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Internal Friction in Rutile Containing Point Defects

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The type of point defect which is introduced into rutile by reduction caused by heating in vacuum is not firmly established although both oxygen vacancies and titanium interstitials have previously been suggested. Symmetry arguments are used to determine the orientation dependence of internal friction for both. A peak with activation energy of 23.5 kcal/mole with a computed standard error of 1 kcal/mole was observed with stress along the [100] direction which is forbidden for isolated oxygen vacancies with the full symmetry of the oxygen sites; oxygen vacancies of lower symmetry might cause this peak, but would also cause another peak which was not observed. The observed peak is permitted for titanium interstitials. Such interstitials should also cause a peak for stress directed along [110], but no such peak was observed. Full agreement with the present experimental results can be obtained by assuming that titanium interstitials are associated in pairs over the temperature range of the peak. This interpretation may not be the only way of explaining the data, particulary since we have not considered the effect of chemical impurities in association with point defects or more complicated phenomena. The evidence strongly suggests that the predominant point defect in vacuum-reduced rutile is neither a simple oxygen vacancy nor a simple titanium interstitial as is frequently assumed.

I. INTRODUCTION

The tendency of rutile (TiO_2) to lose oxygen when heated in vacuum or in hydrogen is well known and a large literature devoted to accompanying changes in physical properties has accumulated and has been surveyed.[1–4] The type of point defect which is formed when rutile is reduced has been the subject of much discussion; most investigators have assumed it to be an oxygen vacancy, but Hurlen[5] has presented crystallographic arguments favoring the titanium interstitial. Chester[6] has presented evidence that the type of defect formed in vacuum-reduced rutile may be different from the type formed in hydrogen-reduced rutile.

Further evidence on the type of defect introduced by a specific reduction process is desirable and the orientation dependence of internal friction provides some additional information. The symmetry of the crystal combined with the symmetry of the defect controls this orientation dependence and defects of different symmetry may lead to different orientation dependence. The writers have worked out the predicted dependence for both the oxygen vacancy and the titanium interstitial. They observed[7] an amplitude-independent internal-friction peak in the kc/sec frequency range with a single relaxation time and interpreted its orientation dependence in terms of titanium interstitials.

Carnahan and Brittain[8] were simultaneously studying amplitude-dependent internal friction in rutile at about 9 cps associated with dislocation motion. They extended[9] their study to confirm the existence and orientation dependence of the amplitude-independent peak with the same activation energy found by the present writers. They went on to study the effect of degree and type of reduction (vacuum or hydrogen) on this peak and of the correlation of peak height with electrical resistivity. Their work thus confirms and considerably extends the experimental work reported here and the present description of experimental work is accordingly very brief. The theory of the orientation dependence for specific types of point defects in rutile has not been given and forms the principle subject of this paper. The relation of defect symmetry to orientation dependence of internal friction can be treated either by the elastic-dipole[10,11] method or the crystallographic method.[12,13] The writers believe the methods to be equivalent insofar as predictions of the presence or absence of internal friction is concerned and the present discussion of the specific case of rutile will be based on the crystallographic method.

II. PREDICTED ORIENTATION DEPENDENCE FOR INTERNAL FRICTION IN RUTILE CONTAINING OXYGEN VACANCIES OR TITANIUM INTERSTITIALS

1. General Rules

The general idea of the crystallographic method of discussing the orientation dependence of internal fric-

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tion is that a point defect, such as an interstitial atom, can occupy any one of a set of equivalent positions in an unstrained crystal, but that strain may cause the positions to become inequivalent and that internal friction may result from the jumping of point defects to the most energetically favorable positions. A general equation [12,13] for the effect of strain upon a set of sites in causing it to split into s inequivalent subsets is

$$s=\frac{n(\mathrm{PG}_0)/n(\mathrm{PPS}_0)}{n(\mathrm{PG}_1)/n(\mathrm{PPS}_1)}, \tag{1}$$

where PG means point group of the crystal, PPS_0 means the point symmetry of the crystal about the defect position as origin, subscript zero means unstrained, subscript 1 means strained, and n indicates the order of the group within parenthesis. The use of this equation will become clear from the examples worked out in the next two sections. The principle underlying Eq. (1) is that a strained crystal will possess only those symmetry elements common to the unstrained crystal and to the strain.[14] Using this principle, one can consider the space group of the unstrained crystal and work out, for a chosen strain, the space group of the strained crystal which gives other information in addition to the s value. Equation (1) provides a quick answer for the s value for a specific set of positions in the structure and can be used as a check on the more general procedure of finding the space group of the strained crystal.

2. Behavior of Defect-Free Rutile Under Selected Stresses

The rutile structure is shown in Fig. 1. The unit cell is primitive tetragonal (not body centered, although there is a Ti atom at the body center) and contains two $\mathrm{TiO_2}$. The space group is $P4_2/mnm$, number 136 of the International Tables,[15] and the point group is $4/mmm$. The Ti atoms are at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and thus occupy the set of special positions designated a in the International Tables. The oxygen atoms are at $(x, x, 0)$, $(1-x, 1-x, 0)$, $(\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ and $(\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2})$ and thus occupy the set of positions designated f. Commonly used values of the lattice constants are[1]: $a=4.594$, $c=2.959$, and the parameter $x=0.306$.

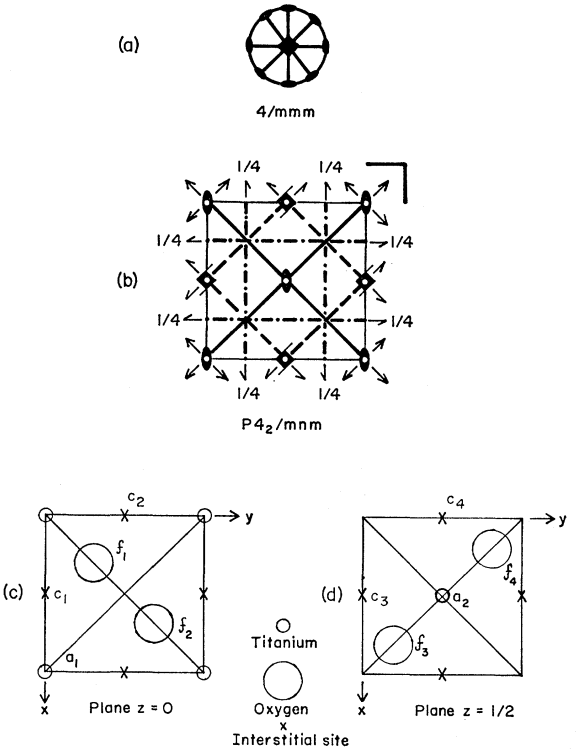

FIG. 1. Unstrained rutile. (a) Point group; (b) elements of space group associated with one unit cell. Heavy lines represent vertical mirror planes, the heavy right angle at upper right represents a horizontal mirror plane, dashed lines indicate axial glide planes, dash-dot lines represent diagonal glide planes, winged squares represent vertical-screw-tetrad axes, small circles represent inversion, ellipses represent vertical diad axes, full arrows represent horizontal diad axes, half arrows represent horizontal-screw-diad axes, horizontal elements are in the plane $z=0$, unless a height is given; (c) the plane $z=0$ of one unit cell showing titanium (small circles) and oxygen (large circles) atoms; (d) the plane $z=\frac{1}{2}$ of one unit cell. The structure is made up of a vertical stacking sequence *cdcd*, etc. In (c) and (d), the lines are used to outline unit cells and show positions of atoms; no symmetry elements are shown. The titanium ions occupy the special positions a (of the International Tables for X-ray Crystallography), the oxygen ions occupy positions f, and the sites suitable for interstitial titanium ions occupy positions c marked with a cross. In each case, only the set of points corresponding to one unit cell (two a type, four f type, and four c type) is labeled. For the unstrained crystal, all a-type positions are equivalent as are all f type and c type.

