Class 9: Polar materials and ferroelectrics

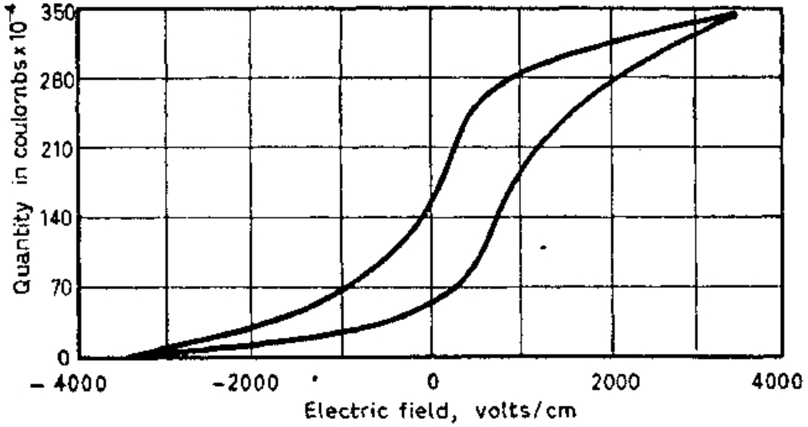

Fig. 1.1. Dielectric hysteresis loop for Rochelle salt (Valasek, 1921).

Valasek, 1921

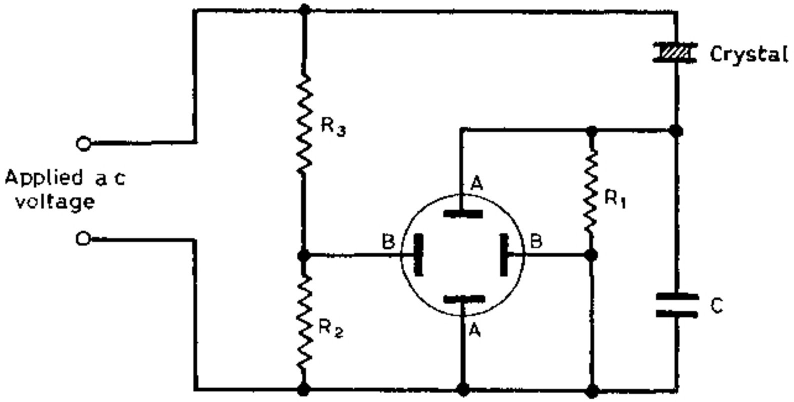

Fig. 1.2. Circuit for investigating hysteresis loop (Sawyer and Tower, 1930).

From Megaw, Ferroelectricity in Crystals.

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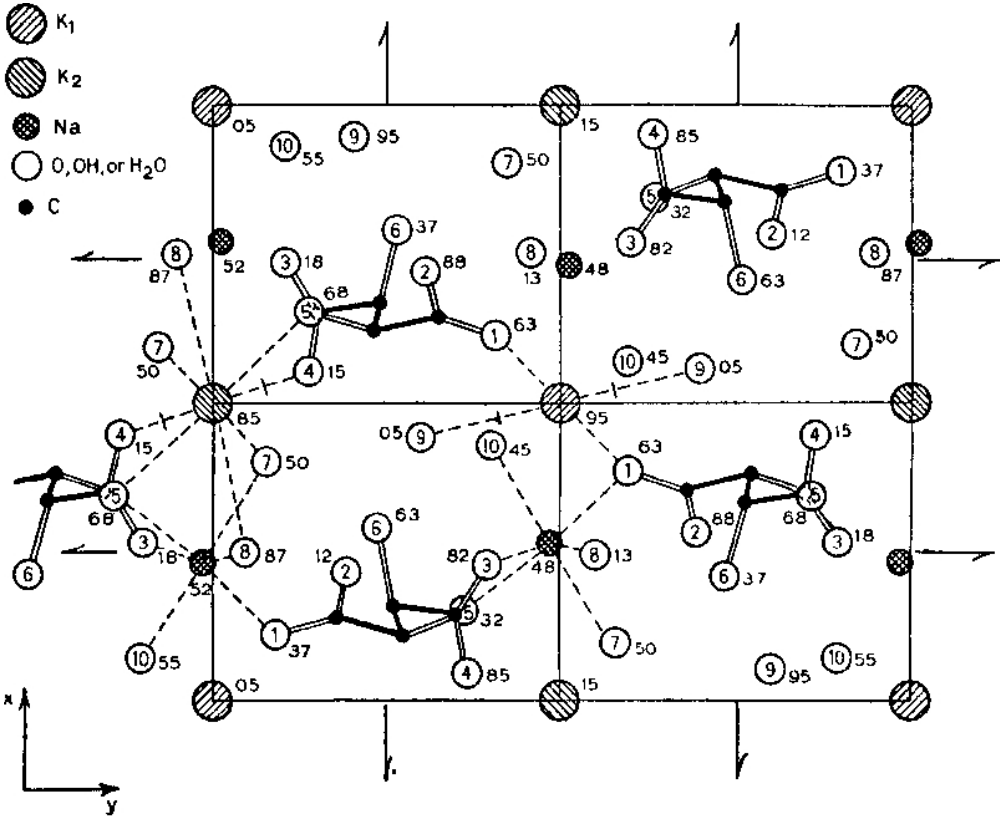

Fig. 2.1. Rochelle salt: projection of structure on 001. Figures beside atom give heights above plane $z = 0$ in hundredths of cell edge; to convert into Ångstrom units multiply by $c/100$. Positions of screw axes indicated by arrows. Environments of representative atoms shown by dotted lines; where these are crossed by a short line at right angles, they involve an atom in the cell vertically above or below that whose height is marked.

Hydrogen-bonded ferroelectricity in Rochelle’s salt.

