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Mechanisms of Impurity Diffusion in Rutile*

N. L. Peterson and J. Sasaki**

Materials Science and Technology Division
Argonne National Laboratory, Argonne, IL 60439

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**Present address: Mitsubishi Chemical, Tokyo, Japan.

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MECHANISMS OF IMPURITY DIFFUSION IN RUTILE*

N. L. Peterson and J. Sasaki**

Materials Science and Technology Division
Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

Tracer diffusion of ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{60}Co , ^{63}Ni , and ^{95}Zr , was measured as functions of crystal orientation, temperature, and oxygen partial pressure in rutile single crystals using the radioactive tracer sectioning technique. Compared to cation self-diffusion, divalent impurities (e.g., Co and Ni) diffuse extremely rapidly in TiO_2 and exhibit a large anisotropy in the diffusion behavior; divalent-impurity diffusion parallel to the c-axis is much larger than it is perpendicular to the c-axis. The diffusion of trivalent impurity ions (Sc and Cr) and tetravalent impurity ions (Zr) is similar to cation self-diffusion, as a function of temperature and of oxygen partial pressure. The divalent impurity ions Co and Ni apparently diffuse as interstitial ions along open channels parallel to the c-axis. The results suggest that Sc, Cr, and Zr ions diffuse by an interstitialcy mechanism involving the simultaneous and cooperative migration of tetravalent interstitial titanium ions and the tracer-impurity ions. Iron ions diffused both as divalent and as trivalent ions.

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**Present address: Mitsubishi Chemical, Tokyo, Japan.

1. INTRODUCTION

The crystal structure and the atomic-defect structure significantly influence the mass-transport process in solids. The crystal structure of rutile is noncubic as may be seen in Fig. 1. The sublattice of the Ti^{4+} ions is body-centered tetragonal. Each Ti^{4+} ion is surrounded by a slightly distorted octahedron of six O^{2-} ions. These TiO_6 octahedra share edges and corners in such a way that each oxygen ion belongs to three neighboring octahedra. The titanium ions lie in rows directly along the c-axis. When the structure is viewed along the c-axis (Fig. 1(b)), it is seen that the rutile lattice has "open channels" parallel to the c-axis; open channels perpendicular to the c-axis are not apparent. The open channels may cause anisotropy in the diffusion process and may allow rapid diffusion of smaller ions parallel to the c-axis.

Fig. 1. (a) A unit cell of the rutile (TiO_2) structure. (b) An end view of the atomic arrangement for the $[001]$ axial direction. The open channel along the c-axis is indicated by the dashed lines.

Rutile is a metal-excess (or oxygen deficient) nonstoichiometric oxide. The extent of the nonstoichiometry and the major defects in rutile are still controversial. Recently Akse and Whitehurst¹ have measured cation self-diffusion over a limited range of oxygen partial pressure p_{O_2} . They conclude that tetravalent interstitial titanium ions $Ti_i^{\bullet\bullet\bullet\bullet}$ are the major atomic defects in rutile. However, measurements of nonstoichiometry and electrical conductivity suggest that oxygen vacancies and possibly trivalent interstitial titanium ions are also important defects in rutile.² In addition, the usual presence of small concentrations of Al and other impurities in rutile crystals further complicates the defect equilibrium near the stoichiometric composition.

In the present study, we present measurements of impurity tracer diffusion in rutile as functions of crystal orientation, temperature, charge state of the impurity ion, oxygen partial pressure, and concentration of Al impurity. These results provide insight into the importance of open channels for diffusion in rutile and help identify the most probable impurity-diffusion mechanisms. Since the defect structure of rutile is of importance in the interpretation of the diffusion data, the defect structure as a function of p_{O_2} , impurity content, and temperature is discussed in the next section before the diffusion measurements are presented.

