



# PROCESSUS DE TRANSPORT DANS LES OXYDESCATION SELF DIFFUSION IN RUTILE

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## CATION SELF DIFFUSION IN RUTILE (\*)

T. S. LUNDY and W. A. COGLAN

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

**Résumé.** — La diffusion dans le rutile ( $\text{TiO}_2$ ) est caractérisée par une extrême anisotropie avec de très grandes vitesses de diffusion parallèlement à l'axe  $c$  dans la structure tétragonale à corps centré pour des éléments interstitiels tels que le lithium et le bore. Au contraire, les éléments substitutionnels semblent diffuser dans les directions  $a$  et  $c$  à des vitesses semblables.

Nous avons examiné l'autodiffusion du cation dans  $\text{TiO}_2$  à la fois théoriquement et expérimentalement et trouvé que les coefficients de diffusion relatifs dans les deux directions peuvent être utilisés avec leurs facteurs de corrélation partiels pour identifier les sauts dans le sous-réseau cationique.

Nous considérons trois types de sauts possibles : direction  $a$ , direction  $c$  et le long de la diagonale de la maille. L'information obtenue montre que le saut diagonal ne peut pas être unique dans ce système mais doit être accompagné par une proportion appréciable de sauts dans la direction  $c$ .

Les vues développées ici peuvent être étendues à d'autres systèmes anisotropiques pour aider à l'identification des mécanismes de transport atomique.

**Abstract.** — Diffusion in rutile ( $\text{TiO}_2$ ) is characterized by extreme anisotropy with very large diffusion rates along the  $c$ -direction in the body-centered tetragonal structure for interstitial elements such as lithium and boron. In marked contrast, substitutional elements appear to diffuse in the  $a$ - and  $c$ -directions at similar rates.

We have examined cation self diffusion in  $\text{TiO}_2$  both theoretically and experimentally and find that the relative diffusion coefficients in the two directions can be used along with their partial correlation functions to identify the jumps taking place in the  $bc$  cation sublattice.

We considered three types of possible jumps :  $a$ -direction,  $c$ -direction, and along the body diagonal. The information obtained shows that the diagonal jump cannot be unique for this system but must be accompanied by a significant fraction of  $c$ -direction jumps.

Concepts developed in this research may be extended to other anisotropic systems to assist in identification of jump mechanisms for the atomic transport processes.

**1. Introduction.** — The crystal structure of rutile is illustrated in figure 1. The sublattice of  $\text{Ti}^{+4}$  ions is body-centered tetragonal with the  $c$  dimension

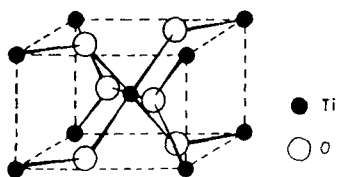


FIG. 1. — The crystal structure of rutile ( $\text{TiO}_2$ ).

much smaller than the  $a$ . According to Bauer [1],  $a = 4.594 \pm 0.003$  Å and  $c = 2.959 \pm 0.002$  Å, so that  $(c/a) = 0.644$ . If the  $c$ -axis of the specimen is oriented to coincide with the  $z$ -axis of a Cartesian coordinate system, a complete description of the diffusion of any species in a system of this crystal structure at a given temperature requires two principal diffusion coefficients, one parallel ( $D_{zz}$ ) and one perpendicular ( $D_{xx}$ ) to the  $z$ -axis. The coefficient in any direction is then given by the relation

$$D = D_{zz} \cos^2 \theta + D_{xx} \sin^2 \theta, \quad (1)$$

where  $\theta$  is the angle between the diffusion direction and the  $z$ -axis.

