

INTERSTITIAL DIFFUSION MECHANISM IN RUTILE*

H. B. Huntington and G. A. Sullivan

Physics Department, Rensselaer Polytechnic Institute, Troy, New York

(Received 7 January 1965)

Considerable study¹⁻⁴ has been given to the reaction by which rutile (TiO_2) takes on a blue coloration when reduced in vacuum or in hydrogen. Controversy has centered on the mechanism responsible for the kinetics of the process with the evidence variously supporting mobile oxygen vacancies or interstitial Ti^{3+} . Recently Shannon⁵ has proposed that the presence of hydrogen and/or water vapor favors the vacancy mechanism and that the titanium interstitials dominate the kinetics of vacuum reduction.

It is the primary purpose of this Letter to point out that the strong anisotropy in diffusion is uniquely compatible with interstitial motion in this lattice. Recent measurements⁶ of the diffusion of lithium in rutile have shown an anisotropy of at least 10^8 to 1 in favor of diffusion along the c axis. A qualitatively similar situation holds for the diffusion of boron.⁷ Clearly, for these cases there must exist a jump mechanism whose net motion is exactly parallel to the c axis. Presumably this occurs along the line $[a/2, 0, X_3]$, where the lattice presents a rather open chimney (see Fig. 1). (It is not necessary, however, that the individual jumps be parallel to the c axis.) Equilibrium positions must occur in the planes $X_3 = (n/4)c$ for either odd or even values of n . The observation that the coloration by vacuum reduction is highly anisotropic⁷ points strongly toward the interstitial mechanism. Similar observations on specimens reduced in hydrogen should give a critical test of Shannon's hypothesis.

The chimney mechanism (unlike most diffusion mechanisms) works best in an ideal crystal. Johnson⁶ has observed that diffusion was strongly inhibited by abrasion of the surface. Clearly, dislocations (or stacking faults) will choke off the chimneys.

In general, internal-friction studies^{8,9} on vacuum-reduced rutile are consistent with our picture. A substantial loss peak was found for specimens stressed in the $[100]$ but not in the $[110]$ nor $[001]$ directions. While these observations appear to rule out vacancy defects for their origin, pairs of interstitials at B sites (n even) have been earlier invoked as a possibility.⁸ We favor single interstitials on A sites

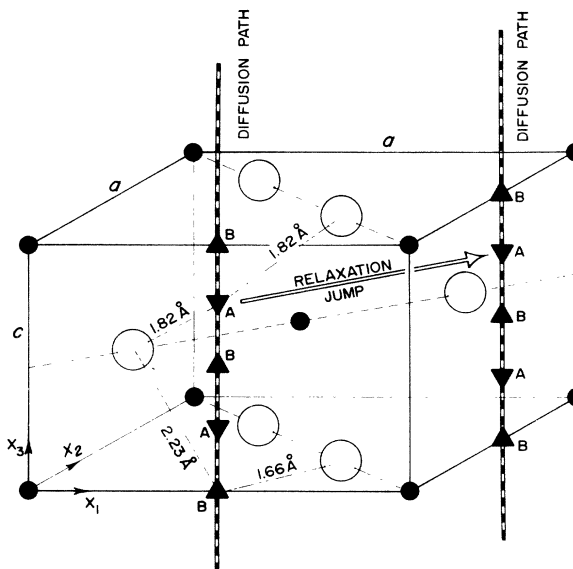


FIG. 1. Interstitial positions in rutile. Solid circles: Ti^{+4} ions; open circles: O^{-2} ions; triangles: titanium interstitials—base up, A site; base down, B site.

(n odd) as a simpler explanation. The symmetry of the A sites is such that the degeneracy between the $(a/2, 0, X_3)$ and $(0, a/2, X_3)$ positions is removed by a uniaxial stress in the $[100]$ direction but not in the $[110]$ direction, in accordance with observation. Moreover, the positions for n odd seem to afford a more suitable environment for the interstitial than do those at B , since for the former there are four nearest neighbors, oxygen atoms at a distance of 1.82 \AA , while at the latter positions (B) the two nearest neighbors are 1.66 \AA distant, and the two next nearest are at 2.23 \AA . It is quite possible that the B site is a potential maximum and that the true potential minima in the basal plane are displaced on either side in approximately the $[110]$ directions. Under these conditions the saddle point for the jump would not be colinear with the initial and final positions. The answer as to the true saddle point in the basal plane rests rather sensitively on the competition between electrostatic ionic interaction and repulsion of inner ion cores.