2. DEFECT STRUCTURE IN RUTILE

Extensive studies of defects in rutile have been conducted as a function of oxygen partial pressure by means of thermogravimetry,³⁻⁷ electrochemical titration,⁸⁻¹⁰ electrical conductivity,^{7,11-14} tracer diffusion,¹ and ion-beam channeling¹⁵ measurements. Many of the results were interpreted in terms of only one defect, usually tetravalent interstitial titanium ions $Ti_i^{\bullet\bullet\bullet\bullet}$ or doubly charged oxygen vacancies $V_O^{\bullet\bullet}$. Kofstad² was one of the first to propose the coexistence of several defects in rutile, namely trivalent interstitial titanium ions $Ti_i^{\bullet\bullet\bullet}$, $Ti_i^{\bullet\bullet\bullet\bullet}$, and $V_O^{\bullet\bullet}$. Although Kofstad's model accurately describes the nonstoichiometry data, it is less consistent with the electrical-conductivity data. Recently Marucco et al.,⁷ using thermogravimetric and conductivity measurements, carried out an extensive study of unusually pure rutile. They obtained a satisfactory fit to the data using a defect model involving $Ti_i^{\bullet\bullet\bullet\bullet}$, $V_O^{\bullet\bullet}$, and $V_O^{\bullet}$. The existence of $V_O^{\bullet}$ is still questionable and is considered to play a significant role in the defect equilibrium only at compositions near stoichiometry. For the

purpose of interpreting the impurity-diffusion data presented in Section 3, it is more reasonable to develop a defect model for rutile based on the simultaneous existence of $Ti_1^{....}$ and $V_O^{..}$.

The formation of the principle atomic defects $Ti_1^{....}$ and $V_O^{..}$ in rutile can be described by the reactions

where Ti_{Ti}^x , O_O^x , and e' denote a neutral cation on a cation site, a neutral anion on an anion site, and an electron, respectively. Application of the law of mass action to these reactions yields

$$K_1 = [Ti_1^{....}][e']^4 p_{O_2} \quad (3)$$

and

$$K_2 = [V_O^{..}][e']^2 p_{O_2}^{1/2}, \quad (4)$$

where the square brackets denote concentrations of defects per mole of TiO_2 , and K_1 and K_2 denote equilibrium constants for reaction 1 and 2, respectively. The deviation from stoichiometry x in TiO_{2-x} is given by

$$x = 2[Ti_1^{....}] + [V_O^{..}]. \quad (5)$$

The effect of impurities may become important to the study of those properties of rutile which are sensitive to the defect concentration. The major impurity in the rutile crystals used in the present study (and a common impurity in most of the previous studies) is Al. In Al-doped rutile, the value of $[e']$ will be lower than in undoped rutile. Hence the reaction

must be considered at high p_{O_2} and low T . Application of the law of mass action to eqn (6) yields

$$K_1 = [e'][h^{\cdot}]. \quad (7)$$

In addition to the reactions expressed in eqns (1), (2), and (6), we must consider the following two reactions for Al-doped rutile

If $\text{V}_0^{\bullet\bullet}$, $\text{Ti}_i^{\bullet\bullet\bullet\bullet}$, Al_{Ti}' , e' , and h' are the primary defects in Al-doped rutile, electroneutrality requires

$$[\text{Al}_{\text{Ti}}'] + [e'] = 4[\text{Ti}_i^{\bullet\bullet\bullet\bullet}] + 2[\text{V}_0^{\bullet\bullet}] + [h'] \quad (10)$$