Both the present investigation and that of Carnahan and Brittain employed flexural vibration in internal-friction experiments. This vibration gives rise to a sinusoidal tensile stress parallel to the axis of the specimen plus small values of other stress components. The internal friction is proportional to the ratio of energy dissipated in one cycle of vibration to the energy stored in the specimen at maximum amplitude of vibration. Both quantities in this ratio are sums involving only squares of stress components. Small stress components thus make only second-order contributions to the internal friction and can be dropped. We therefore take our experimental conditions to be equivalent to a tensile stress along the specimen axis. Specimens used in this work had three orientations of their rod axes: [001], [100], and [110]. These three orientations were chosen for study because a tensile stress along any one of these axes leads to a simple lowering of symmetry. Tensile stress applied in any other nonequivalent direction causes a greater lowering of symmetry, but such an experiment would give no additional information concerning oxygen vacancies or octahedral interstitials

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of full symmetry because the pattern of inequivalence set up by this stress would be a combination of the patterns existing in the crystals with [100] and [110] axes. This result will be shown by tabulating the effect of all types of specimen orientation after the method has been made clear by considering these three orientations in detail.

We now wish to discuss the lowering of symmetry by stress in each of the three specimen orientations. For each type of specimen, we take the symmetry elements of the strained crystal to be those common to the crystal and to the stress for the appropriate relative orientation of crystal and stress. The point symmetry elements of tensile strain have been discussed[13] and those for tensile stress are the same for the crystal orientations considered here. The present symmetry arguments are the same if the discussion is carried out in terms of either an applied tensile stress or strain. We chose stress for this discussion. The point symmetry elements for a tensile stress are those of an ellipsoid of revolution with its unique axis parallel to the axis of the stress. Thus, its point group is ∞/mm and contains an infinitefold axis perpendicular to a mirror plane; every plane through the infinite-fold axis is also a mirror plane.

For the [001] specimen, the infinitefold axis of the stress (which includes a fourfold axis) coincides with the fourfold axis of the original crystal point group and every mirror plane of the original point group also coincides with a mirror plane of the stress. Thus, for the c-axis rod, the stress does not change the point group. The same conclusion holds for the space group. In the latter, glide planes may correspond to mirror planes of the point group, but the glide planes will remain unless the corresponding mirror planes of the point group are destroyed by the stress. The only effect of tensile stress on the [001] crystal is thus to change the c/a ratio.

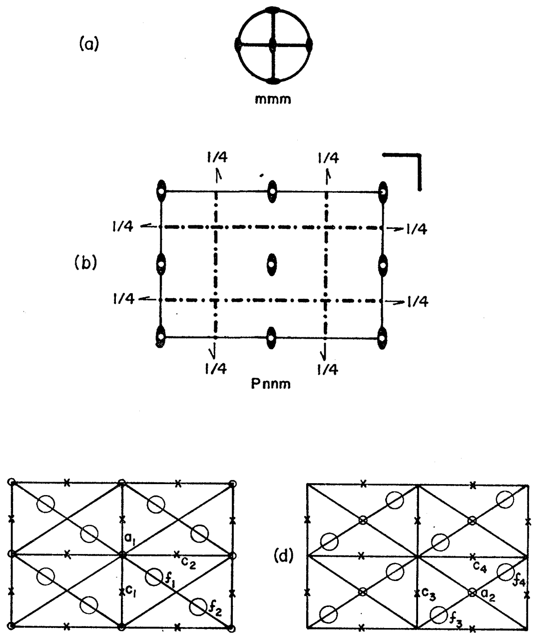

FIG. 2. Rutile under tensile stress along y axis. The point group, space group, and the two layers making up the unit cell are shown as in Fig. 1. The unit cells in (c) and (d) have been drawn to half the scale of (b) so that four unit cells could be shown in both (c) and (d). Examination of the symmetry operations shows that the following equivalences hold: $a_1=a_2$; $f_1=f_2=f_3=f_4$; $c_1=c_4$; and $c_2=c_3$. However, the stress has caused the following inequivalence $c_1\neq c_3$.

For the [100] specimen, the infinitefold axis of the stress coincides with the x or y direction and the point group is lowered to mmm. The point group mmm occurs in two settings as a subgroup of the original point group $4/mmm$. The setting shown in Fig. 2 results because only mirror planes perpendicular or parallel to the direction of tensile stress remain. In the space group, the corresponding mirror planes or glide planes remain and the resulting space group is $Pnnm$ of the International Tables.[14,15] Figure 2 shows the resulting point group, space group, and atomic positions; the tensile stress has been taken along the y axis for convenience in drawing.

For the [110] specimen, the infinitefold axis of the stress is equidistant from two a axes and perpendicular to the z axis. The mirror planes parallel or perpendicular to this infinite-fold axis remain in the point group which yields the point group mmm in the second setting; i.e., at 45° to the setting obtained by tensile stress along the x axis. In the space group, the mirror planes or glide planes corresponding to mirror planes of the point group remain and the resulting space group is $Cmmm$. Figure 3 shows the point group, space group, and atomic positions in the strained [110] crystal. The space group $Cmmm$ has been drawn in the same orientation as the strained crystal; if comparison is made with the International Tables it should be noted that the figure shown there is rotated 45° from our setting.

3. Predicted Orientation Dependence of Internal Friction Assuming Oxygen Vacancies of Highest Symmetry

We first assume that the removal of an oxygen atom to create an oxygen vacancy does not change the symmetry of the surrounding crystal. The oxygen atoms are at positions having point symmetry mm (the full symbol $mm2$ is usually abbreviated as mm) and we assume that, although the neighboring atoms move when an oxygen atom is removed, the motion is constrained by the bulk of the crystal so that the symmetry of the local distortion is still mm. We shall subsequently discuss the effect on our agrument if the local distortion has lower symmetry.

We can now use Eq. (1) to give the splitting factor s for each of the three crystal orientations used in our work. The calculations are shown in Table I. The effect of stress on position point symmetry, PPS is found as before by considering what symmetry elements are common to the stress and to the starting symmetry.

