

substance: titanium oxide (TiO₂)

property: native defects in pure n-type TiO_{2-x} (rutile)

[72H, 73K]

$V_{O}^{\bullet\bullet}$: doubly ionized oxygen vacancy.

Strong relaxation of Ti^{4+} ions away from neighbouring $V_{O}^{\bullet\bullet}$ appears to raise the energy of $V_{O}^{\bullet\bullet}$ above bottom of conduction band; so no direct observation on the defect by ESR is possible.

$Ti_i^{3\bullet}$: triply ionized Ti interstitial; shares two octahedral faces, 4 octahedral edges. A- or C-center in ESR, see following document.

$Ti_i^{4\bullet}$: quadruply ionized Ti interstitial; shares two octahedral faces, 4 octahedral edges.

$(Ti_i^{3\bullet})_2$: di-interstitial = pair of triply ionized Ti in nearest-neighbour interstitial octahedra. Internal friction peak for vibrational stress $\parallel [100]$, no peak for stress $\parallel [110]$ or $[001]$. X center in ESR, see following document.

$(Ti^{3+}-Ti^{3+})$ APB: Ti pairs of face-shared octahedra intersected by antiphase boundary across which normal, interstitial sites become inverted; each Ti octahedron also shares three edges. Ti- pair displacement $\parallel (1/2)[0, -0.90, 0.90]$ instead of "ideal" $1/2 [0, \bar{1}, 1]$ because of electrostatic repulsion force.

$(Ti^{3+}-Ti^{4+})$ APB: as above. W center in ESR, see following document.

$(Ti^{4+}-Ti^{4+})$ APB: as above.

$(Ti^{3+}-Ti^{3+})_{bulk}$: displacements parallel to the *c*-axis to create *c*-axis dimer trapping spin paired electrons in homopolar Ti – Ti bond across a shared octahedral-site edge. Cooperative dimerization and bipolaron formation are both found in homologous series Ti_nO_{2n-1} . See documents on Ti_4O_7 .

$(Ti^{4+}-Ti^{4+})$ CS: Ti pairs of face-shared octahedra intersected by an [hkl] crystallographic shear plane (Fig. 1). Ti-pair same as for APB. Theory suggests CS occurs only in crystals with high static dielectric constant [77J]! Strong cooperative relaxation of Ti^{4+} ions away from CS produces large Ti – Ti separation of face-shared pairs (Magnéli), raising energy of homopolar bond formation above conduction band edge.

Long-range (elastic) attractive force and short-range repulsive force between [312] CS planes (see Fig. 2 for interaction potential) produces clustering of planes into aggregates containing from two to about thirty planes before member of homologous series Ti_nO_{2n-1} is identified in electron microscope. Within an aggregate, the CS spacing D_{sp} varies systematically: $D_{sp} \approx 8.7$ nm for a "lone pair" to $D_{sp} \approx 3.8$ nm at center of largest aggregate, increasing to about 6.3 nm at aggregate edge [72B].

References:

- 72B Bursill, L. A., Hyde, H. G.: Prog. Solid State Chem. 7 (1972) 177.
- 72H Hasiguti, R.: Adv. Mater. Sci. 2 (1972) 69.
- 73K Kersson, J., Volger, J.: Physica 69 (1973) 535.
- 77J James, R., Catlow, C. R. A.: J. Phys. Colloq. 38 (1977) C7-32.
- 77Y Yagi, E., Hasiguti, R. R.: J. Phys. Soc. Jpn. 43 (1977) 1998.

Fig. 1.

TiO₂. Projection of rutile lattice onto the (001) plane intersected by a (312) fault. Ti-ion pairs PQ about the fault, and a single electron trapped at this site produces a W-centre EPR spectrum [77Y]. *R*: Ti-Ti displacement.

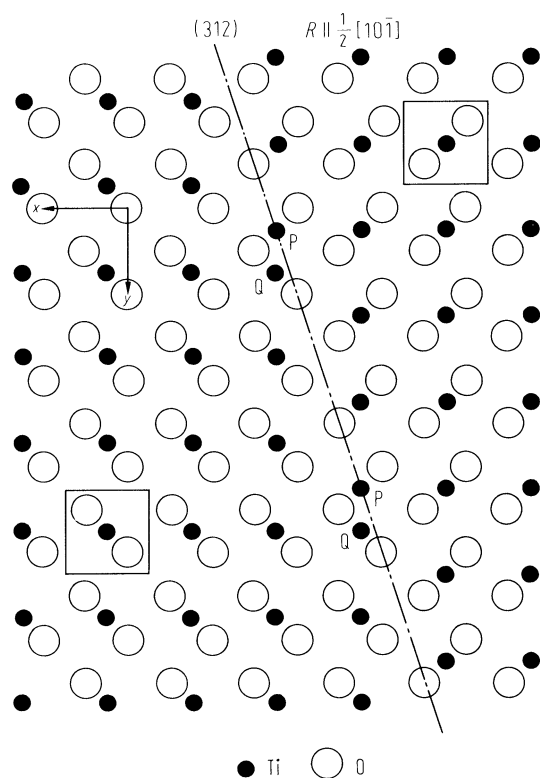


Fig. 2.

TiO₂. Schematic empirical interaction energy between a pair of (312) CS-planes: wave function $\Psi(i,j)$ vs. plane separation D_{ij} [72B].