If Al dissolves substitutionally in $(\text{Ti}_{1-y}\text{Al}_y)\text{O}_{2-x}$, the deviation from stoichiometry is given by eqn (5). Using the definition

$$g \equiv [e'] / [\text{Al}_{\text{Ti}}'] \quad (11)$$

and eqns (3), (4), (7), and (10), one can write

$$[\text{V}_0^{\bullet\bullet}] = \frac{K_2}{4K_1} \left[-1 + \sqrt{1 + \frac{4K_1}{K_2^2} [\text{Al}_{\text{Ti}}'] \left(1 + g - \frac{K_1}{g[\text{Al}_{\text{Ti}}']^2} \right)} \right] \quad (12a)$$

$$[\text{Ti}_i^{\bullet\bullet\bullet\bullet}] = \frac{K_1}{K_2^2} [\text{V}_0^{\bullet\bullet}]^2 \quad (12b)$$

and

$$p\text{O}_2 = \frac{K_1}{[\text{Ti}_i^{\bullet\bullet\bullet\bullet}] g^4 [\text{Al}_{\text{Ti}}']^4} \quad (12c)$$

Using values of K_1 and K_2 estimated from Marucco et al.,⁷

$$K_1 = 3.3 \times 10^{11} \exp\left(-233.3 \frac{\text{kcal}}{\text{mole}} / RT\right)$$

$$K_2 = 3.0 \times 10^2 \exp\left(-105.4 \frac{\text{kcal}}{\text{mole}} / RT\right)$$

and eqn (5), one can assume values of g and calculate $[\text{Ti}_i^{\bullet\bullet\bullet\bullet}]$, $[\text{V}_0^{\bullet\bullet}]$, and x as functions of $p\text{O}_2$, T , and $[\text{Al}_{\text{Ti}}']$. Figure 2 shows the $p\text{O}_2$ dependence of $[\text{Ti}_i^{\bullet\bullet\bullet\bullet}]$, $[\text{V}_0^{\bullet\bullet}]$, and x at 1200°C for $[\text{Al}_{\text{Ti}}'] = 4.74 \times 10^{-4}$ (160 ppm by wt. Al in TiO_2). The contribution to the defect concentrations from eqn (6) is small and has been omitted from the calculations.¹⁶ The asymptotic slopes 1/5 and 1/10 are shown in appropriate locations on Fig. 2. The Magneli

Fig. 2.

Oxygen-partial-pressure dependence of defect concentrations in 160 ppm by wt. Al-doped TiO_{2-x} at 1200°C .

Fig. 3. Oxygen-partial-pressure dependence of $[\text{Ti}_i^{\bullet\bullet\bullet\bullet}]$ in 160 ppm by wt. Al-doped TiO_{2-x} . $[\text{Ti}_i^{\bullet\bullet\bullet\bullet}] > [\text{V}_\text{O}^{\bullet\bullet}]$ in region A, and $[\text{V}_\text{O}^{\bullet\bullet}] > [\text{Ti}_i^{\bullet\bullet\bullet\bullet}]$ in region B.

phases $\text{Ti}_n\text{O}_{2n-1}$ are the stable forms of TiO_{2-x} at low values of p_{O_2} . In this region, the simple point-defect theory is inappropriate, and the defect concentrations are shown as dashed lines. The location of the boundary between $\text{Ti}_n\text{O}_{2n-1}$ and the

Fig. 4. Temperature dependence of the defect concentrations in 160 ppm by wt. Al-doped TiO_{2-x} .

TiO_{2-x} phase is approximate.

Figure 3 shows the p_{O_2} dependence of $[\text{Ti}_i^{\bullet\bullet\bullet}]$ at several temperatures. The value of $[\text{Ti}_i^{\bullet\bullet\bullet}]$ varies with temperature at constant p_{O_2} even in the extrinsic region (Fig. 3); whereas $[\text{V}_\text{O}^{\bullet\bullet}]$ is virtually independent of temperature in the same p_{O_2} region. This behavior is due to the fact that $\text{Ti}_i^{\bullet\bullet\bullet}$ is not the major defect in this p_{O_2} regime. The temperature dependencies of $[\text{Ti}_i^{\bullet\bullet\bullet}]$ and $[\text{V}_\text{O}^{\bullet\bullet}]$ are shown in Fig. 4 in the form of Arrhenius plots.