TABLE I. Number of inequivalent sets s for oxygen sites and for titanium interstitial sites in rutile.

			Tension parallel to		
		Unstrained	[001]	[100]	[110]
Point group	PG	$4/mmm$	$4/mmm$	mmm	mmm
	n(PG)	16	16	8	8
Oxygen sites	PPS	mm	mm	m	mm
	n(PPS)	4	4	2	4
	s	1	1	1	2
Ti interstitial sites	PPS	$2/m$	$2/m$	$2/m$	$2/m$
	n(PPS)	4	4	4	4
	s	1	1	2	2

The s values of Table I for oxygen positions have the following implication for internal friction. For the [001] or [100] crystals under tension, $s=1$, which means that all four oxygen positions per unit cell remain equivalent. Therefore, an oxygen vacancy would have no preference for any particular position and hence no jumping of oxygen vacancies (apart from the random jumping which occurs in the absence of stress) should occur and hence no internal friction should result. For the [110] crystal, $s=2$, so that the oxygen positions split into two sets which are not equivalent. Thus, an oxygen vacancy should prefer sites of one set to those of the other and internal friction should result if the tensile stress on a [110] crystal alternates at a frequency approximately equal to the jump frequency of the oxygen vacancies.

These results have been derived in a formal manner using Eq. (1); these results can be verified by inspection of the drawings of the strained crystals in Figs. 2 and 3, and insight into the actual atomic movements can be obtained. The rutile structure can be described as being being made up of chains O-Ti-O···O-Ti-O. One set of chains runs in the [110] direction and one in the [1$\bar{1}$0] direction. Stress along [100] or [001] affects the two sets of chains equally, but stress along [110] stretches one set of chains and shortens the other (by the Poisson's ratio contraction). The latter stress makes the oxygen positions in one set of chains inequivalent to those of the other set; within either set the oxygen positions remain equivalent. Internal friction might then result from jumps of oxygen vacancies from positions of type f_1 or f_2 to those of type f_3 or f_4 as shown in Fig. 3.

4. Predicted Orientation Dependence of Internal Friction Assuming Titanium Interstitials of Highest Symmetry

Hurlen[5] has pointed out the suitability for occupancy by titanium interstitials of the sites in the centers of the {100} faces and the equivalent sites in the edges of these faces perpendicular to the [001] direction. There are four of these equivalent octahedral positions (labeled c in the International Tables[15]) per unit cell and we take the set c_1, c_2, c_3, c_4, which have coordinates, respectively, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$. We make an assumption for these interstitials corresponding to our assumption for oxygen vacancies. We assume that the initial symmetry, $2/m$, of the crystal seen from the interstitial site is not changed by the insertion of a titanium ion. The effect of lower symmetry will be discussed later.

The calculation of s values from Eq. (1) is outlined in Table I. As before, these results can be verified and understood by reference to Figs. 2 and 3. Each interstitial site is equidistant from two nearest-neighbor oxygen ions and it is the motion of these two ions when the crystal is stressed which is most important in determining the resulting equivalence or inequivalence of interstitial sites. Figures 2(c)–2(d) show that the set of four interstitial sites splits into two sets under tensile stress along [010]. In one set, consisting of c_1 and c_4 (which remain equivalent because a suitable glide plane remains), the interstitial-to-oxygen distance is increased; in the other set, consisting of c_2 and c_3, the interstitial-to-oxygen distance is decreased. One would expect a preference of interstitials for the former set with the crystal under tensile stress along [100] and a driven motion back and forth between the sets of positions if the stress alternates with a frequency equal to, or less than, the jump frequency for interstitials. The pattern of in-

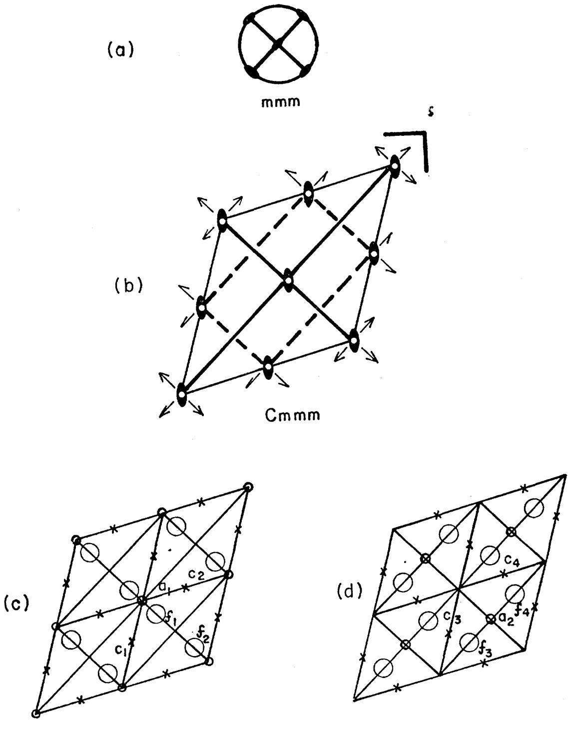

FIG. 3. Rutile under tensile stress which is in the xy plane and which makes equal angles with x and y axes. The unit cells in (c) and (d) have been drawn to half the scale of (b) so that four unit cells could be shown in both (c) and (d). Examination of the symmetry operations shows that the following equivalences hold: $f_1=f_2$; $f_3=f_4$; $c_1=c_2$; and $c_3=c_4$. However, stress has caused the following inequivalences: $a_1 \neq a_2$; $f_1 \neq f_3$; and $c_1 \neq c_3$.

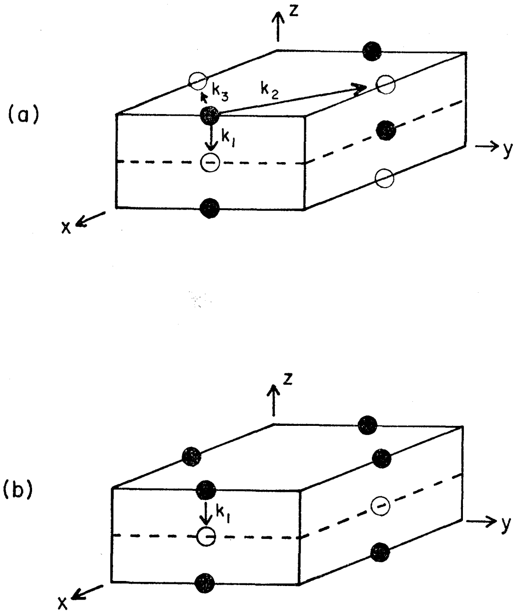

FIG. 4. Pattern of equivalence for Ti-interstitial positions in rutile. (a) Tensile stress along the [100] direction, and (b) tensile stress along the [110] direction.

equivalence set up by [100] tension is shown in Fig. 4(a). Interstitials can jump from one set to a nearest neighbor in the other set in any one of three ways as shown by the paths labeled k_1, k_2, and k_3 in Fig. 4(a). Examination of the atomic positions shows that the three paths are not equivalent, but that for each of these a jump in the opposite direction is equivalent to the jump being considered. There are thus a total of six ways (three pairs) for an interstitial to jump from a site on one set of positions to a nearest neighbor site in the other set.

