substance: titanium oxide (TiO_2)
property: properties of vibrational and Raman modes in rutile

symmetry of optical modes: Fig. 1

phonon dispersion curves: Figs. 2, 3.

frequencies of optical lattice modes

(data in 10^{12} Hz)

$\nu(\Gamma_4^+, B_{2g})$	24.78	R, T = 4 K	R: Raman data from [67P]
	24.72(25)	N	I: IR data from [64E]
$\nu(\Gamma_5^+, E_u)_{LO}$	24.18	I	N: neutron data from [71T]
	25.24 (34)	N	Symmetries of modes are given in
$\nu(\Gamma_1^-, A_{2u})_{LO}$	24.33	I	Koster notation (as in Fig. 2)
	24.30	N	and Mulliken notation.
$\nu(\Gamma_1^+, A_{1g})$	18.36	R	For the correspondence of the
	18.30	N	data between Γ, X, M and Z
$\nu(\Gamma_5^+, E_u)_{TO}$	15.00	I	points, see Figs. 2, 3
	14.81(15)	N	
$\nu(\Gamma_5^-, E_g)$	13.41	R	
	13.339(181)	N	
$\nu(\Gamma_5^+, E_u)_{LO}$	13.74	1	
	12.853(129)	N	
$\nu(\Gamma_4^-, B_{1u}{}^2)$	12.182(122)	N	
$\nu(\Gamma_5^+, E_u)_{TO}$	11.64	I	
$\nu(\Gamma_5^+, E_u)_{LO}$	11.19	I	
	11.232(112)	N	
$\nu(\Gamma_5^+, E_u)_{TO}$	5.49	I	
	5.661(75)	N	
$\nu(\Gamma_1^-, A_{2u})_{TO}$	5.01	I	
	5.177(52)	N	
$\nu(\Gamma_3^+, B_{1g})$	4.29	R	
	4.246(94)	N	
$\nu(\Gamma_4^-, B_{1u})$	3.389(57)	N	
			corresponding to
$\nu(X_1)$	25.38(25)		(Γ_4^+) 71T
$\nu(X_1)$	24.38(25)		(Γ_5^+)
$\nu(X_2)$	13.528(135)		(Γ_5^-)
$\nu(X_1)$	11.756(118)		(Γ_5^+)
$\nu(X_1)$	9.130(125)		(Γ_5^+)
$\nu(X_2)$	9.033(90)		(Γ_4^-) and (Γ_1^-)
$\nu(X_1)$	8.071(81)		(Γ_5^+) and (Γ_3^+)
$\nu(X_1)$	5.821(58)		acoustic LA and TA branches (Γ_5^+)
$\nu(X_2)$	3.084(31)		(Γ_4^-) and acoustic TA branch (Γ_1^-)
$\nu(M_{1,2})$	23.26(23)		(Γ_4^+) and (Γ_5^+)
$\nu(M_9^+)$	13.522(135)		(Γ_5^-)
$\nu(M_9^+)$	9.442(94)		(Γ_5^+)
$\nu(M_{5,6})$	9.398(94)		(Γ_4^-) and (Γ_1^-)
$\nu(M_9^+)$	7.811(78)		(Γ_5^+) and (Γ_3^+)
$\nu(M_{5,6})$	3.058(56)		(Γ_4^-) and acoustic TA branch (Γ_1^-)
$\nu(M_9^+)$	2.936(70)		acoustic LA and TA branches (Γ_5^+)
$\nu(Z_1)$	12.397(124)		(Γ_4^-) and acoustic LA-branch (Γ_1^-)
$\nu(Z_2)$	12.312(123)		(Γ_5^-)

$\nu(Z_4)$	9.720(97)	(Γ_5^+)
$\nu(Z_3)$	9.040(90)	(Γ_3^+)
$\nu(Z_2)$	3.697 (69)	acoustic TA branch (Γ_5^+)

temperature dependence of vibrational modes: A_{2u} and E_u(TO) modes, with displacements along [001] and [110], have an anomalous increase in intensity and decrease in frequency with decreasing temperature (Fig. 4) characteristic for mode softening on the approach to a ferroelectric catastrophe. These modes are responsible for the high dielectric constant.

pressure dependence of Raman modes: E_g (417 cm^{-1}) and A_{1g} (612 cm^{-1}) peaks shift with rates of + 0.43 and + 0.41 cm^{-1} $kbar^{-1}$, but the B_{1g} (145 cm^{-1}) mode softens by – 0.36 cm^{-1} $kbar^{-1}$ [71N]. Above 26 kbar a transition to a new spectrum is observed [71N, 79H], which has been interpreted as a transition from an anharmonic to a harmonic material at high pressure [79H] and as a transition to a new phase of PbO_2 structure [71N, 80M] or $CaCl_2$ structure [78N]. Uniaxial stress measurements [80M] show that all modes displace linearly with pressure, but the B_{1g} mode shows non-classical behaviour. At very high pressures (> 300 kbar) another phase is observed in Raman spectrum whose structure is unknown [81M].

References:

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Fig. 1.