Impurities may dissolve interstitially and diffuse as a freely migrating interstitial ion. The diffusion coefficient for impurity diffusion by this mechanism may be expected to be highly anisotropic with rapid transport parallel to the c-axis and may be independent of p_{O_2} .

Impurities may prefer to dissolve substitutionally and diffuse by the interstitialcy mechanism. In this mechanism, an interstitial titanium ion may jump to a substitutional site displacing the substitutional impurity ion into a neighboring interstitial site. The interstitial impurity ion may then jump to a neighboring substitutional site displacing the lattice titanium ion into a neighboring interstitial site. The diffusion coefficient for impurities diffusing by the interstitialcy

mechanism should vary with p_{O_2} and $[Al'_{Ti}]$ in the same manner as does $[Ti_i^{''''}]$. Hence, the variation of the impurity diffusion coefficient with varying p_{O_2} , $[Al'_{Ti}]$, temperature, and crystallographic direction may identify the mechanism of diffusion.

3. EXPERIMENTAL PROCEDURE

The tracer-sectioning technique has been used to determine the tracer-diffusion coefficients of ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{60}Co , ^{63}Ni , and ^{95}Zr as functions of p_{O_2} , temperature, and crystallographic orientation in single crystals of rutile. Several single-crystal rutile boules were purchased from Commercial Crystal Laboratories, Inc. The major impurity Al was specifically analyzed for, and found to be, 160 ppm by wt. in one boule and 50 ppm by wt. in a second boule. The details of the experimental

Fig. 5. Temperature dependencies of impurity diffusion coefficients in rutile in air. Cation¹⁷ and anion^{18,19} self-diffusion in air, chemical diffusion $\tilde{D}$ in CO/CO_2 gas mixtures,²⁰ lithium chemical diffusion in vacuum,²¹ and hydrogen chemical diffusion in H_2/H_2O gas mixtures²² are also shown. Diffusion lc is denoted by dashed lines.

procedures may be found in Ref. 16.

4. RESULTS AND DISCUSSION

4.1 Impurity Diffusion in Rutile in Air

The values of D^* for the diffusion of ^{60}Co , ^{63}Ni , ^{59}Fe , ^{54}Mn , ^{51}Cr , ^{46}Sc , and ^{95}Zr in rutile in air are plotted in Fig. 5 in the form of Arrhenius plots. Diffusion coefficients for other impurities reported by previous investigators are also shown in Fig. 5.

The magnitude of the diffusion coefficient is very sensitive to the charge states of the impurity. Generally, the tracer diffusion coefficient for monovalent impurities (Li,H) is larger than that for divalent impurities (Co,Ni), which is larger than that for trivalent impurities (Cr,Sc), which is larger than that for tetravalent impurities (Zr). Also, the larger the diffusion coefficient, the greater the anisotropy in the diffusion coefficient. Although the data for Li diffusion in pure rutile are not well established (the published values involve considerable concentration gradients), the value of $D_{||c}(\text{Li})$ is very large, and Johnson¹ suggests that $D_{||c}(\text{Li}) \sim 10^8 D_{\perp c}(\text{Li})$. For the diffusion of divalent impurities like Co in rutile, $D_{||c}^*(\text{Co}) > 10^3 D_{\perp c}^*(\text{Co})$. Rather little anisotropy is observed for the diffusion of the trivalent impurities Sc and Cr. Impurities that commonly coexist in both the divalent and trivalent states (Fe,Mn) diffuse at rates and with anisotropies that lie between the values observed for divalent impurities (Co,Ni) and trivalent impurities (Cr,Sc). The anisotropy in the diffusion of the tetravalent impurity Zr is opposite to that observed for the divalent impurities; $D_{\perp c}^*(\text{Zr})$ is nearly 5 times larger than $D_{||c}^*(\text{Zr})$. The mechanisms of diffusion responsible for this diverse impurity-diffusion behavior in rutile are considered in the next section where the p_{O_2} dependence of the impurity diffusion coefficients is discussed.