If there are initially n more interstitials per cm^3 on one set than the other, this difference will decay (in the unstressed crystal) according to

$$dn/dt=-4(k_1+k_2+k_3)n \tag{2}$$

which has the solution

$$n(t)=n(o)\exp(-t/\tau) \tag{3}$$

where τ, the relaxation time, is equal to $1/4(k_1+k_2+k_3)$.) Relaxation processes described by this type of equation are very familiar in electrical[16] or mechanical[17–19] studies. In either case, the mathematics is formally the same and need not be repeated here. The result for the internal friction Q^{-1} times absolute temperature T can be obtained following the method of Ref. 19 and is

$$TQ^{-1}=C(\partial u/\partial\sigma)^2\omega\tau/(1+\omega^2\tau^2)\,, \tag{4}$$

where $C=YN/4k$, Y is Young's modulus, N is the number of interstitials per cm^3, and k is Boltzmann's constant; u is the difference in energy between sites caused by stress σ, and ω is frequency. Each of the k_i appearing in τ is thermally activated and can be written

$$k_i=k_{io}\exp(-E_i/kT)\,, \tag{5}$$

where k_{io} is a constant with the dimensions of frequency, E_i is the activation energy, and k is Boltzmann's constant. If two of the three k_i appearing in τ can be neglected compared to the third, then τ can be written as a single term involving an exponential and the function on the right-hand side becomes a hyperbolic secant. Our data fit this functional form and lead us to believe that one of the three k_i is predominant; examination of the structure suggests that k_1 is predominant because it appears to involve the least displacement of the surrounding ions. For most atomic-jump processes in solids, k_{io} is 10^{12}/sec or greater. In our work, k is about 1×10^{17}/sec and ω is about 10^4/sec, which means that the exponential is of order 10^{-13} at the internal friction peak. We find an activation energy of about 1 eV for the predominant process, presumably the k_1 jump. If the activation energies for the k_2 and k_3 jumps are only 20% larger than for k_1, their exponential factors decrease to 0.002 of the k_1 value. It thus appears reasonable to drop k_2 and k_3, and take $\tau=1/4k_1$. For the [100] crystal, Eqs. (4), (5), and the definition of the hyperbolic secant give

$$TQ_{100}^{-1}=A_{100}\left(\frac{\partial u}{\partial\sigma_{100}}\right)^2\operatorname{sech}\left(\frac{E}{kT}+S\right)\,, \tag{6}$$

where $E=E_1$, $S=\ln(\omega/4k_1)$, and $A_{100}=Y_{100}N/8k$.

The application of tensile stress along the [110] direction also splits the original set of four interstitial positions into two sets but the pattern of inequivalence is different. The mirror planes are retained, as shown in Fig. 2(b), and we have $c_1=c_2$, $c_3=c_4$, and $c_1\neq c_3$. The resulting pattern is shown in Fig. 4(b). Only the k_1 jump is effective now and we have $\tau=1/4k_1$. The reasoning goes as before and we obtain

$$TQ_{110}^{-1}=A_{110}\left(\frac{\partial u}{\partial\sigma_{110}}\right)^2\operatorname{sech}\left(\frac{E}{kT}+S\right)\,, \tag{7}$$

where E and S are the same as in Eq. (6) because the same atomic jumps are involved and $A_{110}=Y_{110}N/8k$. Then

$$A_{110}/A_{100}=Y_{110}/Y_{100}\,, \tag{8}$$

and we have

$$(Q_{110}^{-1}/Q_{100}^{-1})=Y_{110}\left(\frac{\partial u}{\partial\sigma_{110}}\right)^2\bigg/Y_{100}\left(\frac{\partial u}{\partial\sigma_{100}}\right)^2. \tag{9}$$

To evaluate $(\partial u/\partial\sigma)$, we assume that the change in u with strain depends primarily on the change in the distance to the nearest-neighbor oxygen ions. For interstitial positions c_1 and c_3 with corresponding energies

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u_1 and u_3 for titanium ions, we have $u=u_1-u_3$ and

$$\frac{\partial u}{\partial \sigma}\cong\frac{\partial u_1}{\partial d_1}\frac{\partial d_1}{\partial \sigma}-\frac{\partial u_3}{\partial d_3}\frac{\partial d_3}{\partial \sigma}. \tag{10}$$

Now both u_1 and u_3 depend on their respective d in the same manner, and because the partials are to be evaluated at $d_1=d_2$ and $\sigma=0$, we have

$$\frac{\partial u}{\partial \sigma}=\frac{\partial u_1}{\partial d_1}\left(\frac{\partial d_1}{\partial \sigma}-\frac{\partial d_3}{\partial \sigma}\right). \tag{11}$$

It is convenient to use $\partial d_i/\partial\sigma=(\partial d_i^2/\partial\sigma)/2d_i$ and work with d_i^2. The partials of d_1^2 and d_2^2 can be approximated by assuming that macroscopic elasticity describes the ionic motions under stress. Thus, under σ_{100} the oxygen ion originally at $(\alpha, \alpha, 0)$ moves to $(\alpha(1+s_{11}\sigma_{100}), \alpha(1+s_{12}\sigma_{100}),0)$ and the interstitial position c_1 originally at $(0.5, 0, 0)$ moves to $(0.5(1+s_{11}\sigma_{100}), 0, 0)$, where the s_{ii} are the elastic compliances.[20] Then d_1^2 becomes

$$d_1^2=(\alpha-(0.5)^2(1+s_{11}\sigma_{100})^2+\alpha^2(1+s_{12}\sigma_{100})^2, \tag{12}$$

and the partial derivative evaluated at zero stress becomes

$$\partial d_1^2/\partial\sigma_{100}=2s_{11}(\alpha-0.5)^2+2s_{12}\alpha^2. \tag{13}$$

The same line of reasoning applies to position c_3 and one finally obtains

$$\partial(d_1-d_3)/\partial\sigma_{100}=(s_{11}-s_{12})[(\alpha-0.5)^2-\alpha^2]/d. \tag{14}$$

The same calculation can be carried out for a tensile stress in the [110] direction. In this case, it is convenient to use a rotated coordinate system having x' along [110] and use the elastic compliances s'_{ij} expressed in this rotated system. The result is

$$\partial(d_1-d_3)/\partial\sigma_{110} =(s'_{11}-s'_{12})[4(\alpha-0.25)^2-0.125]/d. \tag{15}$$

We now note that $Y_{100}=1/s_{11}$, $Y_{110}=1/s'_{11}$, and define the Poisson ratio values $\nu_{100}=-s_{12}/s_{11}$ and $\nu_{110}=-s'_{12}/s'_{11}$. Combining Eqs. (9), (11), (14), and (15) gives

$$\frac{Q_{110}^{-1}}{Q_{100}^{-1}}=\left(\frac{Y_{100}}{Y_{110}}\right)\frac{(1+\nu_{110})^2}{(1+\nu_{100})^2}\left[\frac{4(\alpha-0.25)^2-0.125}{(\alpha-0.5)^2-\alpha^2}\right]^2. \tag{16}$$

Using the elastic constant of rutile,[20] one obtains $Y_{100}/Y_{110}=0.404$, $\nu_{100}=0.605$, and $\nu_{110}=0.0715$. Using $\alpha=0.306$ gives $Q_{110}^{-1}/Q_{100}^{-1}=0.73$.

