substance: Ti_2O_3
property: band structure, energy gap

band structure: Fig. 1, Brillouin zone: Fig. 2. Calculations reported in [69N, 71N, 75A]. Phenomenological band scheme: Fig. 3.

The symmetry at each Ti is D_3 and the degeneracy of the $t_{2\pi}$ orbitals lifted to form $a_1 + e_\pi$. The a_1 orbitals on the two face-sharing Ti interact strongly to form a_1 and a_1* bands that are broadened considerably to form two bands 1 eV wide.

The e_π orbitals form a narrow band essentially confined to the basal planes and ca. 1/3 eV wide. As the temperature is raised, the Ti – Ti separation across a shared face increases whereas the basal-plane separation remains constant. The effect is to stabilize the e_π band with respect to the a_1 band, and the two bands intersect at 460 K (Fig. 4). This behaviour can be fitted quantitatively to the elastic-constant variation [73C], resistivity and Seebeck experiments [73S] and heat capacity data [61N, 72P, 73B] (Fig. 5). Further support to this model comes from optical data (see below) and from the photoelectron spectrum [78V] which shows a shift of 0.6 eV to lower binding energy of the Ti 3d peak.

energy gap

E_g	0.13 eV	T = 300 K	estimates using the model	73B
	0.027...0.050 eV		discussed above. [68H, 59M, 61Y]	68H
	0.056...0.079 eV		are determined from activation	61Y
	0.079 eV		energies of conductivity	59M
	0.14 eV		(100...300 K) and Hall data	66A
	0.10...0.23 eV		(100...300 K), respectively	73S

References:

59M Morin, F. J.: Phys. Rev. Lett. 3 (1959) 34.
61N Nomura, S., Kawakubo, T., Yanayi, T.: J. Phys. Soc. Jpn. 16 (1961) 706.
61Y Yahia, J., Frederikse, H. P. R.: Phys. Rev. 123 (1961) 1257.
66A Adler, D.: Phys. Rev. Lett. 17 (1966) 139.
68H Honig, J. M., Reed, T. B.: Phys. Rev. 174 (1968) 1020.
69N Nebenzahl, I., Weger, M.: Phys. Rev. 184 (1969) 936.
71N Nebenzahl, I., Weger, M.: Philos. Mag. 24 (1971) 1119.
72P Paukov, I. E., Berezovskii, G. A.: Zh. Fiz. Khim. 46 (1972) 2683.
73B Barros, H. L., Chandrashekhar, G. V., Chi, T. C., Honig, J. M., Sladek, R. J.: Phys. Rev. B7 (1973) 5147.
73C Chi, T. C., Sladek, R. J.: Phys. Rev. B7 (1973) 5080.
73S Shin, S. H., Chandrashekhar, G. V., Loehman, R. E., Honig, J. M.: Phys. Rev. B8 (1973) 1364.
75A Ashkenazi, J., Chuchem, T.: Philos. Mag. 32 (1975) 763.
75H Honig, J. M., van Zandt, L. L.: Annu. Rev. Mater. Sci. 5 (1975) 225.
78V Vaandevan, S., Hedge, M. S., Rao, C. W. R.: Solid State Commun. 27 (1978) 131.

Fig. 1.

Ti_2O_3. Band structure in the region of the t_{2g} levels [75A].

