprising when best analyses of crystals from a given source are compared. However, as has been shown above, the ranges of chemically created defects which occur in crystals from any given source overlap to large degree. This is particularly the case in argon (the atmosphere in which all high temperature experiments have been performed) where much of the iron-group impurity will probably be in a divalent state. Not much more can be said about this aspect of the data in view of the lack of detailed chemical analyses of the actual crystals used in experiments.

As we have seen, coefficients for diffusion in MgO are generally in qualitative agreement to the extent that different investigators have examined a given system. Two very different interpretations of the results have arisen from this body of data, each of which is self-consistent within certain bounds. On the one hand we have the interpretation of Harding, the main points of which are:

(a) Over a wide temperature range, regions of impurity precipitation and perhaps dislocation enhancement (IV), extrinsic (II) and, above 1900°C, intrinsic diffusion are observed.

(b) $H_f = 3.8$ eV; $H_m = 1.5, 3.1$ and 3.9 eV for divalent, trivalent and quadrivalent ions, respectively, independent of ion size.

This interpretation is consistent with the purity of available crystals, and the interpretation given to dislocation-climb experiments⁽⁴⁹⁾ and certain oxygen self-diffusion results^(19,50).

Another interpretation, and that suggested by the writer holds:

(a) Intrinsic diffusion has not been observed for MgO.

(b) H_m is ca. 2.8 eV for both Mg^{2+} and O^{2-} , and of the order of 1.6 to 2.7 eV for divalent impurity cations.

(c) H_f is in excess of 4.5 eV.

(d) A general correlation between diffusion rates and ionic size exists for ions of similar electron configuration⁽²⁸⁾, although ions with polarizable d electrons may depart from this relationship⁽³⁶⁾.

This interpretation is consistent with the lack of a dependence of diffusion rates on atmosphere, with the observation that interdiffusion coefficients - almost certainly controlled by chemically-created cation vacancies - extrapolate smoothly to tracer values at zero concentration, agrees with the empirical relation between H_m , H_f and melting temperature^(6,7) and is consistent with recent theoretical calculations of H_f . Further support is provided by the fact that activation energies of ca 2 eV are of the same order as the activation energies for a given ion in transition metal oxides with virtually identical.

lattice constants⁽⁵¹⁾, and for which it seems probably (although not absolutely certain) that cation vacancy concentrations in equilibrium with the atmosphere comprise the defect structure.

Either interpretation hinges critically upon the significance given to hints of structure contained in Arrhenius plots, and which have been illustrated by Figs. 3 and 6. Are these real or merely artifacts caused by the extreme difficulty of performing experiments at very high temperatures? A few of the questions connected with specific results described in this review might be answered with further experimentation. But, if the recent theoretical estimates of $H_f = 7$ to 8 eV are correct, MgO crystals with total aliovalent impurity contents less than 0.6 ppm must be grown and preserved during high temperature experiments if a definitive transition to intrinsic behavior is ever to be observed. With this stringent requirement on purity, questions about the defect structure of "simple" oxides will be better resolved through recourse to experiments with ideally-imperfect oxides in which defect structure may be controlled through variation in atmosphere.

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Captions for Figures

- Fig. 1. Distribution of tracer after annealing under various initial or boundary conditions for sample preparation.
- Fig. 2. Results of tracer-type diffusion measurements with single-crystal MgO.
- Fig. 3. Plot of cation self-diffusion coefficients in single-crystal MgO as a function of reciprocal temperature.
- Fig. 4. Oxygen self-diffusion coefficients for MgO plotted as a function of reciprocal temperature. The three sets of results were obtained at different oxygen partial pressure. To facilitate comparison, data have been scaled to a pressure of 150 Torr by assuming a $1/6$ powder dependence.
- Fig. 5. Plot of Ca^{2+} diffusion coefficients in single-crystal MgO as a function of reciprocal temperature.
- Fig. 6. Plot of Ni^{2+} diffusion coefficients in single-crystal MgO as a function of reciprocal temperature. The data of Harding were determined from ^{63}Ni residual activity, the data of Wuensch and Vasilos through electron microprobe spectroscopy. The results of Blank and Pask and of Appel and Pask are interdiffusion coefficients extrapolated to zero Ni concentration.