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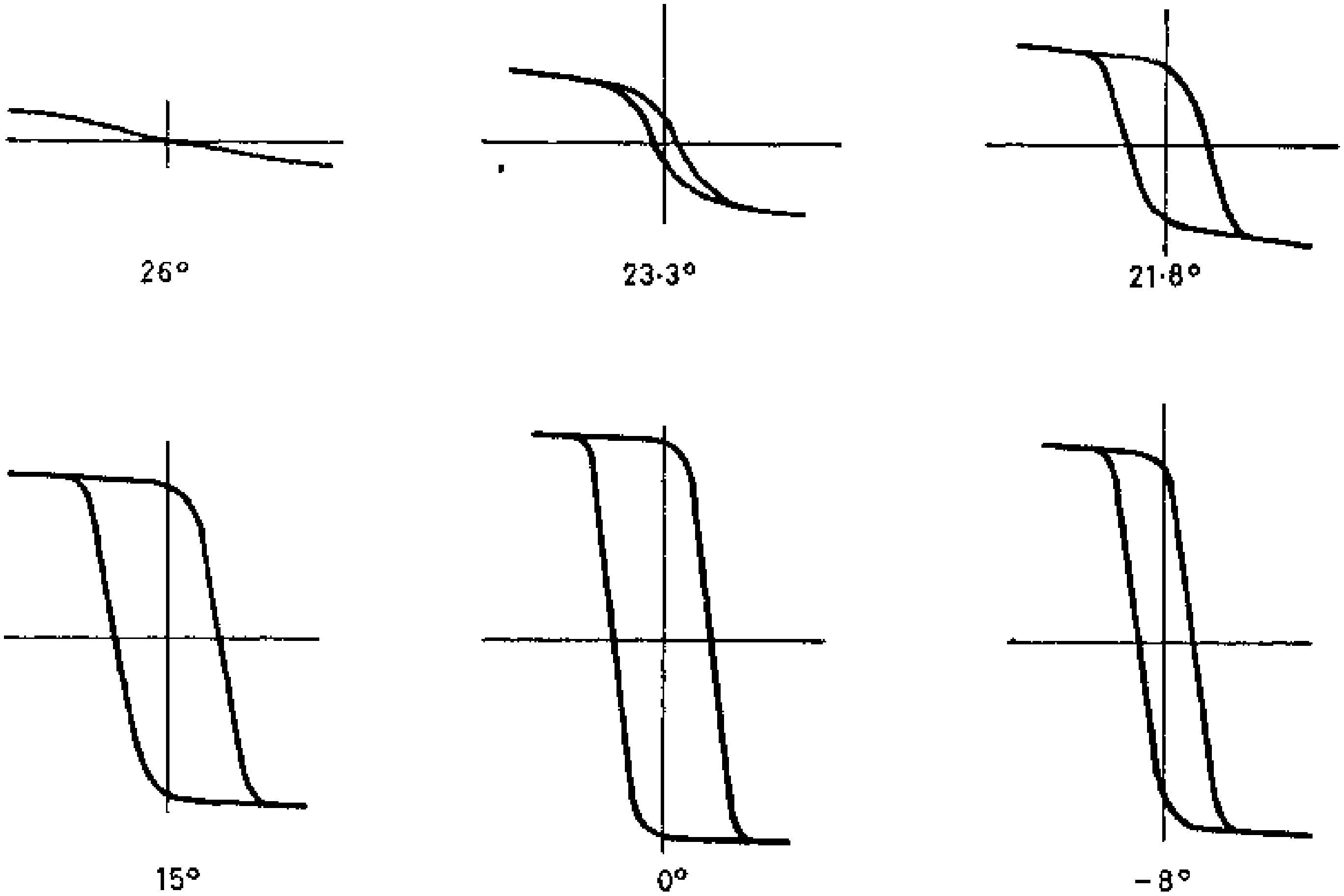

Fig. 1.5. Dielectric hysteresis loops for Rochelle salt at different temperatures (Sawyer and Tower, 1930).

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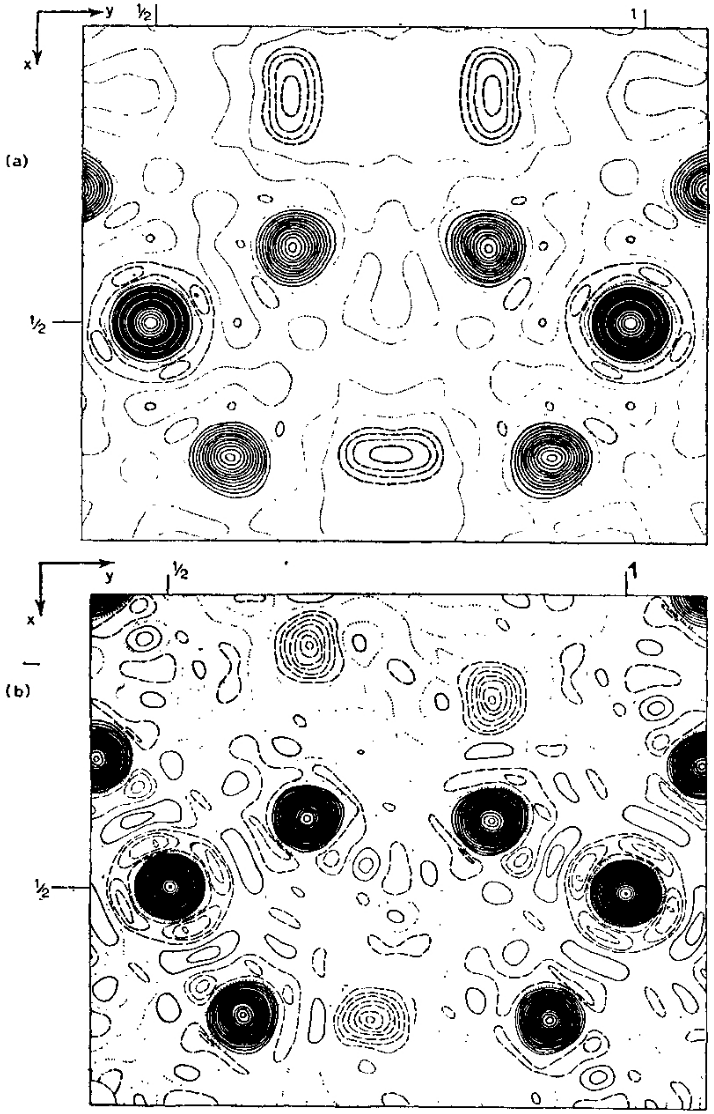

Fig. 3.3. Fourier synthesis, (001) projection, from neutron diffraction (Bacon and Pease, 1953, 1955). (*a*) at room temperature, (*b*) at 77°K.

The heaviest peaks are K + P, with O only slightly weaker; the peaks indicated by dashed contours are H. For comparison with Fig. 3.1, put the K + P peaks at $x = \frac{1}{2}$, $y = \frac{1}{2}$ and $x = \frac{1}{2}$, $y = 1$.

Hydrogen-bonded ferroelectricity in potassium dihydrogen phosphate (KDP).