4.2. p_{O_2} Dependence of Impurity Diffusion in Rutile

The impurity tracer-diffusion coefficients in rutile have been measured as a function of p_{O_2} for the diffusion of ^{60}Co , ^{46}Sc , ^{59}Fe , ^{51}Cr , and ^{95}Zr . The results are particularly useful in identifying the mechanism of diffusion and are discussed in detail for ^{60}Co and ^{46}Sc . Due to space limitations the results for ^{59}Fe , ^{51}Cr , and ^{95}Zr are only mentioned.

4.2.1. ^{60}Co diffusion in rutile. Our first measurements of the p_{O_2} dependence of ^{60}Co diffusion were limited to 800 and 1000°C because of the very large values of $D_{||c}^*(\text{Co})$ at high temperatures. These values of $D_{||c}^*$ were independent of p_{O_2} because they were predominantly in the extrinsic region. Recent measurements of $D_{||c}^*(\text{Co})$ at 1100 and 1200°C in the more pure rutile (50 ppm by wt. Al) by Hoshino and Peterson²³ are shown in Fig. 6. The concentration of $\text{Ti}_i^{\bullet\bullet\bullet}$, calculated from eqn (12) for rutile containing 50 ppm by wt. trivalent ions, is also shown in the figure.

There are two features of the data in Fig. 6 that must be considered. First, the p_{O_2} dependencies of $D_{||c}^*(\text{Co})$ and $[\text{Ti}_i^{\bullet\bullet\bullet}]$ are identical. The large anisotropy in the diffusion coefficients, $D_{||c}^*(\text{Co}) \gg D_{\perp c}^*(\text{Co})$ (Fig. 5), results from rapid interstitial migration along the open channels parallel to the c-axis in the rutile structure. The p_{O_2} dependencies of $D^*(\text{Co})$ and $[\text{Ti}_i^{\bullet\bullet\bullet}]$ suggest that cobalt prefers to dissolve substitutionally in TiO_2 ; the cobalt ion is pushed into the open channels by an interstitialcy mechanism involving the simultaneous motion of

Fig. 6.

Oxygen-partial-pressure dependence of ^{60}Co diffusion in rutile containing 50 ppm by wt. Al.

$Ti_i^{\bullet\bullet\bullet}$ defects and Co ions.

Second, both the earlier data at 800°C and the data at 1100 and 1200°C in Fig. 6 show a considerable change in $D_{||c}^*(Co)$ near $p_{O_2} = 10^{-2}$ atm. This same behavior is noted in Sec. 4.2.3 for Fe diffusion in rutile. A possible explanation for this behavior is as follows. As the p_{O_2} increases, the value of $[e']$ decreases and the point of intrinsic electronic equilibrium (eqn (6)) is reached in trivalent-impurity doped TiO_2 . According to Yahia²⁴ and Rudolph,²⁵ trivalent-impurity doped rutile shows a change of electronic conductivity from n type to p type in the range $10^{-4} < p_{O_2} < 10^{-2}$ at 800°C, precisely the region where the diffusion coefficient changes rapidly with varying p_{O_2} . This change in conduction mechanism may produce an increase in the $[Co^{3+}]/[Co^{2+}]$ ratio. Since Co^{3+} may be expected to diffuse by the interstitialcy mechanism (with little anisotropy in D^*) and Co^{2+} may diffuse by an interstitial mechanism along the open channels at a much more rapid rate, a small increase in the $[Co^{3+}]/[Co^{2+}]$ ratio may produce a significant decrease in $D_{||c}^*(Co)$. The fact that the effective activation energy for $D^*(Co)$ is at least 10 kcal/mole smaller at $p_{O_2} = 10^{-4}$ atm than at p_{O_2} for air is consistent with this explanation. No change in D^* is observed in this p_{O_2} regime for impurities whose charge state is expected to be independent of the conduction mechanism.