Our conclusions concerning internal friction caused by jumping of isolated titanium ions can now be summarized: For the [001] crystal, the internal friction due to this cause should be strictly zero. Internal friction should occur for both the [100] crystal and the [110] crystal; the present theory can not predict the absolute size of the peak but is capable of a rough prediction of the relative sizes of the peaks for the [110] and [100] crystals. A numerical estimate indicates that the value for the [110] crystal should be about 0.73 of the value for the [100] crystal.

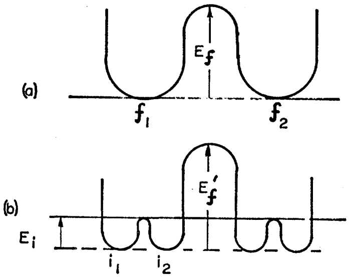

FIG. 5. Potential-energy curves: (a) represents the situation for an oxygen vacancy which occupies the oxygen sites f_1 or f_2 with full symmetry of the oxygen position; (b) represents the situation for an oxygen vacancy which can occupy either of two sites i_1 and i_2 of lower symmetry neighboring a single oxygen position f_1.

5. Predicted Orientation Dependence of Internal Friction Assuming Isolated Oxygen Vacancies of Lower Symmetry

It was convenient to divide our discussion of the behavior of point defects into two parts corresponding to two situations. First, a point defect may occupy a site in such a way that the full site symmetry is preserved. Each oxygen ion in rutile has point symmetry *mm*. Removal of an oxygen ion to form a vacancy will be accompanied by some displacement of the neighboring ions, but it is geometrically possible for the point symmetry *mm* to be preserved. In this situation, the potential-energy curve for an oxygen vacancy can be represented as in Fig. 5(a). Here E_f is the activation energy for a jump from one oxygen site of full symmetry to another. The detailed predictions for this first situation have been given in the last two sections. Second, the energy may be reduced if the local distortion is such that the point symmetry of the defect is lowered to a subgroup of the original point symmetry. If so, there must be a number of equivalent ways for this to happen equal to the order of the group of the original point symmetry divided by the order of the group of the final point symmetry. Thus, if an oxygen site with symmetry *mm* and order 4 goes to a vacancy with symmetry *m* of order 2, there must be two equivalent ways for this to happen. In this situation, the potential energy curve can be represented as in Fig. 5(b). Here E'_f represents a jump from one oxygen position to another and E_i represents a jump between the two oxygen vacancy positions corresponding to a single oxygen ion position. We now explore the ways that the second situation can arise and determine which can lead to internal friction.

The symmetry of the oxygen site *mm* can be lowered to *m* in two ways. First, the vertical mirror plane (i.e., the plane parallel to the *z* axis) may be lost. This cor-

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[20] J. B. Wachtman, Jr., W. E. Tefft, and D. G. Lam, Jr., J. Res. Natl. Bur. Std. (U. S.) **A66**, 465 (1962).

TABLE II. Splitting of all types of sites in rutile under all types of stress.

Wycoff symbol	PPS	Number of inequivalent sets resulting from tension parallel to						
		[001]	[100]	[110]	[*hk*0]	[*h*0*l*]	[*hhk*]	[*hkl*]
a	*mmm*	1	1	2	2	1	2	2
b	*mmm*	1	1	2	2	1	2	2
c	2/*m*	1	2	2	4	2	2	4
d	$\bar{4}$	1	1	1	2	1	1	2
e	*mm*	1	1	2	2	1	2	2
f	*mm*	1	1	2	2	1	2	2
g	*mm*	1	1	2	2	1	2	2
h	2	1	2	2	4	2	2	4
i	*m*	1	2	2	4	2	2	4
j	*m*	1	1	2	2	2	3[a]	4
k	1	1	2	2	4	4	4	8

[a] Unequal splitting, 8 → 4+2+2. For specification of Wycoff positions in the rutile space group, see space group No. 136 in Ref. 15. The *a* sites are occupied by titanium, the *f* sites are occupied by oxygen, and the *c* sites are the octahedral interstitial positions which may be occupied by excess titanium.

responds to going from the original Wycoff position[15] *f* to either of two equivalent Wycoff positions, i_1 or i_2, symmetrically placed with respect to the lost vertical mirror plane. These two positions are equivalent because the bulk of the crystal retains the vertical mirror plane and a local distortion on one side of it will have the same relationship to the rest of the crystal as a symmetrical distortion on the other side. Internal friction can arise from jumps of the type i_1 to i_2 only if the applied stress removes the vertical mirror plane in the bulk of the crystal. This plane remains under tensile stress on the [001] or [110] crystal, but is removed by tensile stress on the [100] crystal.

The symmetry *mm* of the oxygen site can alternatively be lowered to *m* by removing the horizontal mirror plane (i.e., the plane perpendicular to *z*). This corresponds to going from the original Wycoff position *f* to either of two equivalent Wycoff positions,[15] j_1 or j_2, symmetrically placed with respect to the lost horizontal mirror plane. To remove the equivalence of j_1 and j_2 would require removal of the horizontal mirror plane from the bulk of the crystal and this cannot be done by homogeneous tensile stress on any one of the three crystals used.

Such a lowering of symmetry is predicted by the Jahn-Teller theorem and is known to occur for some ions in crystals.[21] The magnitude of the corresponding energy reduction depends on the details of the situation, but estimates up to 0.1 eV have been given.[21] This is a rather low value compared to the activation energy for motion of point defects of the type important in material transport processes, which is found[22] to range upward from above 0.4 eV for the alkali halides and is probably higher for rutile. If E_i of Fig. 5(b) is significantly different from E'_f, one might expect to see two internal-friction peaks in rutile containing oxygen vacancies. One peak should occur only in the [100] crystal and at a temperature for which the jump frequency ν_1 between the *i*-type sites neighboring a single *f*-type site approximately equals the experimental frequency. If the temperature is raised sufficiently to make ν_f, the jump frequency corresponding to E'_f, equal to the experimental frequency, a second peak should occur only in the [110] crystal.