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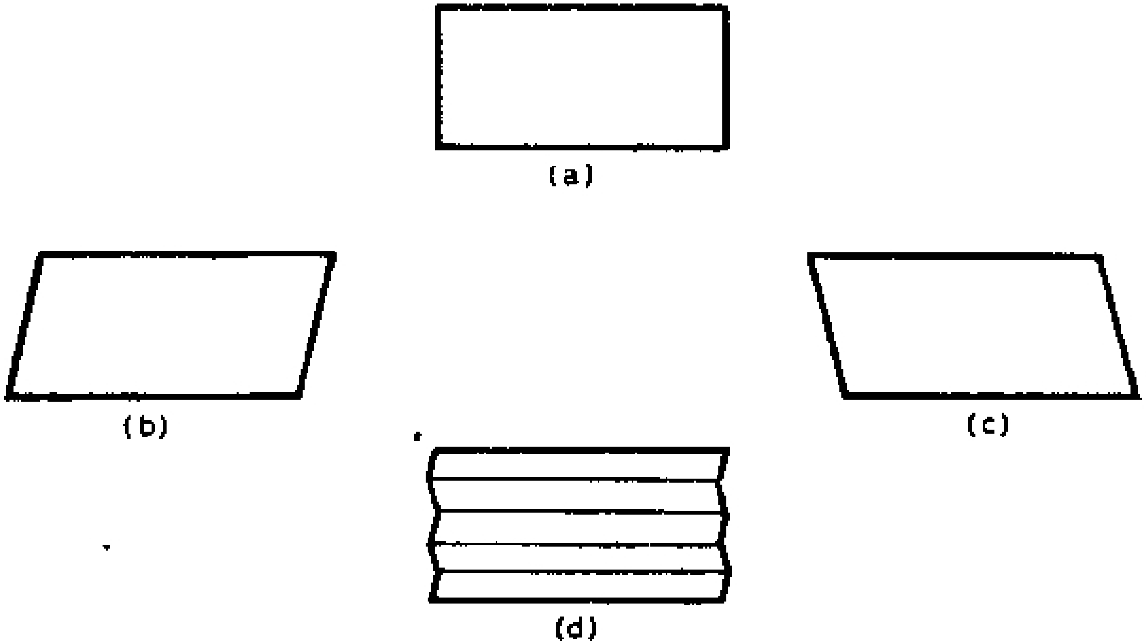

Fig. 1.6. Diagrammatic illustration of twinning in a pseudosymmetric structure.

(*a*) Crystal above transition point (high-symmetry form)
(*b*), (*c*) Low-symmetry form: two possible orientations
(*d*) Twinned crystal, with low-symmetry form in both orientations.

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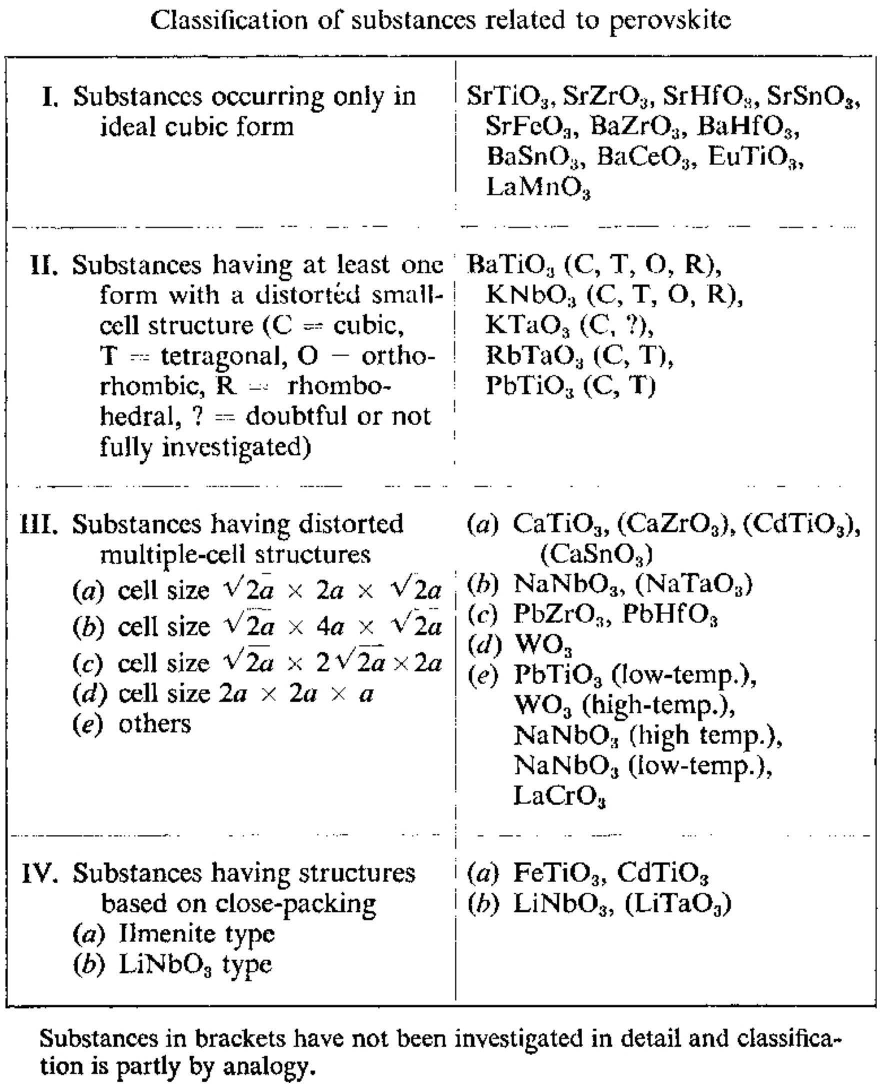

Classification of substances related to perovskite

I. Substances occurring only in ideal cubic form	$SrTiO_3$, $SrZrO_3$, $SrHfO_3$, $SrSnO_3$, $SrFeO_3$, $BaZrO_3$, $BaHfO_3$, $BaSnO_3$, $BaCeO_3$, $EuTiO_3$, $LaMnO_3$
II. Substances having at least one form with a distorted small-cell structure (C = cubic, T = tetragonal, O = orthorhombic, R = rhombohedral, ? = doubtful or not fully investigated)	$BaTiO_3$ (C, T, O, R), $KNbO_3$ (C, T, O, R), $KTaO_3$ (C, ?), $RbTaO_3$ (C, T), $PbTiO_3$ (C, T)
III. Substances having distorted multiple-cell structures (*a*) cell size $\sqrt{2}a \times 2a \times \sqrt{2}a$ (*b*) cell size $\sqrt{2}a \times 4a \times \sqrt{2}a$ (*c*) cell size $\sqrt{2}a \times 2\sqrt{2}a \times 2a$ (*d*) cell size $2a \times 2a \times a$ (*e*) others	(*a*) $CaTiO_3$, ($CaZrO_3$), ($CdTiO_3$), ($CaSnO_3$) (*b*) $NaNbO_3$, ($NaTaO_3$) (*c*) $PbZrO_3$, $PbHfO_3$ (*d*) WO_3 (*e*) $PbTiO_3$ (low-temp.), WO_3 (high-temp.), $NaNbO_3$ (high temp.), $NaNbO_3$ (low-temp.), $LaCrO_3$
IV. Substances having structures based on close-packing (*a*) Ilmenite type (*b*) $LiNbO_3$ type	(*a*) $FeTiO_3$, $CdTiO_3$ (*b*) $LiNbO_3$, ($LiTaO_3$)

Substances in brackets have not been investigated in detail and classification is partly by analogy.