TiO_2. Symmetry of the optical modes in rutile at $q = 0$. Projection drawn down the c-axis [71T]

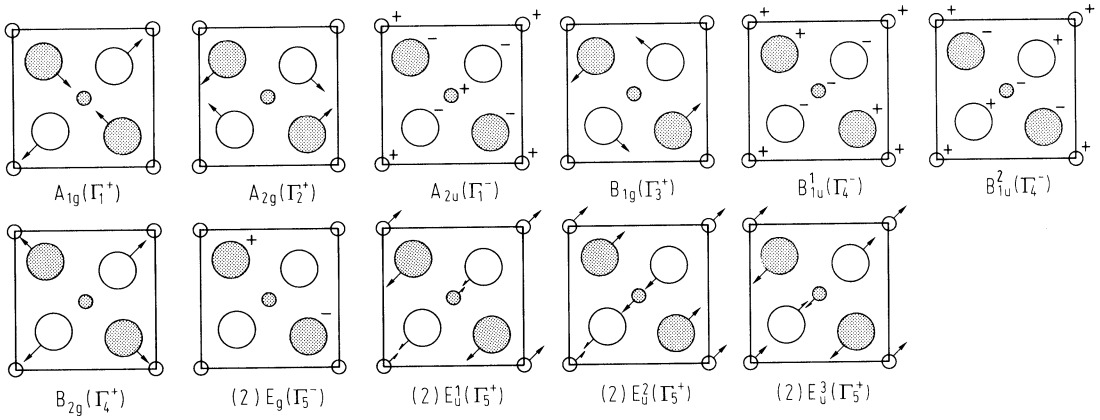

Fig. 2.

TiO_2. Low-frequency phonon dispersion curves for rutile. Lines through the points are guide lines only. Solid (open) points represent measurements made under predominantly longitudinal (transverse) scattering conditions. Circular (square) points indicate that the scattering vector *q* lay predominantly normal to (parallel to) the *z*-axis. Triangular points are modes with displacements normal to *z*, but which may not be classified as longitudinal or transverse [71T].

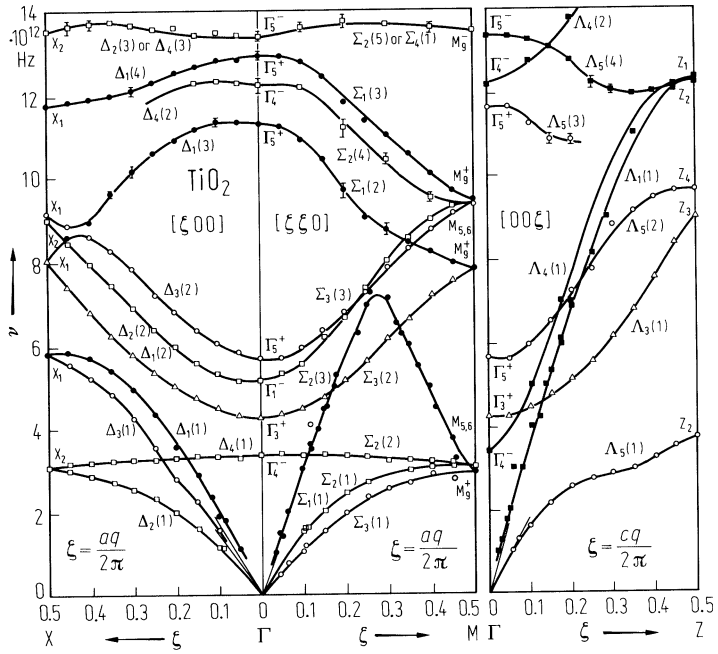

Fig. 3.

TiO_2. High-frequency phonon dispersion spectrum. Notation as in Fig. 2 [71T].

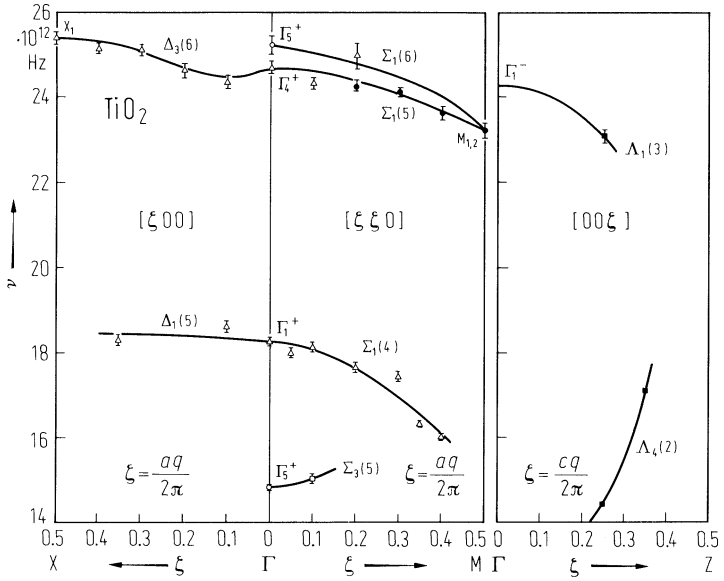

Fig. 4.

TiO_2. Square of the A_{2u}-mode frequency vs. temperature. Solid line calculated from dielectric measurements [61P], circles from neutron scattering [71T].