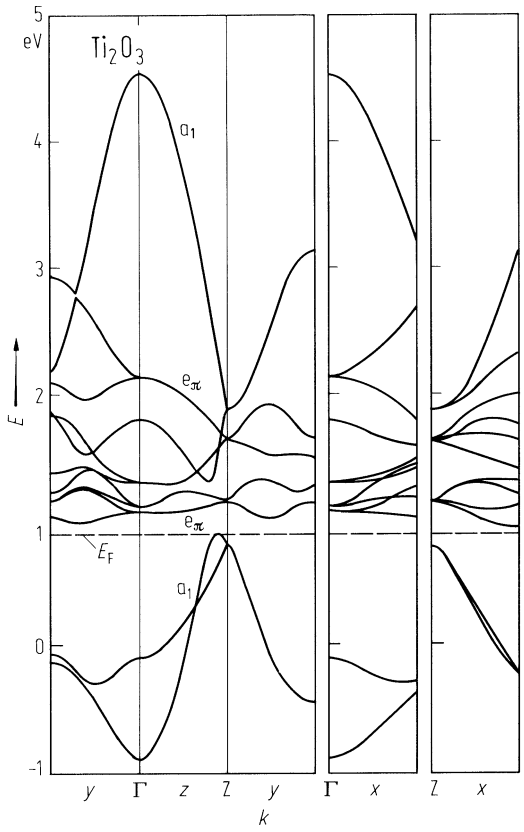

Fig. 2.

Ti_2O_3. Brillouin zone [75A].

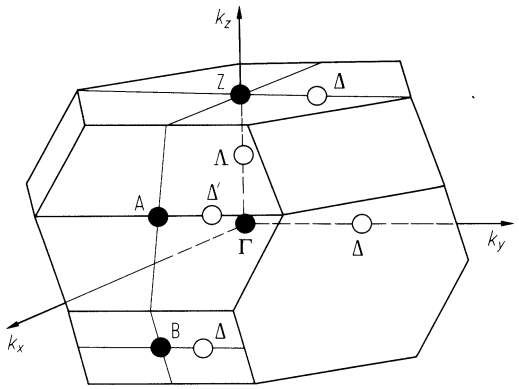

Fig. 3.

Ti_2O_3. Phenomenological band structure [75H].

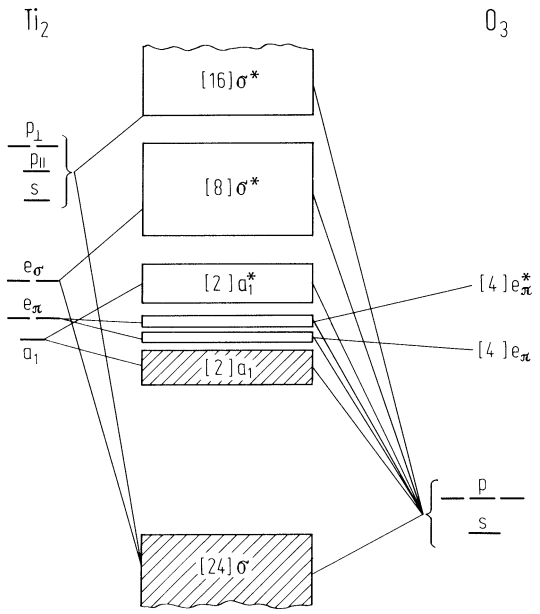

Fig. 4.

Ti_2O_3. Density of states vs. energy showing band crossing with raising temperature [73B]. The vertical dashed line is the calculated Fermi energy.

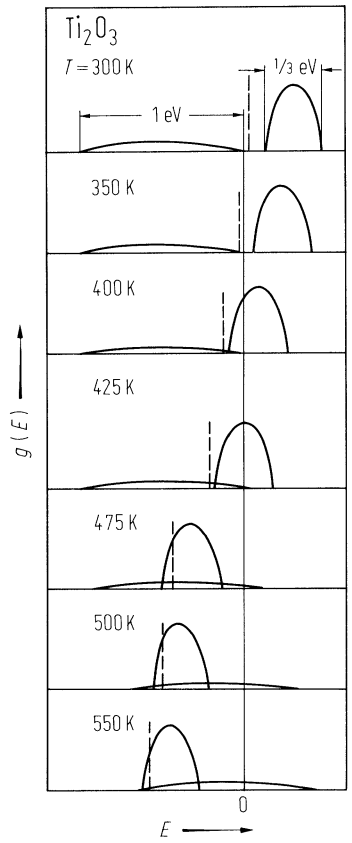

Fig. 5.

Ti_2O_3. Heat capacity per formula unit vs. temperature. Different curves: data of various authors [73B].