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Type of Specimen	Conditions	Concentration as a function of Penetration	Solutes studied in MgO	Fractional residual activity upon removal of layer x'	Solutes studied in MgO
Initial thin film between two slabs of host crystal	$C(x,0) = 0$ for $x > 0$ $\int C(x,t)dx = S$ for $t \geq 0$	$S(4\pi D^*t)^{-1/2} \exp [-x^2 (4D^*t)^{-1}]$	Cr (27), Ni (11,33,34), ^{28}Mg (17), Co (34), Fe (34,37) Mn (37), ^{91}Y (38), ^{45}Ca (26), Ca (36)	$\text{erfc } x' (4D^*t)^{-1/2}$	^7Be (25,29), ^{68}Ge (30), ^{63}Ni (23), ^{28}Mg (13,16), ^{46}Sc (31), ^{115}Cd (27)
				Gruzin (15)	^{45}Ca (30)
Initial thick film between two slabs of host crystal	$C(x,0) = C_0$ for $ x < h/2$ $C(x,0) = 0$ for $ x > h/2$	$\frac{1}{2}C_0 \{ \text{erf}(h-x)(4D^*t)^{-1/2} + \text{erf}(h+x)(4D^*t)^{-1/2} \}$	^{26}Mg (10)		
Exchange with vapor, or incompletely dissolved initial film of solute with limited solubility	$C(0,t) = C_0$ for $t \geq 0$	$C_0 \text{erfc}[x(4D^*t)^{-1/2}]$	Ni (11,33,34), ^{26}Mg (10), Zn (35), Co (34), Ca (36)	$1.772 \text{ierfc } x' (4D^*t)^{-1/2}$	^{68}Ge (30), ^{85}Sr (28), ^{133}Ba (14,23)
Diffusion across boundary between host crystal and slab containing uniform concentration C_0	$C(x,0) = C_0$ for $x < 0$, $C(x,0) = 0$ for $x \geq 0$	$\frac{1}{2}C_0 \text{erfc}[x(4D^*t)^{-1/2}]$	^{26}Mg (10)		

Ion	Radius (Å) ^a	Tracer	Method	Material ^b	Atmosphere	Temperature range (°C)	D_0 (cm ² /sec)	E (eV)	Reference
25^{2+}	0.27	^7Be	Residual activity (solubility)	M	air	1000°-1700°	$1.41^{+0.50}_{-0.36} 10^{-5}$	1.60 ± 0.04	Harding and Mortlock (1966) (25) ✓
		^7Be from HCl solution	Residual activity (solubility)	V	air, argon	636°-2340°	$1.99^{+0.24}_{-0.22} 10^{-5}$	1.68 ± 0.02	Harding (1973) (29) ✓
56^{4+}	0.540	^{68}Ge	Residual activity (sol. and insol.)	M, V	argon	1850°-2400°	$3.4^{+7.0}_{-2.3} 10^{-1}$	$4.0 \pm .2$	Harding (1973) (30) ✓
9^{3+}	0.615	Cr_2O_3 from calcined deposit from CrO_3 solution	Thin film; microprobe	N	air	1300°-1700°	$9.8 10^{-4}$	2.95	Tagai et al (1965) (37) ✓
51^{2+}	0.700	NiO from calcined deposit from NiCl_2 solution Exchange with vapor over NiO	Thin film or vapor - exchange; microprobe	N	air	1000°-1850°	$1.80 10^{-5}$	2.10	Wuensch and Vasilos (1960, 1962) (33, 34) ✓
				N, S	argon	1900°-2460°	$1.80 10^{-5}$	2.10	Wuensch and Vasilos (1971) (41) ✓
		^{63}Ni from HCl solution	Residual activity (solubility)	V, M	air, argon	1100°-1600°	$\ln D(\frac{1}{T})$ curved		Harding (1972) (23) ✓
						1600°-1900°	$1.3 10^{-6}$	1.6	
						1900°-2500°	$1.4^{+4.8}_{-1.1} 10^{-2}$	$3.3 \pm .3$	
$^{24}\text{Mg}^{2+}$	0.720	^{28}MgO from evaporation of HCl solution, or vaporization-condensation of MgO	Thin film, sectioning	N, I	air(?)	1429°-1616°	$2.49^{+3.20}_{-1.40} 10^{-1}$	$3.43 \pm .13$	Lindner and Parfitt (1957) (17) ✓
		^{28}Mg from 0.1N HCl solution	Residual activity (solubility)	M, V	air	1132°-1400°	$5.4^{+6.4}_{-2.9} 10^{-1}$	$3.2 \pm .1$	Harding et al (1971) (18) ✓
				V	air	1400°-1742°	$1.6 10^{-5}$	1.8	
				M	air	1400°-1742°	$1.2 10^{-5}$	1.6	
		^{28}Mg from 0.1N HCl solution (diluted 20X) + Ca^{2+}	Residual activity (solubility)	V	argon	1540-1900°	$7.49 10^{-6}$	$1.56 \pm .03$	Harding and Price (1972) (16) ✓
					argon	1905-2342°	$7.43^{+12.17}_{-4.61} 10^{-2}$	$3.46 \pm .19$	