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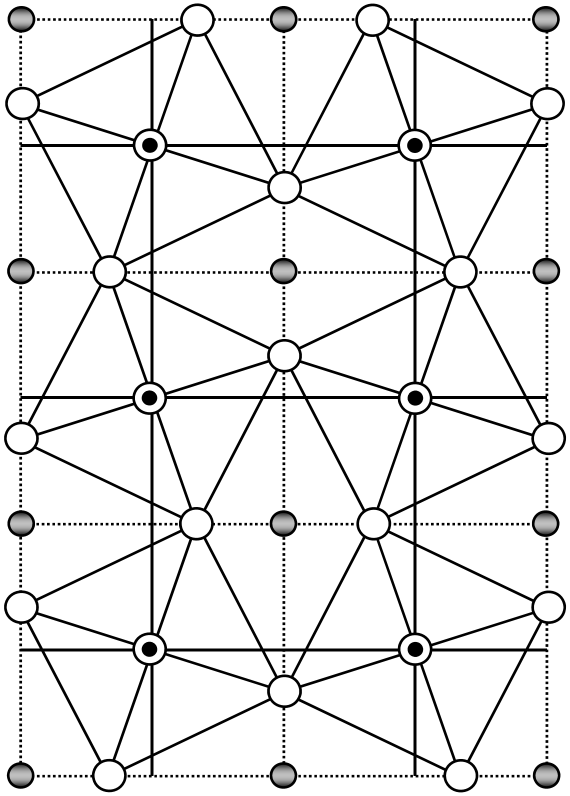
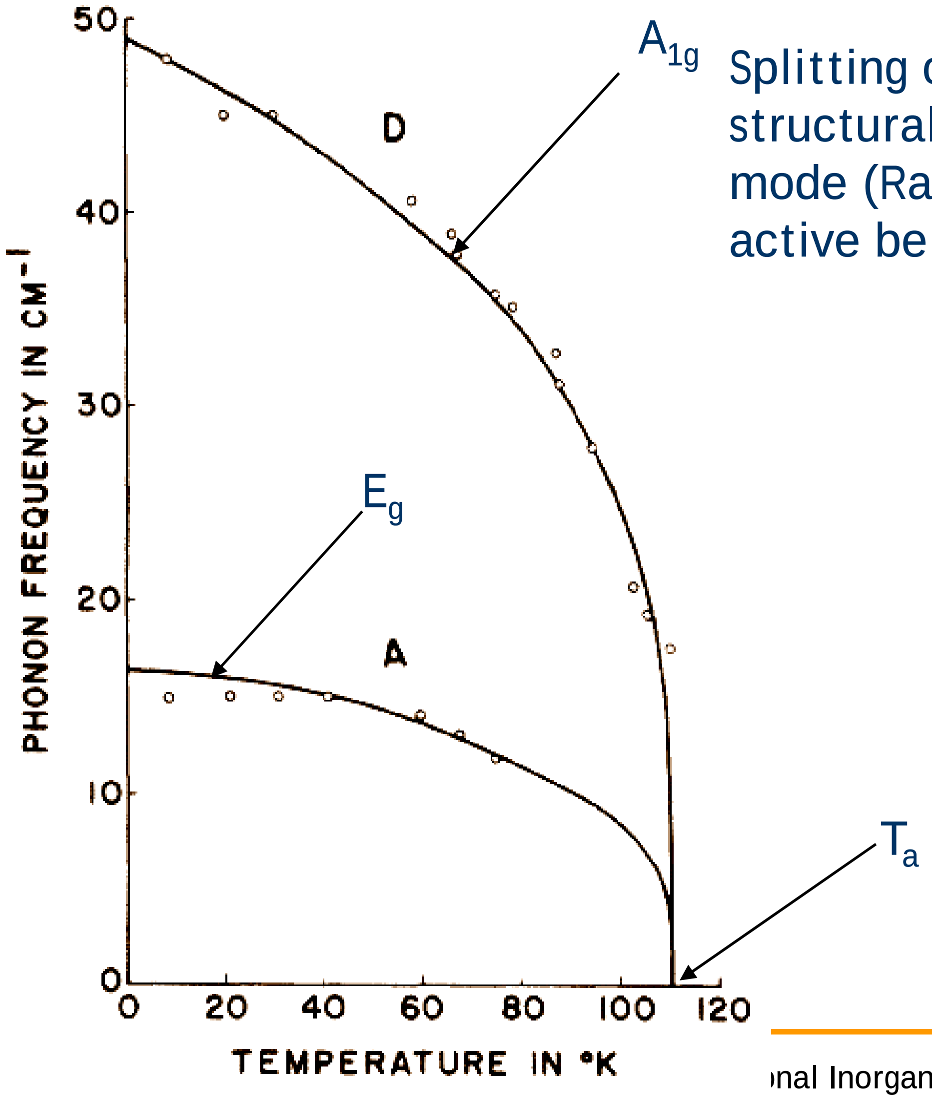
Antiferrodistortive transition in $SrTiO_3$ in R-point of the Brillouin zone





Splitting of the structural soft mode (Raman active below T_a)

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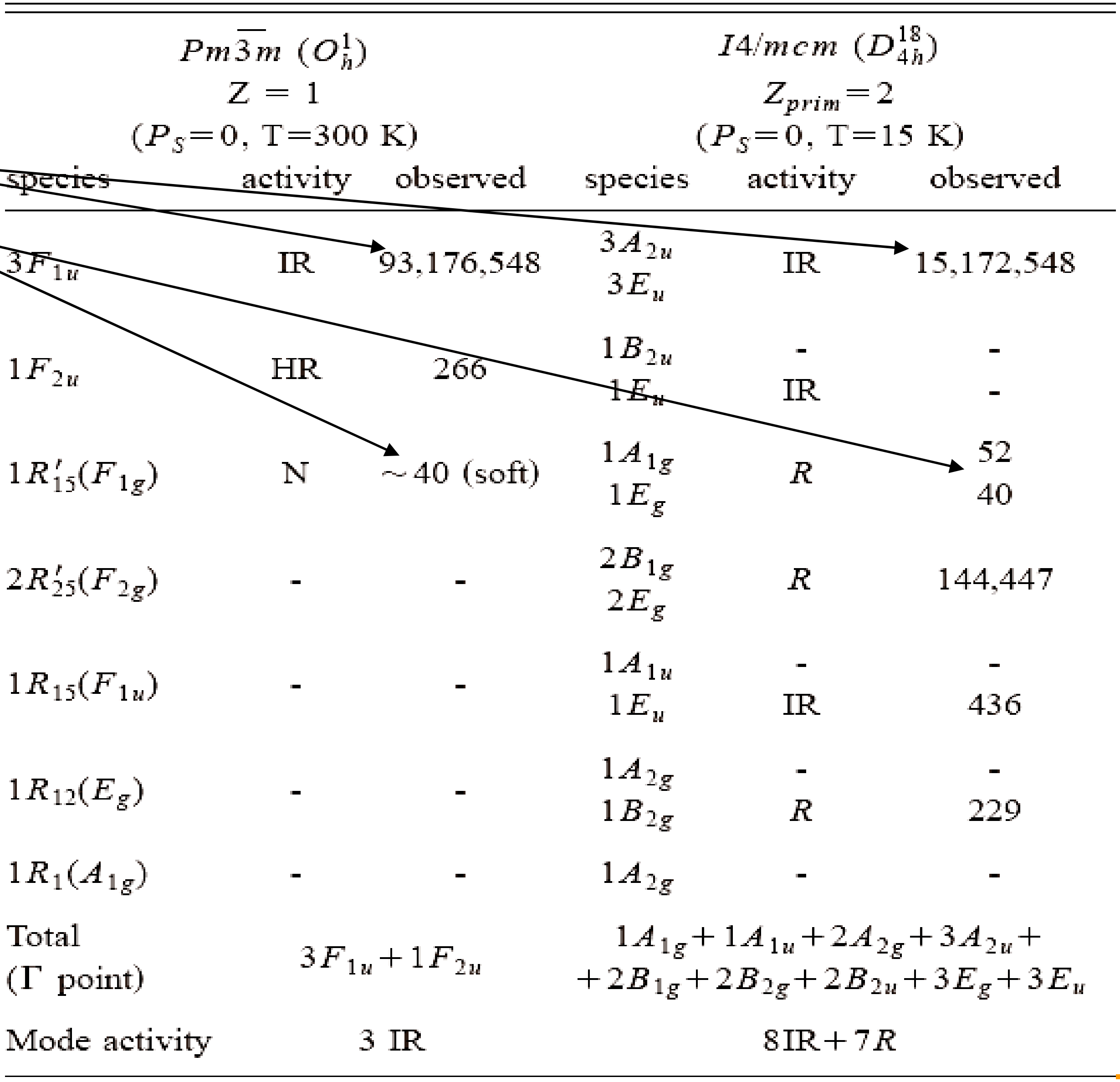
Ferroelectric SM