Deviations from stoichiometry for rutile can occur only for values of  $x$  less than 2 in  $\text{TiO}_x$  [2]. The stability range has been found to be  $1.992 \leq x \leq 2.000$  with the corresponding oxygen pressure needed to maintain the lower value of  $x$  being only  $10^{-25.7}$  atmospheres at 727 °C [3]. Two types of defects have been widely considered for substoichiometric rutile. Either oxygen vacancies or titanium interstitials are formed. Some evidence has been presented to show that below about 600 °C the oxygen vacancy dominates while above this temperature enhancement of the titanium in interstitial concentration is of prime importance [4]. The oxygen vacancy itself may be associated with two trapped electrons and two  $\text{Ti}^{+3}$  ions or it may contain only one trapped electron and be paired with a  $\text{Ti}^{+3}$  ion on a normal  $\text{Ti}^{+4}$  site. In either case, a blue coloration results from the formation of  $\text{Ti}^{+3}$  color centers with reduction of rutile by appearance of a broad absorption band in the infrared region centered at 1.2  $\mu$ . The growth kinetics of this absorption peak have been attributed to self-diffusion of titanium via a mechanism involving both cation interstitials and cation vacancies [5]. Nominally stoichiometric  $\text{TiO}_2$  is obtained by firing rutile in air at 1 100 °C [3].

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Several diffusion studies have been reported for rutile. Venkatu and Poteat [6] measured cation self-diffusion coefficients along the  $c$ -direction in rutile doped with  $\text{Al}_2\text{O}_3$  by techniques similar to those reported herein. The near-surface portions of their curved penetration plots were assumed to be related to lattice diffusion and the Arrhenius equation for the four resulting data was

$$D_{zz} = 0.064 \exp\left(-\frac{61\,400}{RT}\right) \text{ cm}^2/\text{s}. \quad (2)$$

No cation self-diffusion measurements were made for  $D_{xx}$ .

Haul and Dümbgen [7] examined the self diffusion of oxygen in  $\text{TiO}_2$  by using  $^{18}\text{O}$  and an isotope exchange technique for the temperature range 710–1350 °C. Their measurements were also made with  $\text{Al}_2\text{O}_3$ -doped rutile and, in order to explain the absence of an oxygen pressure dependence, they concluded that the impurity-induced oxygen vacancy concentration dominated. Oxygen diffusion parallel to the  $c$ -axis of the crystal was slightly slower than that perpendicular with  $(D_{zz}/D_{xx}) = 0.6$  at 1347 °C. Recently, Iguchi and Yajima [8] used electrical resistivity measurements to measure oxygen vacancy diffusion coefficients in  $\text{TiO}_2$  and found this same ratio to be approximately 2 in the temperature range of 800–1100 °C. In both cases, the slight anisotropy is dramatically in contrast with various works on impurity cation diffusion in  $\text{TiO}_2$ . For example, Johnson [9] reported that lithium diffuses along the  $c$ -axis at a rate at least  $10^8$  times faster than perpendicular to the  $c$ -axis. This phenomenon has been explained by Huntington and Sullivan [10] as diffusion along a « *rather open chimney* » in the  $[a/2, 0, z]$  direction. This chimney mechanism also appears to dominate for the diffusion of boron [11] and the transition metal ions Cr, Fe, Co and Ni in rutile [12].

In the present paper, we will examine both theoretical and experimental aspects of cation self diffusion in rutile with emphasis on identification of the atomic jump.

**2. Theory.** — Mullen [13] used the Einstein relation for a random walk mechanism, modified to include Bardeen-Herring correlation concepts, to yield theoretical expressions relating diffusion coefficients with lattice parameters, jump frequencies, vacancy concentrations, and correlation functions. He determined the effect of correlation on vacancy diffusion for several anisotropic structures by assuming allowed types of jumps and using matrix arrays of jump possibilities. For the body-centered tetragonal structure, possibilities considered were the diagonal jump ( $B$ -jump in our notation) and those along the edges of the square base ( $A$ -jumps) of the tetragonal structure. Due to the relatively small  $c$ -dimension for the  $bct$  cation sublattice of rutile, Coghlan [14] added a possible jump in this direction ( $C$ -jump,