The limited data for the diffusion of ^{63}Ni in TiO_2 (see Fig. 5) would suggest that other divalent transition-metal impurities may diffuse rapidly by the same diffusion mechanism responsible for ^{60}Co migration in rutile, with considerable anisotropy in D^* .

4.2.2. ^{46}Sc diffusion in rutile. The p_{O_2} dependence of the diffusion of ^{46}Sc in rutile is shown in Fig. 7; the results by Akse and Whitehurst¹ for cation self-diffusion in TiO_2 are also shown. Values of $D_{||c}^*(Sc)$ are proportional to $p_{O_2}^{-1/5}$ in the intrinsic region, and the anisotropy and p_{O_2} dependence of $D^*(Sc)$ are quite similar to those for cation self-diffusion in TiO_2 . The p_{O_2} dependence of $[Ti_i^{\bullet\bullet\bullet}]$ in 160 ppm by wt. Al-doped rutile is represented by the solid lines in Fig. 7; the values of $D_{||c}^*(Sc)$ are in good agreement with these lines. At 1100°C,

Fig. 7. Oxygen-partial-pressure dependence of ^{46}Sc diffusion parallel to the c-axis in rutile. All data are for rutile containing 160 ppm by wt. Al except for three points at 1100°C for rutile containing 50 ppm by wt. Al. The data for cation self-diffusion at 1058.4°C are also shown.¹

rutile samples containing two different amounts of Al impurity were used. The dot-dash line in Fig. 7 shows the theoretical curve for $D_{||c}^*(\text{Sc})$ estimated from the theory described in Section 2 (see eqn (12)) for a sample containing 50 ppm by wt. Al. Clearly, $D_{||c}^*(\text{Sc})$ is strongly coupled to the $[\text{Ti}_i^{\bullet\bullet\bullet}]$ which suggests that Sc ions move by the interstitialcy mechanism involving the simultaneous motion of Ti defects and Sc ions. This also suggests that cation self-diffusion in rutile occurs by the interstitialcy mechanism.

The temperature dependence of $D^*(\text{Sc})$ involves the temperature dependence of $[\text{Ti}_i^{\bullet\bullet\bullet}]$. Figure 8 shows Arrhenius plots for $D^*(\text{Sc})$ in rutile in air and in $p_{\text{O}_2} = 10^{-8}$ atm. Using the temperature dependencies of $[\text{Ti}_i^{\bullet\bullet\bullet}]$ for air and for $p_{\text{O}_2} = 10^{-8}$ atm shown in Fig. 4, one may obtain values of $D_{||c}^*(\text{Sc})/[\text{Ti}_i^{\bullet\bullet\bullet}]$ as a function of temperature (see Figure 8). The slope of the Arrhenius plot for $D_{||c}^*(\text{Sc})/[\text{Ti}_i^{\bullet\bullet\bullet}]$, 16.7 kcal/mole, gives the migration energy for Sc^{3+} ions via the interstitialcy mechanism plus the impurity-defect binding energy minus the temperature dependence of the correlation factor for impurity diffusion; the latter two terms tend to cancel one another and are generally small compared to the

Fig. 8. Temperature dependence of ^{46}Sc diffusion parallel to the c-axis in rutile containing 160 ppm by wt. Al. The values of $D^*(\text{Sc})/[\text{Ti}_i^{\bullet\bullet\bullet}]$ are also shown.

migration energy. The near equality of $D_{||c}^*(\text{Sc})/[\text{Ti}_i^{\bullet\bullet\bullet}]$ at $p_{\text{O}_2} = 10^{-8}$ atm and at p_{O_2} for air suggests that the mobility of Sc^{3+} ions is independent of p_{O_2} and that $\text{Ti}_i^{\bullet\bullet\bullet}$ is the principle cation defect at both values of p_{O_2} .