Structural SM (doublet)

Mode frequencies on STO ceramics

(Petzelt et al., PRB **64**, 184111 (2001))



$Pm\bar{3}m$ (O_h^1) Z = 1 (P_S=0, T=300 K)			$I4/mcm$ (D_{4h}^{18}) Z_{prim}=2 (P_S=0, T=15 K)		
species	activity	observed	species	activity	observed
$3F_{1u}$	IR	93,176,548	$3A_{2u}$ $3E_u$	IR	15,172,548
$1F_{2u}$	HR	266	$1B_{2u}$ $1E_u$	- IR	- -
$1R'_{15}(F_{1g})$	N	~40 (soft)	$1A_{1g}$ $1E_g$	R	52 40
$2R'_{25}(F_{2g})$	-	-	$2B_{1g}$ $2E_g$	R	144,447
$1R_{15}(F_{1u})$	-	-	$1A_{1u}$ $1E_u$	- IR	- 436
$1R_{12}(E_g)$	-	-	$1A_{2g}$ $1B_{2g}$	- R	- 229
$1R_1(A_{1g})$	-	-	$1A_{2g}$	-	-
Total (Γ point)	$3F_{1u}+1F_{2u}$		$1A_{1g}+1A_{1u}+2A_{2g}+3A_{2u}+$ $+2B_{1g}+2B_{2g}+2B_{2u}+3E_g+3E_u$		
Mode activity	3 IR		8IR+7R		

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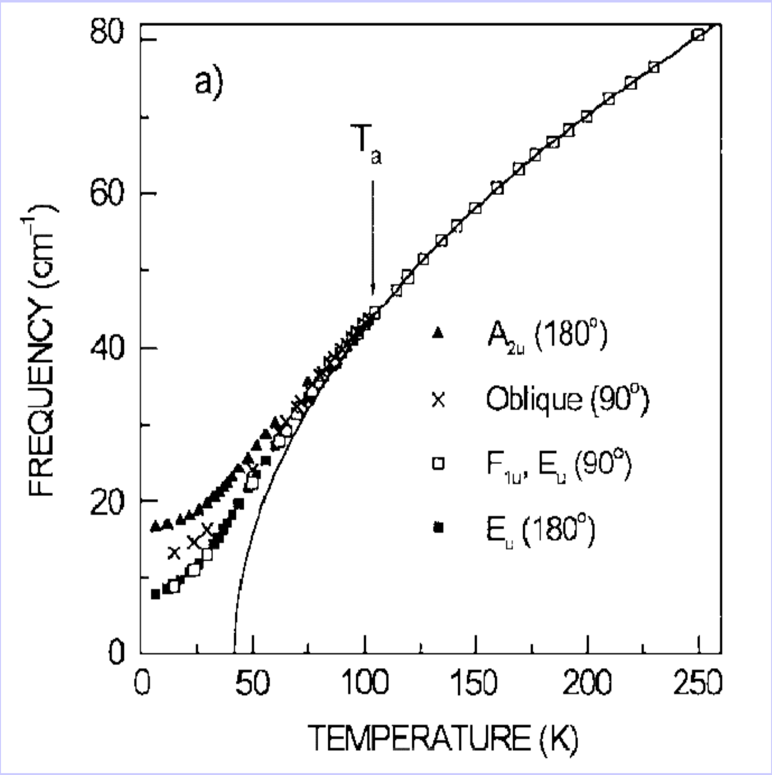