to the Mullen model, and thereby considered all three possible atomic jumps. For this situation) the modified Einstein equations are

$$D_{zz} = c^2 N_v (v_B f_{Bz} + v_C f_{Cz}) \quad (3)$$

and

$$D_{xx} = a^2 N_v (v_A f_{Ax} + v_B f_{Bx}), \quad (4)$$

where  $c$  and  $a$  are the lattice parameters,

$N_v$  is the vacancy concentration,

$v_i$  are the jump frequencies, and

$f_{jk}$  are the partial correlation functions with  $J$  referring to the type of jump and  $k$  to its influence on the diffusion coefficient in the  $k$  direction.

The  $f_{jk}$ 's are functions of the relative jump frequencies  $v_i$  as well as of the crystal structure itself. Note that the  $A$ -jump has no influence on  $D_{zz}$  and the  $C$ -jump none on  $D_{xx}$ . Therefore  $f_{Az}$  and  $f_{Cx}$  are both absent from the expressions. The ratio of diffusion coefficients

$$\frac{D_{zz}}{D_{xx}} = \left(\frac{c}{a}\right)^2 \frac{(v_B f_{Bz} + v_C f_{Cz})}{(v_A f_{Ax} + v_B f_{Bx})} \quad (5)$$

reduces to simpler forms in limiting cases. For example, if only the  $B$ -jump is allowed, the values of  $f_{Bz}$  and  $f_{Bx}$  are equal and eq. (5) becomes

$$\frac{D_{zz}}{D_{xx}} = \left(\frac{c}{a}\right)^2 \quad (6)$$

so that lattice parameter information can be used in comparison with diffusion coefficients to verify or deny the uniqueness of this type of jump. Coghlan [14] used the assumptions and techniques of Mullen with larger arrays of atoms to perform computer calculations of  $f_{jk}$  for the  $bct$  system. Those results are illustrated in figure 2 for  $f_{Ax}$  where ratios of jump frequencies for each type of jump to the total jump

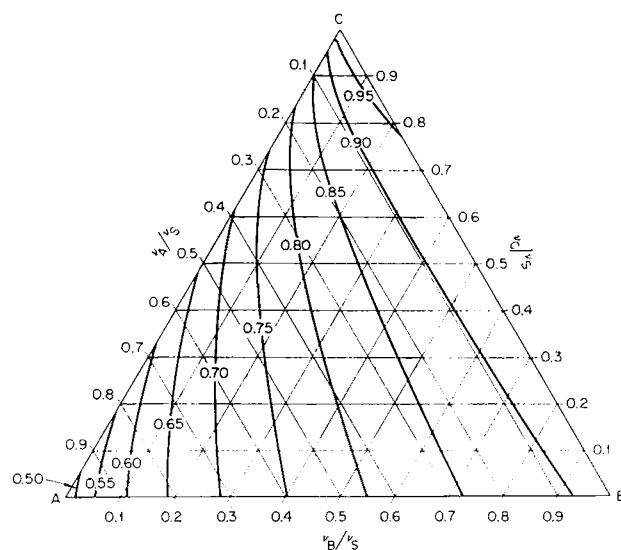


FIG. 2. — The correlation function  $f_{Ax}$  versus fractional atomic jump frequency ratios for self diffusion in a body-centered tetragonal lattice.

frequency ( $\nu_s = \nu_A + \nu_B + \nu_C$ ) are plotted along the axes. Note that for this example, as one approaches the case where only the  $A$ -jump is important for the  $bct$  lattice, the correlation function  $f_{Ax}$  approaches that for a 2-D square array of atoms, namely a value of about 0.467. For all other limiting cases such as that where the lattice changes to simple cubic ( $A$ -jumps allowed in 3-D) or body-centered cubic ( $B$ -jumps only), results of these calculations always agreed to within 0.3 % of accepted correlation factors.