Scandium and other trivalent ions such as Cr (Sec. 4.2.4) diffuse through the rutile lattice by an interstitialcy mechanism and avoid the open channels parallel to the c-axis even though Cr^{3+} has a smaller ionic radius than Co^{2+} [26]. Hence the charge state of the impurity ion plays a more major role than does the size of the ion in determining the site occupancy for impurity ions in rutile.

4.2.3. ^{59}Fe diffusion in rutile. As observed for ^{60}Co tracer diffusion in rutile, the p_{O_2} dependence of ^{59}Fe diffusion

shows a large change near $p_{O_2} = 10^{-2}$ atm. The same explanation offered to account for this phenomenon for $D^*(Co)$ should also be appropriate for $D^*(Fe)$ in rutile.

The rather large anisotropy in the diffusion coefficients, $D_{||c}^*(Fe) \gg D_{\perp c}^*(Fe)$ (Fig. 5), suggests that at least a fraction of the iron ions diffuses as Fe^{2+} along the open channels parallel to the c-axis as observed for other divalent ions (Co, Ni). However, the p_{O_2} dependence of $D^*(Fe)$ suggests that a significant fraction of the iron ions dissolves substitutionally as Fe^{3+} and diffuses by the interstitialcy mechanism, as observed for other trivalent ions (Sc, Cr). The magnitude of $D^*(Fe)$ is between $D^*(Co)$ and $D^*(Sc)$, which adds further support to the idea that iron dissolves both as Fe^{2+} and as Fe^{3+} . For a detailed analysis of Fe diffusion in rutile, see Ref. 16. The limited data available for ^{54}Mn diffusion in rutile in air (Fig. 5) are very similar to those for $D^*(Fe)$, thus suggesting that both Mn^{2+} and Mn^{3+} ions contribute to diffusion.

4.2.4. ^{51}Cr and ^{95}Zr diffusion in rutile. The p_{O_2} dependencies of ^{51}Cr and ^{95}Zr diffusion were determined both parallel to and perpendicular to the c-axis. $D^*(Cr)$ and $D^*(Zr)$ are proportional to $p_{O_2}^{-1/5}$, in good agreement with the p_{O_2} dependence of $[Ti_i^{***}]$. Hence, like scandium, chromium and zirconium ions move by the interstitialcy mechanism involving the simultaneous motion of a titanium ion and an impurity ion. The slopes of the Arrhenius plots for $D^*/[Ti_i^{***}]$ suggest that the activation energy for impurity migration by the interstitialcy mechanism exhibits very little anisotropy.

5. CONCLUSIONS

The experimental results for diffusion of ^{46}Sc , ^{51}Cr , ^{54}Mn , ^{59}Fe , ^{60}Co , ^{63}Ni , and ^{95}Zr as functions of crystal orientation, oxygen partial pressure, and temperature in rutile suggest the following conclusions. (1) Compared to cation self-diffusion, divalent impurity ions (Co and Ni) diffuse extremely rapidly in rutile and exhibit a large anisotropy in the diffusion coefficients. The divalent impurity ions diffuse rapidly along open channels parallel to the c-axis and are knocked into the channels by an interstitialcy mechanism involving interstitial Ti ions. (2) Trivalent (Sc, Cr) and tetravalent (Zr) impurity ions dissolve substitutionally in rutile and diffuse by an interstitialcy mechanism involving the simultaneous and cooperative

motion of titanium ions and impurity ions. (3) Mixed-valence impurity ions (Fe,Mn) diffuse both as divalent ions by the interstitial mechanism along the channels and as trivalent ions by the interstitialcy mechanism. (4) The charge state of the impurity ion seems to play a more important role than does the size of the impurity ion in determining whether an impurity ion enters the open channels parallel to the c-axis in the rutile structure. Small trivalent impurity ions avoid the open channels; whereas larger divalent ions diffuse rapidly along these channels.

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