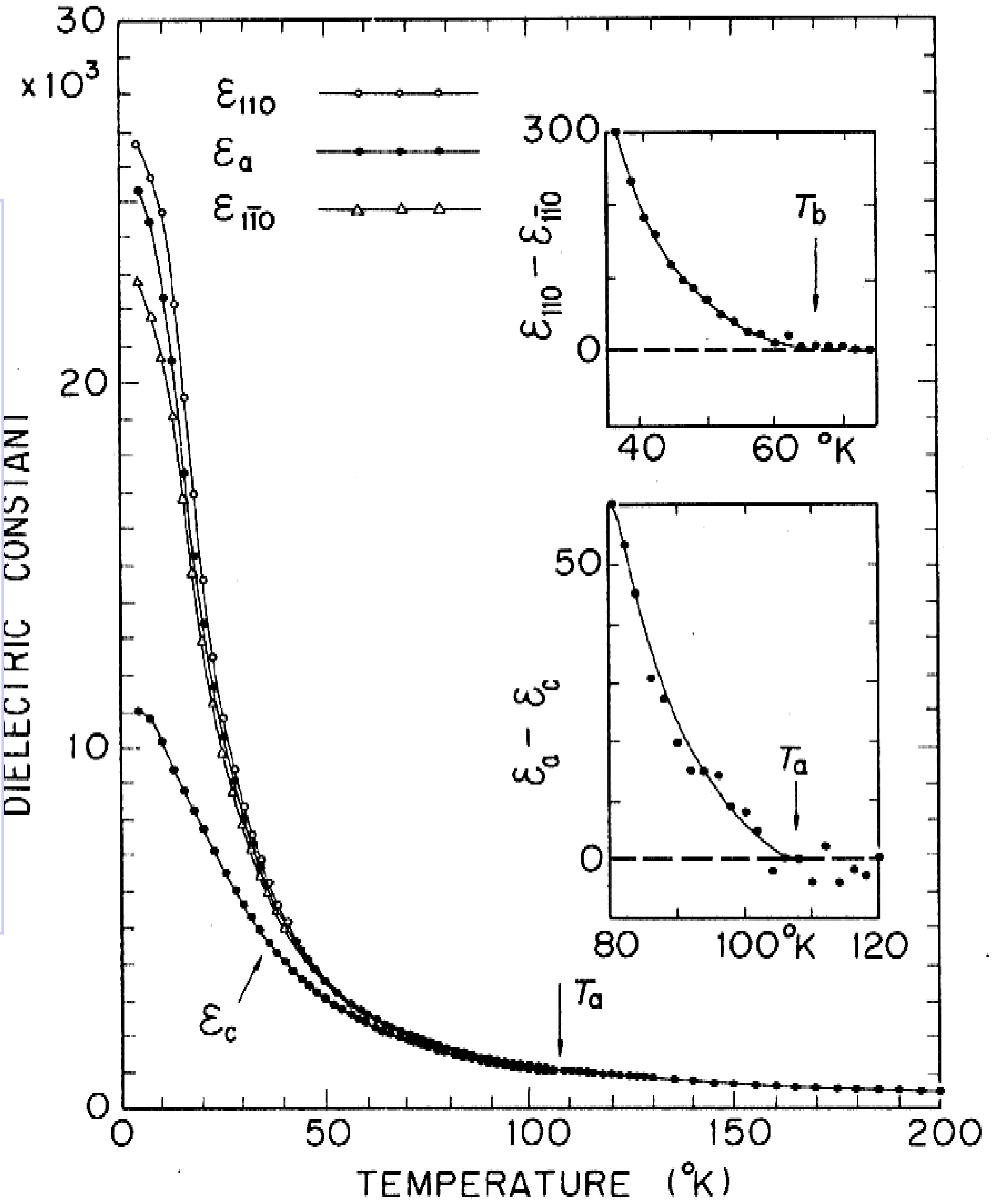

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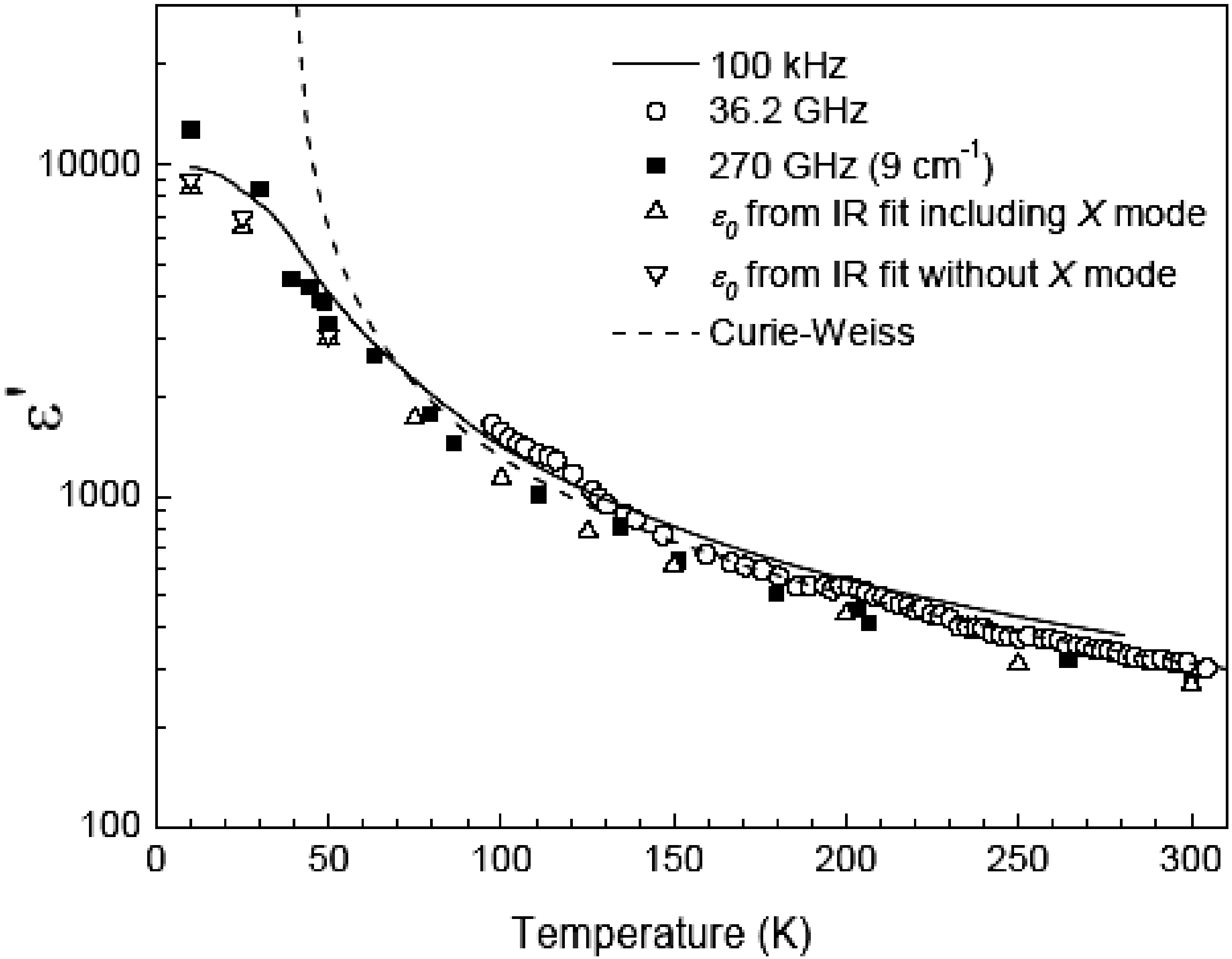
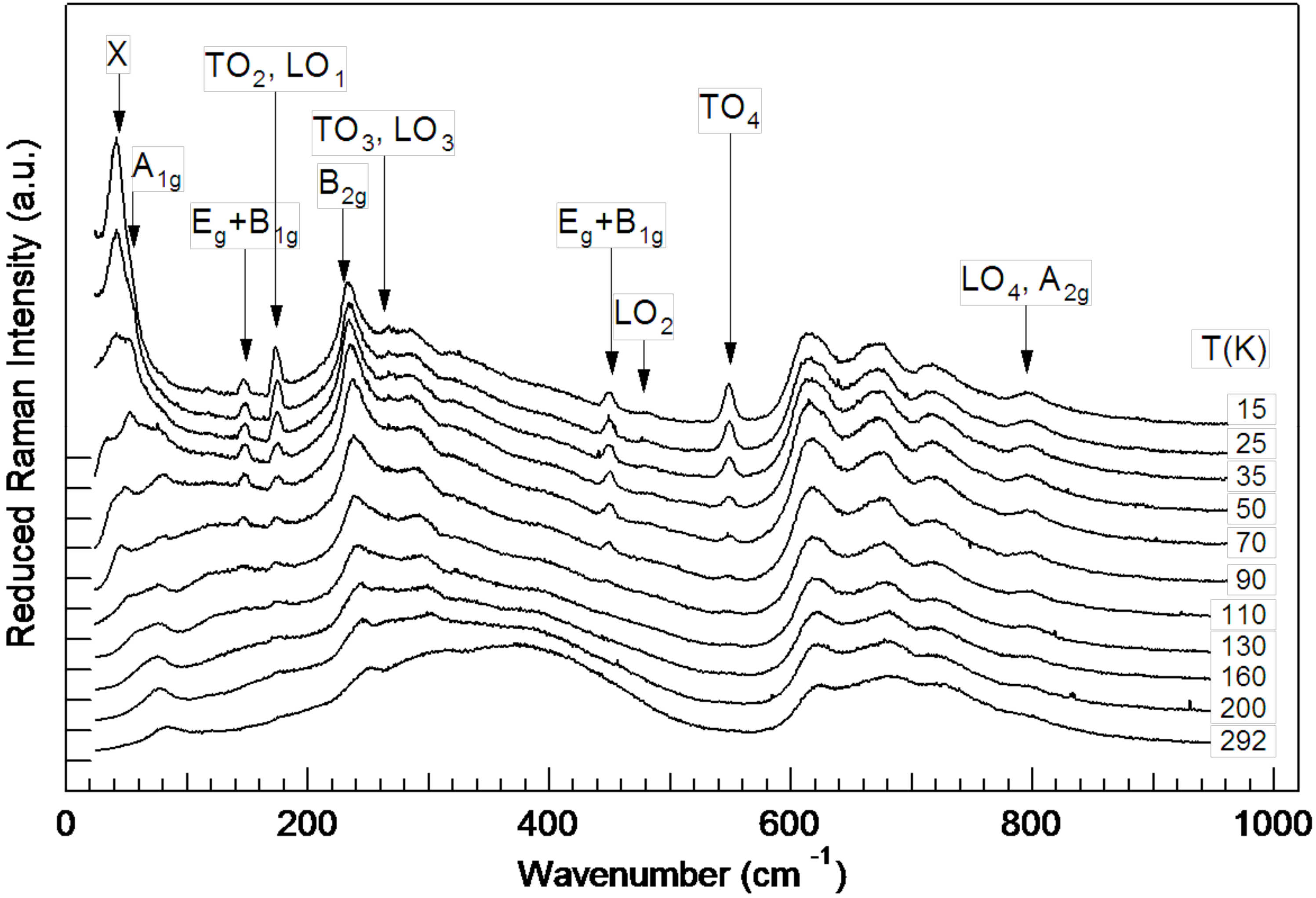