6. Predicted Orientation Dependence of Internal Friction for Titanium Interstitials of Lower Symmetry

The titanium interstitial sites of symmetry 2/*m* could be lowered either to 2 or to *m* by local distortion accompanying insertion of the titanium ion. The former possibility corresponds to going from Wycoff position *c* to either of the positions h_1 or h_2 symmetrically placed with respect to the horizontal mirror plane possessed by the bulk crystal, but not by the local distortion. Production of internal friction by jump from h_1 to h_2 requires loss of this horizontal mirror in the bulk of the crystal and this cannot be accomplished by tensile stress on any of the three crystals considered. The latter possibility corresponds to going from Wycoff position *c* to either of the two positions i_3 or i_4 symmetrically placed with respect to the twofold axis through the *c* position which is possessed by the bulk of the crystal, but not by the defect. Production of internal friction by jump from i_3 to i_4 requires removal of this twofold axis and this cannot be accomplished by tensile stress on any of the three crystals considered. Thus, the lowering of symmetry of the titanium interstitial site leads to no new possibility of internal friction caused by the jumping of titanium interstitials for the three crystal orientations considered here.

In the above discussion, positions i_3 and i_4 were used to distinguish from positions i_1 and i_2 used in the discussion of possible low-symmetry oxygen vacancy sites. In each case, the set of eight *i*-type Wycoff positions is being considered, but it is considered with different pairings and different locations in the crystal; for oxygen vacancies it is the symmetrical pairs neighboring four *f*-type positions and for titanium interstitials, it is the symmetrical pairs neighboring four *c*-type positions.

7. Summary of Predictions Concerning All Isolated Sites of Full Symmetry for All Types of Homogeneous Stress

The point group of rutile, 4/*mmm*, can go to the subgroup *mm* in either of two settings depending on whether tensile stress is applied parallel to [100] or [110]. We have considered these possibilities, but there remain [12] the possibilities of further reduction to 2/*m* or still further to $\bar{1}$. The subgroup 2/*m* can be obtained in three inequivalent setting depending on whether tensile stress is applied parallel to the [*h k* 0], [*h* 0 *l*], or

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[21] D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 399.

[22] J. S. Dryden and R. J. Meakins, Discussions Faraday Soc. 23, 39 (1957).

[*h h k*] directions. For each case, the number of inequivalent sets into which any given set splits can be worked out as previously shown. The results are summarized in Table II for every type of position in the rutile space group. One curiosity is the behavior of the set of eight *j*-type positions which split under tensile stress parallel to [*h h k*] into three subsets of four, two, and two positions instead of splitting into equal subsets as for all other stresses and positions. Such behavior is fairly common in some space groups.

The results concerning splitting of full-symmetry oxygen vacancy or titanium interstitial sites have been confirmed by Bhagavantam and Pantulu[23] by an argument which has the same physical basis, but which uses representation theory in the manner of Ref. 19.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. Specimens

The three crystals used in this investigation were taken from a set previously used in a determination of single crystal elastic constants. The reader is referred to the text and to Table I of that paper[20] for a complete specification of the crystals; in the notation of that table our [001], [100], and [110] crystals are, respectively, specimens numbers 41, 49, and 44. The specimens were machined into cylinders and heated for about 24 h at 800°C in flowing O_2 at 1 atm pressure. The resulting crystals were regarded as stoichiometric. Reduced crystals were produced by heating on platinum in an Al_2O_3 tube in vacuum (mechanical pump producing about 20 μ with a liquid-nitrogen cold trap to prevent oil from reaching the specimen.) Specimens were held for 1–3 h at temperatures near 1260°C. The temperature was then reduced to 975°C at an approximately constant rate of 2° per min and the furnace was then shut off. The objective was to produce a large degree of reduction consistent with remaining in the single-phase field. Two terminal resistance measurements indicated resistivities around 5–10 Ω-cm on the [001] and [110] crystals. The resistivity of the [100] crystal was not determined, but its weight loss was only about one-third as great, indicating a proportionately higher resistivity. The weight loss of the [100] crystal indicated a composition of $TiO_{1.995}$.

Carnahan and Brittain[9] have found that our data on this [100] axis crystal are consistent with their plot of peak temperature as a function of frequency if a resistivity of 21 Ω-cm is assumed. The present writers have not attempted to study the observed phenomena as a function of resistivity because this has been done by Carnahan and Brittain.[9]

2. Experimental Technique

The variation of internal friction and of Young's modulus with temperature was determined by Forster's method in which a bar is suspended horizontally from two threads (fiberglass was used in this investigation) tied near the nodes of flexural vibration. One thread was driven by a magnetic record-cutting head and the other was attached to a piezoelectric pickup. The driving frequency was varied until resonance occurred. The drive was then shut off and the resulting damped oscillation was recorded on a storage oscilloscope. The internal friction value was then calculated from the time for the amplitude to decay to one half its original value. Measurements were made in vacuum of about 50 μ and the background value of Q^{-1} was as low as 2 or 3×10^{-5} when the specimen was carefully hung.

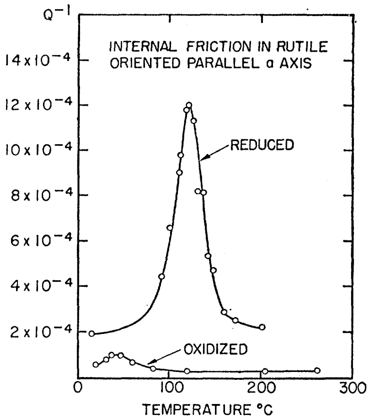

Fig. 6. Internal friction of a [100] rutile crystal as a function of temperature.

IV. RESULTS

1. Unreduced Specimens

Measurements on unreduced specimens gave a small peak for the [100] crystal ($Q^{-1}=10\times10^{-5}$ at 50°C and 1842 cps) and for the [110] crystal ($Q^{-1}=21\times10^{-5}$ at 60°C and 5629 cps), but no peak was observed for the [001] crystal. Figure 6 shows the small peak for the [100] specimen. Measurement on a polycrystalline specimen also revealed this peak ($Q^{-1}=14\times10^{-5}$ at 53°C and 2583 cps) and a curve-fitting procedure was used to obtain an activation energy from peak shape of 14±0.4 kcal/mole[24] and a pre-exponential value of $2.7\times10^{+14}$ $\sec^{-1}$. The changes in peak temperature caused by measurement at different frequencies are too small compared to the uncertainty of peak temperature to permit a reliable calculation of activation energy from peak shift. This peak diminished in amplitude or disappeared entirely when the specimens were vacuum reduced and reappeared when they were reoxidized.

2. Vacuum-Reduced Specimens

No peak was found for the [001] or [110] crystals. The latter was carefully examined and the damping

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[23] S. Bhagavantam and P. V. Pantulu, Proc. Indian Acad. Sci. **58**, 183 (1963).

[24] In expressions of the form $a\pm b$, "a" is a constant fitted by the method of least squares through 16 data points, and "b" is the computed standard error of "a." The thermochemical calorie defined as 4.184 J is used here.