Mg^{2+} (cont.)		^{26}MgO chemical vapor transport or vapor exchange	semi-infinite source, thick film, vapor exchange; mass spectrometry	N, S	argon	1100-1400	---	---	Wuensch et al (1973) (40)
						1400-2400	$4.19^{+2.45}_{-1.55} 10^{-4}$	$2.76 \pm .03$	
Sc^{3+}	0.730	^{46}Sc						2.2	Solaca (1972) (32) Solaca and Mortlock (1970) (31)
Co^{2+}	0.735	CoO from calcined deposit of $CoCl_2$ solu- tion	thin film, vapor exchange; microprobe	N	air	1000°-1810°	$5.78 10^{-5}$	2.06	Wuensch and Vasilos (1962) (34)
Zn^{2+}	0.745	exchange with vapor over ZnO	vapor exchange microprobe	N	air	1000°-1650°	$1.48 10^{-5}$	1.85	Wuensch and Vasilos (1965) (35)
Fe^{2+}	0.770	FeO from calcined deposit of $FeCl_2$ solu- tion	thin film, microprobe	N	air	1050°-1720°	$8.83 10^{-5}$	1.81	Wuensch and Vasilos (1962) (36)
		FeO from calcined deposit of $FeCl_3$ solu- tion	thin film, microprobe	N	air	1310°-1690°	$3.2 10^{-4}$	1.82	Tagai et al (1965) (37)
		FeO from oxidized metallic film	thin film, microprobe	N	air	1300°-1690°	$1.3 10^{-3}$	2.12	
Mn^{2+}	0.820	Mn_2O_3 from calcined deposit from nitrate solution	thin film, microprobe	N	air	1300°-1700°	$4.1 10^{-7}$	1.21	Tagai et al (1965) (37)
Y^{3+}	0.892	^{91}Y as oxide	thin film	GE	argon	1400°-1760°	$2.11^{+1.18}_{-1.0} 10^{-2}$	$3.10^{+0.07}_{-0.05}$	Berard (1971) (38)
Cd^{2+}	0.95	^{115}Cd	residual activity (solubility)	V	argon	1778-2267°	$1.7^{+6.0}_{-1.4} 10^{-2}$	$3.4 \pm .3$	Harding and Bhalla (1967) (27)
Ca^{2+}	1.00	^{45}Ca from HCl solution	thin film, auto- radiography	M	air	910°-1700°	$2.95^{+2.6}_{-1.5} 10^{-5}$	$2.13 \pm .10$	Rungis and Mortlock (1966) (26)
		CaO-MgO film or exchange with vapor over MgO	thin film, vapor exchange microprobe	N	air	790°-1850°	$8.9 10^{-4}$	2.76	Wuensch and Vasilos (1966) (36)
		^{45}Ca	residual activity (Gruzin)	M, V	argon	1850°-2400°	$3.43^{+4.95}_{-2.03} 10^{-3}$	$3.2 \pm .2$	Harding (1973) (30)

Sr ²⁺	1.16	⁸⁵ Sr	residual activity (in complete solubility)	M	?	1000°-1600°	6.0 ^{+10.7} _{-3.8} 10 ⁻⁴	2.91 ^{±.13} ^c	Mortlock and Price (1973) (28)
							3.3 ^{+11.1} _{-2.5} 10 ⁻¹	3.09 ^{±.19} ^d	
Ba ²⁺	1.36	¹³³ BaCl ₂ solution plus NH ₄ OH	residual activity (incomplete solubility)	M	air	1003°-1724°	7 ⁺³ ₋₂ 10 ⁻²	3.38 ^{±.05} ^c	Harding (1967) (16)
							6.3 ^{+4.2} _{-2.5} 10 ⁻⁵	1.85 ^{±.07} ^d	
				V,M	argon, air	1008°-1422°	4.2 ^{+5.4} _{-2.3} 10 ⁻²	3.3 ^{±.1}	Harding (1972) (23)
						1900°-2450°	2.8 ^{+13.2} _{-2.3} 10 ⁻²	3.5 ^{±.3}	
O ²⁻	1.40	¹⁸ O exchange	depletion from atmosphere through mass spectrometry	?	150 Torr O ₂	1300°-1750°	2.5 10 ⁻⁶	2.71	Oishi and Kingery (1960) (19)
				N	1 Torr O ₂	975°-1150°	4.3 10 ⁻⁵	3.56	Zovner (1966) (19)
						750°-975°	4.8 10 ⁻¹⁴	1.31 ^{±.13}	
				SE	1 Torr O ₂	875°-1150°	2.4 10 ⁻⁵	3.56 ^{±.13}	
				Cr-doped N (330 ppm)	1 Torr O ₂	1000-1150°	4.8 10 ⁻¹²	1.47 ^{±.17}	
						834°-1000	1.5 10 ⁻⁸	2.36 ^{±.13}	
				Li-doped SE (380 ppm)	1 Torr O ₂	1040°-1150	1.4 10 ⁻¹¹	1.85 ^{±.22}	
				crushed sintered compact	40 Torr O ₂	1050°-1438°	4.5 10 ⁻⁷	2.61	Hashimoto et al (1972) (20)

^aShannon and Prewitt, Ref (21)

^bMorton Company, Chippewa, Ontario, Canada; S=W. & C. Spicer Ltd, Winch Comb, Gloucestershire, England; M=Monocrystals, Inc.,

Cleveland, Ohio; V=Ventron Electronics Corp., Bradford, Pennsylvania; SE=Semi Elements Inc., Saxonburg, Pennsylvania;

IR=Infra Red Development Corp., Welwyn Garden City, England; GE-General Electric Co., Schenectady, New York

^cSmall solute penetrations

^dLarge solute penetrations.

Fig 3

Fig 4

Fig. 5

Fig 6

Fig 6