From the results of these correlation function calculations, one can construct the master plot, shown in figure 3, to be used with experimental results

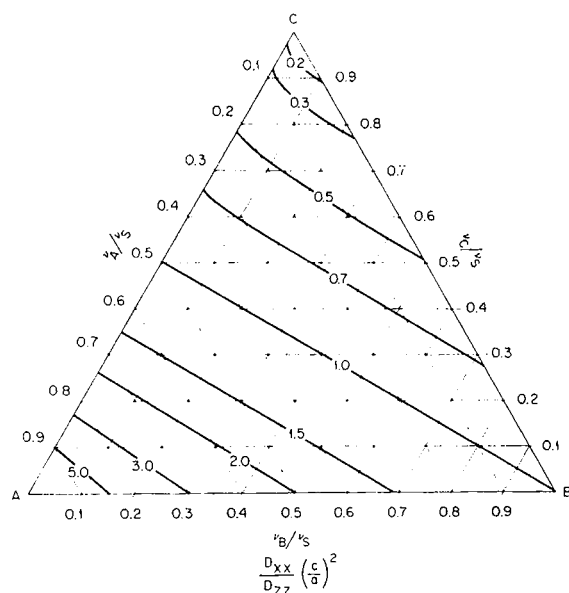


FIG. 3. — Normalized diffusion coefficient ratios versus fractional atomic jump frequencies for self diffusion in a body-centered tetragonal lattice.

of diffusion coefficient measurements to yield information on the relative importance of the different kinds of atomic jumps.

**3. Experimental.** — The diffusion coefficient measurements reported herein were performed using 99.99 % pure single crystals obtained from the Nakazumi Crystals Corp. and carrier-free  $^{44}\text{Ti}$  radioactive tracer received in 0.2  $N$  HF, 0.5  $N$  HCl solution from the International Chemical and Nuclear Corp. The crystals were cut into right-circular disks of the desired orientation with the faces subsequently polished flat. Tracer was deposited onto those faces by flash evaporations in an evacuated belljar from a tantalum filament. Isothermal diffusion anneals in air or in a flowing oxygen atmosphere were followed by serial sectioning by hand grinding. The relative tracer content of each section was found by use of a NaI(Tl) detector in conjunction with a multichannel analyzer. A semi-micro balance was used for finding section weights. This information combined with

measured diameters, material density, and normalized section activities to yield penetration profiles which were plotted as  $\ln A$  versus  $X^2$  in the usual fashion. The slopes of the linear portions of these Gaussian plots (excluding influences of short-circuiting at large penetrations) were related to the diffusion coefficients using the thin-film solution to Fick's second law. Results of this series of experiments are listed in table I and summarized in the Arrhenius

TABLE I

Diffusion coefficients for  $^{44}\text{Ti}$  in  $\text{TiO}_2$

$T^\circ\text{C}$	$D_{zz}$ $\text{cm}^2/\text{s}$	$D_{xx}$ $\text{cm}^2/\text{s}$	$D_{zz}/D_{xx}$
1 197	$0.59 \times 10^{-10}$	$1.617 \times 10^{-10}$	0.36
1 247	$1.36 \times 10^{-10}$	$2.74 \times 10^{-10}$	0.50
1 293	$1.64 \times 10^{-10}$	$5.88 \times 10^{-10}$	0.28
1 347	$3.56 \times 10^{-10}$	$4.4 \times 10^{-10}$	0.81
1 350	$4.08 \times 10^{-10}$	$4.7 \times 10^{-10}$	0.87
1 398	$6.74 \times 10^{-10}$	—	—
1 455	$9.53 \times 10^{-10}$	—	—
1 477	$1.825 \times 10^{-9}$	$2.8 \times 10^{-9}$	0.65
1 510	$2.36 \times 10^{-9}$	$2.9 \times 10^{-9}$	0.81
	Average		0.61

plots in figure 4 for both  $D_{zz}$  and  $D_{xx}$ . The temperature dependences are given by