It should be noted that a jump along the c axis leads to no stress relaxation. Such relaxation can only be accomplished by a jump

from one A site to an adjoining one in the same basal plane as shown by the arrow. We then identify the observed activation energy⁸ for the internal-friction peak, 23.5 kcal/mole, with this jump. Again it is consistent with the general picture not to assign this activation energy to the motion parallel to the c axis. The diffusivity in this direction has been estimated⁷ to be about 10^{-5} cm²/sec at 520°C, which is far too high to be consistent with such a large activation energy.

We wish to thank Dr. J. H. Rosolowski for showing us the marked anisotropy of the blue coloring reaction and for drawing our attention to the work of Bogomolov.⁷ We are indebted also to Dr. R. C. DeVries for illuminating discussion.

*Work supported by the U. S. Atomic Energy Commission.

¹F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).

²A. Von Hippel, J. Kalnais, and W. B. Westphal, J. Chem. Phys. Solids **23**, 779 (1962).

³H. P. R. Frederikse, J. Appl. Phys. Suppl. **32**, 2211 (1961).

⁴J. H. Becker and W. R. Hosler, J. Phys. Soc. Japan **18**, Suppl. II, 152 (1964).

⁵Robert D. Shannon, J. Appl. Phys. **35**, 3414 (1964).

⁶O. W. Johnson, Phys. Rev. **136**, A284 (1964).

⁷V. N. Bogomolov, Soviet Phys.—Solid State **5**, 1468 (1964).

⁸J. B. Wachtman, Jr., and L. R. Doyle, Bull. Am. Ceram. Soc. **41**, 275 (1962); Phys. Rev. **138**, A276 (1964).

⁹R. D. Carnohan and J. O. Brittain, J. Appl. Phys. **34**, 3095 (1963).

DIRECT OBSERVATION OF PHONONS IN SILICON BY ELECTRIC-FIELD-MODULATED OPTICAL ABSORPTION*

Andrea Frova and Paul Handler

Materials Research Laboratory, University of Illinois, Urbana, Illinois
(Received 4 January 1965)

In silicon, phonon-assisted transitions from the top of the valence band to the minima of the conduction band have been observed by a number of workers: Macfarlane *et al.*¹ by optical absorption, Holonyak *et al.*,² Esaki and Miyahara,³ Chynoweth, Logan, and Thomas,⁴ and most recently Logan, Rowell, and Trumbore⁵ by phonon-assisted tunneling in p - n junctions; and also Haynes and coworkers by means of recombination radiation.^{6,7} The values of the phonon energies obtained agree quite well with those found by Brockhouse by neutron-scattering experiments.⁸ In addition to single-phonon processes, multiple-phonon processes have been observed,^{4,7} which are also in good agreement with the data of Brockhouse. The most successful experiments have been performed at liquid-nitrogen temperature and below. In this paper we show that some rather accurate determination of the phonon energies can be made at room temperature by means of the electric-field-modulated optical absorption (Franz-Keldysh effect^{9,10}). The effect in silicon may be described as photon-plus-phonon-assisted tunneling across the energy gap.

The experimental technique makes use of the electric field in a reverse-biased silicon p - n junction. Since the absorption coefficient

of the crystal depends on the magnitude of the field, a monochromatic light beam incident on the plane of the junction can be modulated by application of a small ac voltage superimposed upon the dc reverse bias. The relative modulation of the light intensity is proportional to the change in absorption coefficient $\Delta\alpha$ corresponding to the maximum field E in the junction. This has been discussed in previous papers,^{11,12} where this technique was used to investigate the properties of germanium and a detailed description of the experimental arrangement was presented. The silicon samples were n -type wafers of about 50-100 ohm-cm resistivity (~ 1 cm² area, ~ 70 -150 microns thick). A highly doped p layer was diffused on one side to produce a step junction, while on the other side an n^+ region was created to provide a good ohmic contact. The electric field was in the (111) direction, so that all the conduction band minima were equivalent. The reverse dc currents were of the order of 10^{-6} A, and the currents due to the ac modulation at 20 cps were at least an order of magnitude less.

Figure 1(a) shows $\Delta\alpha$ vs photon energy at room temperature. The position of the peaks is practically independent of the magnitude of the electric field. Since both the height and