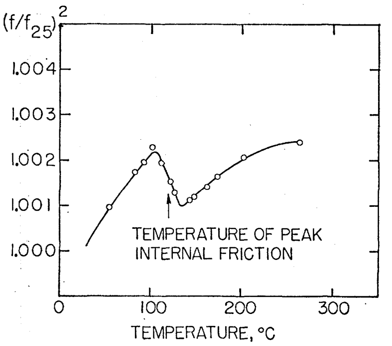

FIG. 7. Resonance frequency ratio for a [100] rutile crystal after reduction. Curve is for same state of reduction as reduced curve of Fig. 6.

was not greater than 3×10^{-5} from 100 to 575°C. In contrast, a large peak was found in the [100] crystal ($Q^{-1}=120\times10^{-5}$ at 120.8°C and 1838 cps). The curve-fitting procedure gave an activation energy of 23.5±1.0 kcal/mole and a pre-exponential value of $k_{10}=1.2\times10^{17}$ sec.

The curve of Young's modulus as a function of temperature for unreduced rutile shows a small increase with increasing temperature from 25°C up to about 300°C. For vacuum-reduced rutile, we expect to see a drop in this curve associated with the internal friction peak (predicted by the usual model of the standard linear solid[17,18]) and this was found as shown in Fig. 7.

V. DISCUSSION

1. Small Peak

The small peak, characterized by an activation energy of 14 kcal/mole, is apparently not caused by the point defect which vacuum reduction introduces into rutile. Gerritsen[25] has examined the spin-resonance spectra resulting from various impurity ions in rutile. It was found [25,26] that most of the nickel in solid solution is in the octahedral interstitial positions; i.e., the type *c* sites. Such ions should give an internal friction peak for both [100] and [110] directions as observed. Routine spectroscopic analysis of a crystal prepared in the same manner as the [100] crystal did not show the presence of nickel,[20] but this evidence alone was not considered to be conclusive proof and the possibility remains that the observed peak is due to a trace of undetected Ni. Preliminary measurements[26] on specimens containing 0.1% Ni show an internal friction peak for both [100] and [110] directions. The results obtained so far indicate that the activation energy and peak temperature agree with those observed for the present small peak and suggest that the latter may be caused by Ni despite the negative result of the spectroscopic analysis. Further work on the dependence of peak height on Ni content is needed. Preliminary results on specimens doped with chromium show a similar peak so that the small peak reported here cannot be definitely assigned either to Ni or Cr.

2. Implications of Large Peak Concerning the Type of Defect in Vacuum-Reduced Rutile

The large peak is well established experimentally and the present value of 23.5±1 kcal/mole for the activation energy agrees with the average value of 24 kcal/mole obtained by Carnahan and Brittain, who also obtained the same orientation dependence found in the present work. Comparison of the observed orientation dependence with the results summarized in Table II leads to the conclusion that no "isolated" defect can be invoked to explain these data without difficulty arising because there is no position in the rutile structure that splits into subsets under tensile stress along [100] which does not also split into subsets for tensile stress along [110]. The existence of the peak for [100] stress compels us to associate it with the *c*, *h*, *i*, or *k* sites because no other sites split into subsets under this stress. The fact that no peak was observed for the [110] stress requires some further explanation and there appear to be three types of possible explanation: (a) That an internal friction peak does occur for [110] stress at the same temperature as the [100] peak, but is too small to be observed. (b) That a peak occurs under [110] stress but that Jahn-Teller distortion of the site caused the jump frequencies for the pattern of inequivalence set up by [110] stress to be sufficiently different from that set up by [100] stress that the [110] peak lies outside the temperature range of present observations. This possibility has already been discussed in connection with oxygen vacancies or octahedral titanium interstitials. (c) That the point defects responsible are not "isolated" but are associated into pairs or groups in such a way that the pattern of inequivalence of sites set up by [100] stress still leads to inequivalent positions for the group, but that the various possible arrangements of the group all have the same energy under the pattern of inequivalence set up by [110] stress. This possibility will be clarified by subsequently discussing the possible pairing of titanium interstitials.

We now consider the possibilities of reconciling either oxygen vacancies or titanium interstitials with the experimental results.

(1) Isolated oxygen vacancies with the full symmetry of the oxygen positions cannot cause the peak occurring in the [100] crystal as shown by the symmetry argument in Sec. II. 3.

(2) Isolated oxygen vacancies of lower symmetry could give a peak with the observed orientation dependence, but the observed peak is very unlikely to have this origin. As noted in Sec. II. 5, oxygen vacancies with symmetry corresponding to Wycoff position *i*, would be driven back and forth between two *i*-type positions neighboring a single oxygen atom position for

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[25] H. J. Gerritsen, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), pp. 3–12.

[26] H. J. Gerritsen and E. S. Sabisky, Phys. Rev. **125**, 1853 (1962).

stress along [100], but not for stress along [001] or [110]. This model fits the observed orientation dependence exactly, but is not likely to be the correct explanation for several reasons. First, the value of 23 kcal/mole appears to be rather high for jumps between Jahn-Teller inequivalent positions in an ionic crystal in view of the numerical values mentioned in Sec. II. 5. Second, such motion alone cannot account for material transport. Oxidation of titanium with an activation energy of 26 kcal/mole has been reported[27] for conditions in which diffusion through the oxide layer is presumably rate controlling. The similarity of the present activation energy value suggests that the internal-friction peak is due to a process capable of causing material transport. Third, if oxygen vacancies do exist, there should be a peak for stress in the [110] direction corresponding to jumps between oxygen atom positions in addition to any peak resulting from motion between Jahn-Teller inequivalent sites both neighboring a single oxygen atom position. Such a peak was not found in measurements up to 575°C.

(3) Pairs of oxygen vacancies could give the observed orientation dependence but the model which must be assumed does not seem reasonable. This model requires that oxygen vacancies exist in nearest-neighbor pairs half a cell height apart in the [001] direction (say positions f_1 and f_3 of Fig. 1) and that the observed [100] peak results from motion between two i-type positions as hypothesized in (2) above. For this model, the first two difficulties mentioned in (2) remain, but the third has been removed. In this case, application of stress along [110] would not cause an internal-friction peak because neither vacancy alone can jump to an inequivalent position without destroying the pairing $c/2$ apart and if both jump simultaneously, there is no change in energy. This model cannot be definitely ruled out, but seems most unlikely because, in addition to the two difficulties previously mentioned, there seems to be no reason why pairing should occur.

(4) Isolated titanium interstitials with the full symmetry of the interstitial position are not likely to be responsible for the observed peak. This conclusion rests on the agrument given in Sec. II. 4 that such interstitials should give a peak for the [110] crystal with height 0.73 that for the [100] crystal and on the experimental observation that the peak for the [110] direction, if it occurs at all, is not more than 0.025 times as high as that for the [100] crystal.

(5) Isolated titanium interstitials with symmetry lower than the full symmetry of the interstitial site give no more possibilities of internal friction for the crystals used here than interstitials of full symmetry and so come under the heading of (4) above.