$SrTiO_3$ ceramics



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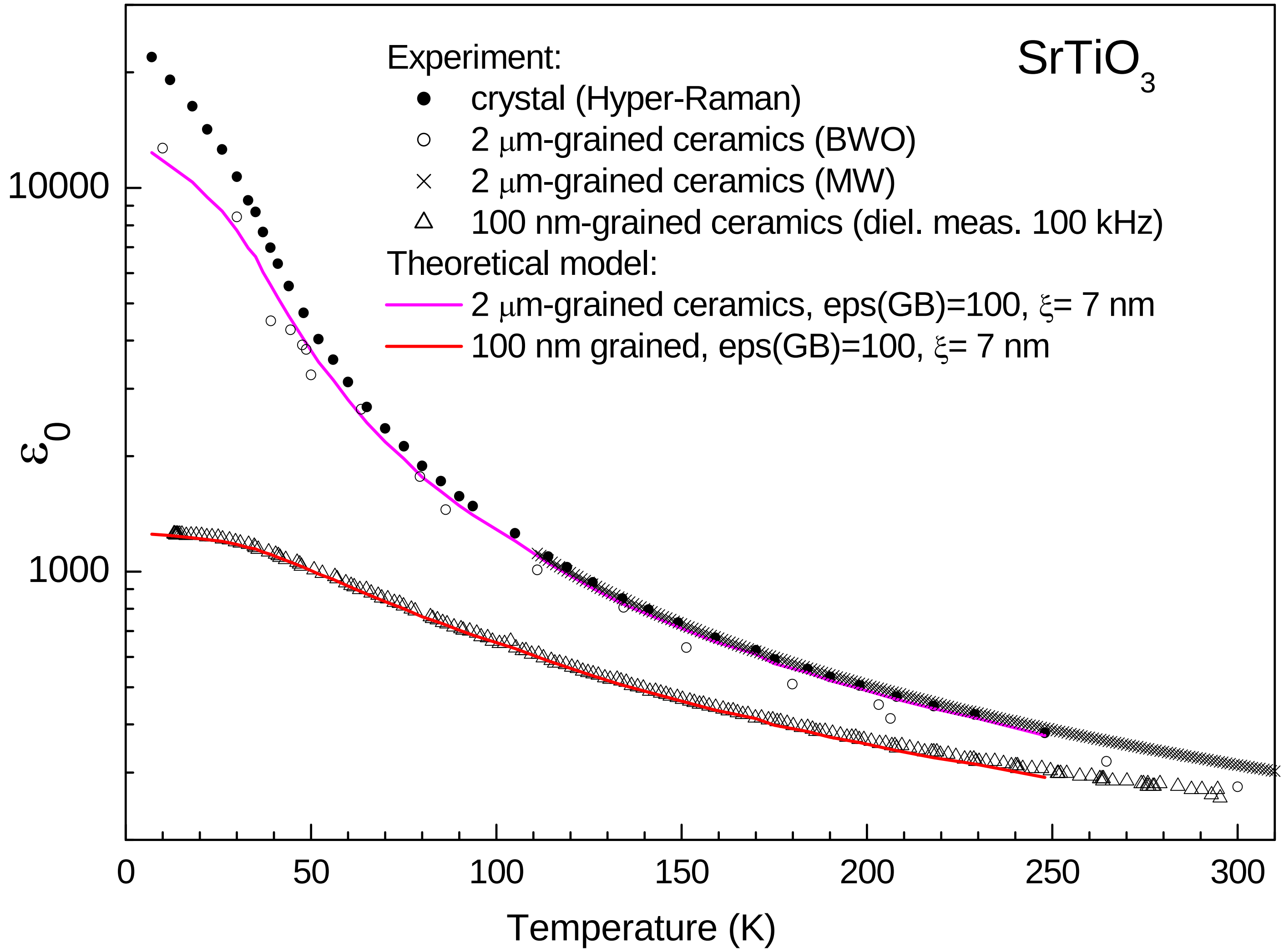
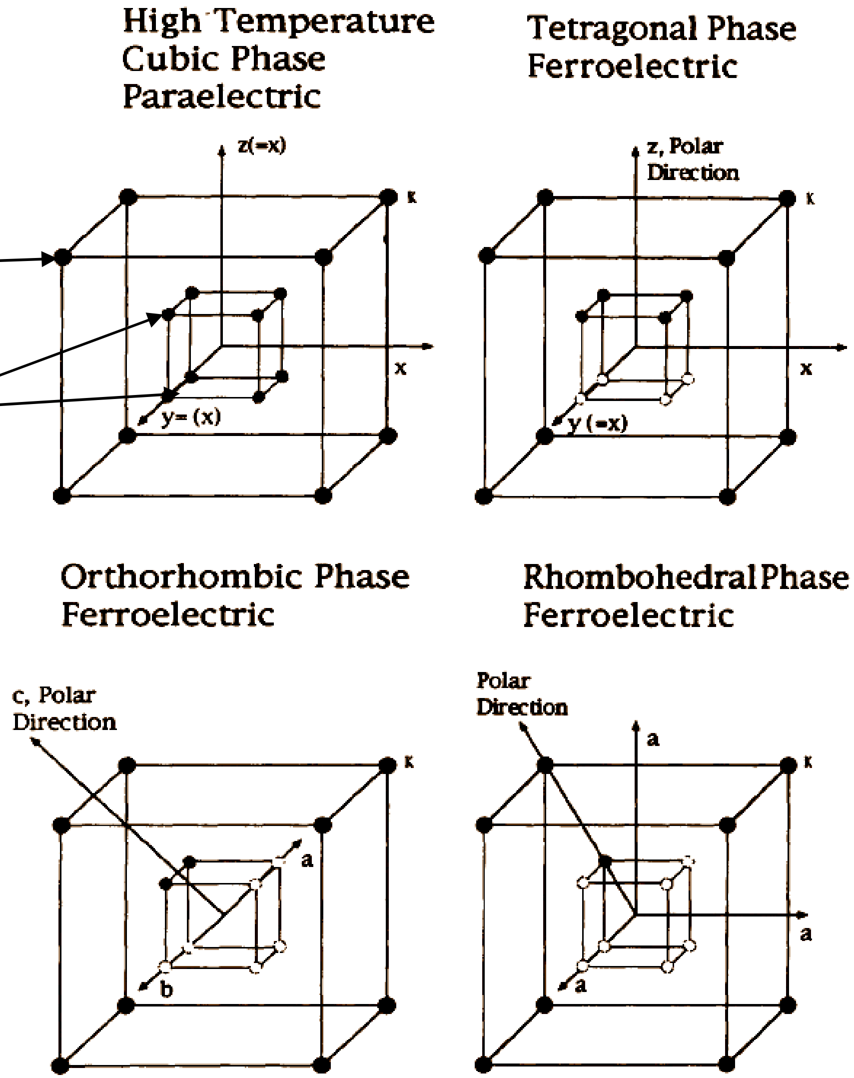
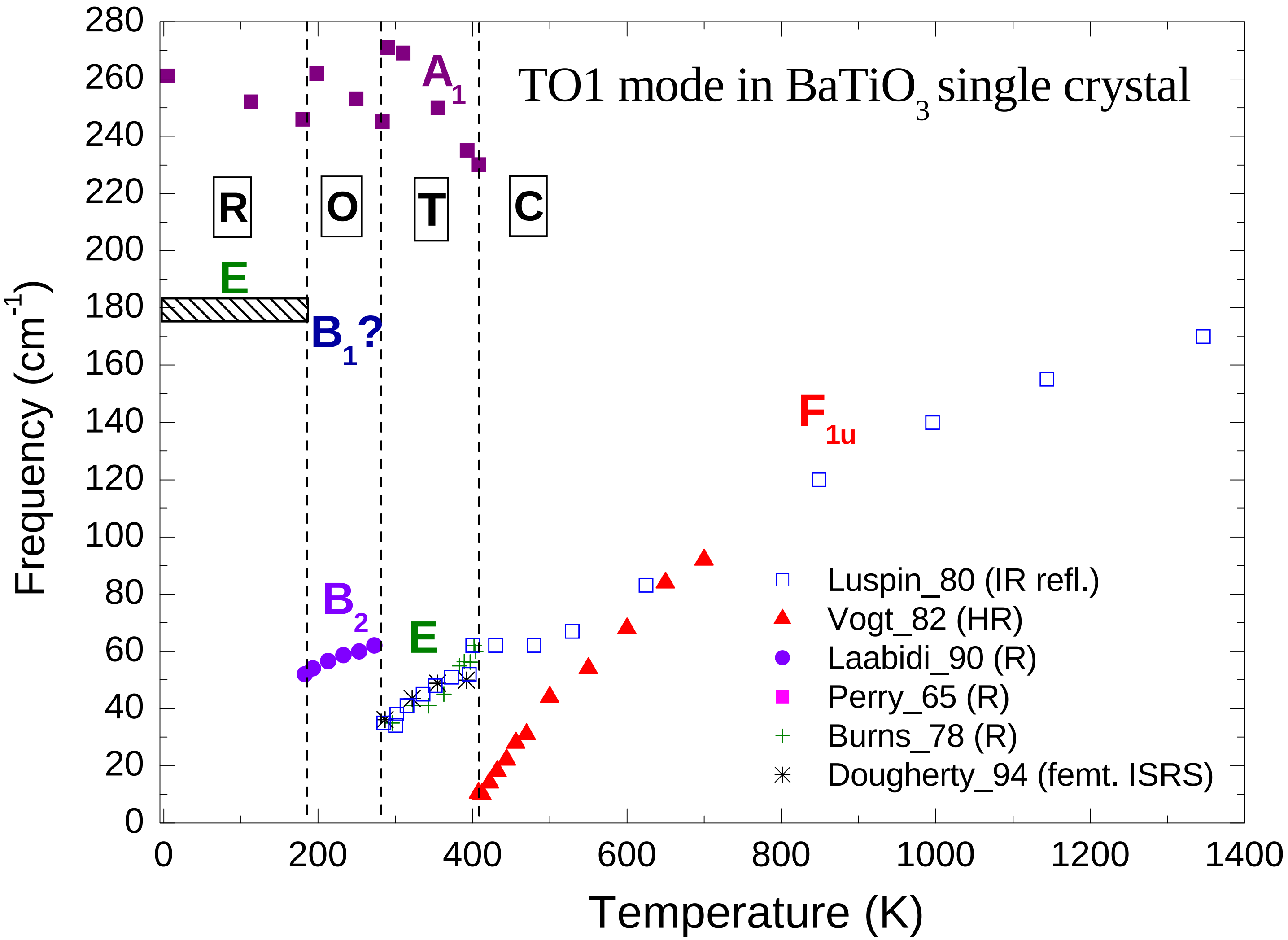


Order-disorder model for BaTiO$_3$ phase transitions

Ordered Ba

Dynamically disordered Ti




TO1 mode in BaTiO$_3$ single crystal
Frequency (cm^{-1})
Temperature (K)
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
0
200
400
600
800
1000
1200
1400
R
O
T
C
A$_1$
E
B$_1$?
B$_2$
E
F$_{1u}$
□ Luspin_80 (IR refl.)
▲ Vogt_82 (HR)
● Laabidi_90 (R)
■ Perry_65 (R)
+ Burns_78 (R)
✳ Dougherty_94 (femt. ISRS)

Class 9: Polar materials and ferroelectrics

Unpolarized Raman spectra of $BaTiO_3$ crystals (after Perry and Hall 1965)