$$D_{zz} = 0.046 \exp(-59\,900/RT) \text{ cm}^2/\text{s},$$

and

$$D_{xx} = 0.0024 \exp(-48\,500/RT) \text{ cm}^2/\text{s}.$$

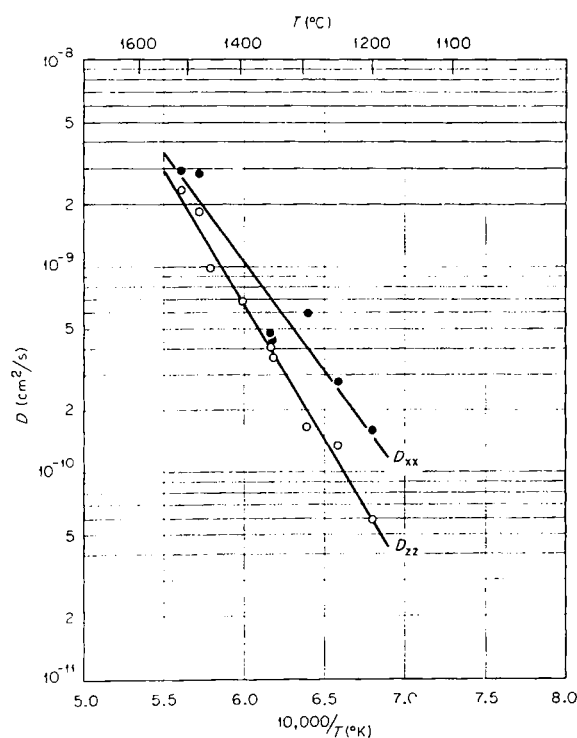


FIG. 4. — Arrhenius plots for the diffusion of Ti in  $\text{TiO}_2$ .

4. **Discussion.** — At all temperatures and for all pairs of specimens tested, the diffusion coefficient  $D_{zz}$  was smaller than  $D_{xx}$ . This result is in sharp contrast to the very large diffusion rates along the  $c$ -axis of  $\text{TiO}_2$  crystals for Li, B, Cr, Fe, Co and Ni. The «chimney» mechanism for very rapid diffusion along the  $c$ -axis does not seem to have been available to the Ti tracer. Titanium ions in the stoichiometric  $\text{TiO}_2$  would appear, therefore, to have no significant interstitial-site residence.

As previously shown in eq. (6), the ratio  $D_{zz}/D_{xx}$  can be calculated directly from lattice parameter information for the special case where only  $B$ -type jumps occur. For this situation the ratio is 0.415. Included in table I are the various experimentally determined ratios where specimens were paired. These data are plotted in figure 5 along with a smoothed curve calculated from ratios of the Arrhenius equations over the range of temperatures. The dashed horizontal line is for the diagonal  $B$ -jump. It appears that the  $B$ -jump may dominate near the lower end of the temperature range covered but that significant numbers of  $C$ -jumps must occur at higher temperatures. This can happen either by  $C$ -jumps alone

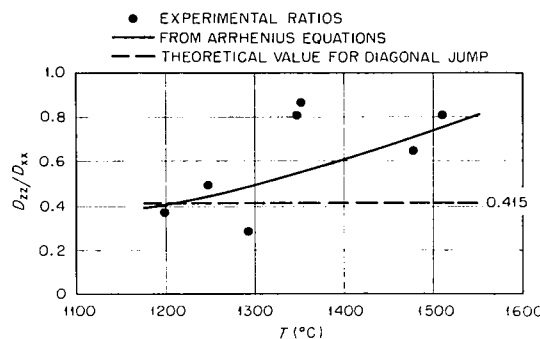


FIG. 5. — Ratios of diffusion coefficients versus temperature for Ti diffusion in  $\text{TiO}_2$ .

or by a particular combination of  $C$ - and  $A$ -jumps. Since the  $A$ -jump would be the longest of the three possible jumps, we prefer to think that  $B$ - and  $C$ -jumps are dominant for this system.

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