(6) Pairs of titanium interstitials can give the observed orientation dependence and this model seems reasonable. Consider an interstitial at site c_1 of Fig. 1. The distance from this site to the center of the nearest oxygen ion at f_1 is 1.664 Å, but the shortest Ti-O bond in the normal structure is 1.944 Å according to Grant.[1] The oxygen ion at f_1 must be displaced away from c_1 toward c_2 so that occupancy of c_2 by a second interstitial is unlikely. On the other hand, this oxygen motion should make c_4 a more favorable site for occupation by an interstitial than a c-type site which is not near any other interstitial ion. This motion is favorable for site c_4 in two ways. First, the distance f_1 to c_4 was originally 2.227 Å so that little repulsion is expected and decreasing this distance should increase the electrostatic binding between a titanium interstitial at c_4 and the oxygen ion originally at f_1. Second, motion of the oxygen originally at f_1 would require some movement of the oxygen at $(-x, x, \frac{1}{2})$ because the original center-to-center distance of these two oxygens was 2.78 Å which corresponds to hard-sphere contact if the radius of oxygen is taken as 1.39 Å. This second motion increases the shortest oxygen-to-interstitial site distance for c_4 and so should make it easier for an interstitial atom to occupy c_4 assuming that this effect outweighs the electrostatic repulsion between charges of like sign on c_1 and c_4. The idea which is being proposed may be clearer if restated in the language used by Hurlen[5] in discussing the interstitial sites. He points out that the octahedron surrounding the interstitial site is distorted with respect to the octahedron surrounding a normal titanium site in that two oxygens are closer and four are more distant. We are suggesting that insertion of a titanium interstitial at c_1 causes the octahedron at c_4 to distort in such a way that the cation-oxygen distances closely resemble those in the octahedron surrounding the normal titanium site and the site c_4 is therefore more favorable for occupation by a titanium ion. Thus, we suggest that interstitial titanium ions, if they exist at all, are likely to exist as pairs $c_1\,c_4$ or equivalently $c_2\,c_3$ unless the temperature is high enough to cause dissociation.

The arrangement of ions found in phases neighboring rutile in the titanium oxygen system resembles the interstitial pair postulated here and lends some plausibility to assuming its existence. It has been shown[28] that phases of composition Ti_nO_{2n-1} where $n=4,5,6,7,8,$ 9, or 10 exist. Each of these can be looked upon as blocks of rutile structure joined together along planes.[5,28] On a joining plane, the titanium ions in normal positions with respect to the material on one side are in interstitial positions with respect to the material on the opposite side and vice versa. Two successive titanium ions which appear as interstitials when viewed from one side have the $c_1\,c_4$ relationship postulated here. The situation in a phase with a definite structure is, of course, different from that in slightly reduced rutile, but if planes of "interstitials" form upon greater re-

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[27] D. H. Whitmore and Toshihiko Kawai, J. Am. Ceram. Soc. **45**, 375 (1962).

[28] S. Anderson, B. Collén, U. Kuylenstierna, and A. Magnéli, Acta Chem. Scand. **11**, 1641 (1957).

duction, it seems reasonable for pairs of interstitials to exist in slightly reduced rutile.

The observed orientation dependence of the internal friction is consistent with the existence of pairs of titanium interstitials in vacuum reduced rutile. Stress along [001] causes no inequivalence of interstitial sites and so causes no peak. Stress along [100] causes the pattern of inequivalence shown in Fig. 4(a), so that the pair $c_1\, c_4$ is not equivalent to the pair $c_2\, c_3$ and a peak should occur as it does. Stress along [110] causes the pattern of inequivalence shown in Fig. 4(b), so that the pair $c_1\, c_4$ remains equivalent to the pair $c_2\, c_3$; no peak should occur and none is observed. We conclude that the internal-friction peak occurring in vacuum reduced rutile is probably caused by pairs of interstitial titanium ions. The present work gives no direct evidence concerning the charge on these ions.

In comparing the present work with that of Carnahan and Brittain[9] the areas of agreement should first be noted. The same orientation dependence and activation energy of the large peak were found; there is no disagreement in the data. The interpretations agree up to a point. Carnahan and Brittain think the peak is probably caused by interstitial titanium, but disagree with the present interpretation in their explanation for the lack of observation of a peak for the [110] direction. They suggest that stress in the [110] direction does not change the environment of the interstitial titanium ions enough to cause a measurable peak. We, however, have given a calculation in Sec. II. 4 which indicates that the peak for the [110] direction should be observable; we are therefore forced to assume pairs of interstitial titanium ions rather than isolated interstitials as assumed by Carnahan and Brittain. The calculation of Sec. II. 4 may be questioned both with respect to the energy change for the titanium interstitial can be taken as a function only of the nearest-neighbor oxygen distance and with respect to the use of macroscopic elasticity to compute the change in this distance with stress. This calculation is, however, a comparison of two states of stress and the same percentage errors would cancel. Some confidence in this calculation seems justified by the observation[29] of peaks of the same magnitude for the [100] and [110] directions for rutile containing interstitial nickel.

3. The Large Pre-exponential Factor

The internal-friction peak occurring in vacuum reduced rutile is characterized by a relaxation time τ_r given by $1/\tau_r = k_{10} \exp(-E/RT)$, where R is the gas contant, $E = 23.5 \pm 1$ kcal/mole, and $\ln k_{10} = 39.3 \pm 1.8$. For the linear chain of positions along which a titanium interstitial could jump under stress $\tau_r = \tau/2$, where τ is the mean time of stay on one position. The Eyring theory of reaction rates has been applied by Wert and Zener[30] and by Wert[31] to the jumping of atoms in crystals. They obtain $1/\tau = n\nu \exp(\Delta S/R) \exp(-E/RT)$ where n is the number of nearest neighbor sites for the jumping atom, ($n = 2$ for interstitial titanium), ν is the frequency of vibration, and ΔS is the activation entropy. They estimate ν from $\nu = (E/2m\lambda^2)^{1/2}$. Here λ is the distance between atomic sites ($\lambda = c/2 = 1.480$ Å for interstitial titanium.) We obtain $\nu = 6.4 \times 10^{12}$ sec which gives $\exp(\Delta S/R) = 4.6 \times 10^3$ or $\Delta S/R = 8.4 \pm 1.8$. The largest experimental value of $\exp(\Delta S/R)$ quoted by Wert and Zener is the value of 100 for N in Ta so the present result is unexpectedly high. Reducing $\exp \Delta S/R$ by a factor of 48 to bring it within the range of experimental values tabulated by Wert and Zener requires reducing $\Delta S/R$ by 3.6, which is just twice the standard error determined by curve fitting as previously described.[19] This standard error does not include possible systematic error or uncertainty in the knowledge of ν. The uncertainty in $\Delta S/R$ is thus so large that further speculation about the large value of $\Delta S/R$ itself seems unjustified.

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[29] J. B. Wachtman, Jr., W. S. Brower, S. Spinner, and T. Fridinger (to be published).

[30] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[31] C. A. Wert, Phys. Rev. **79**, 4, 601 (1950).