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HIFAR 1958 - 2007

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Determination of the symmetry of ferroelectric phase of SrTi^{18}O$_3$ from lattice dynamics calculations

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STO16 = SrTi^{16}O3 STO18 = SrTi^{18}O3

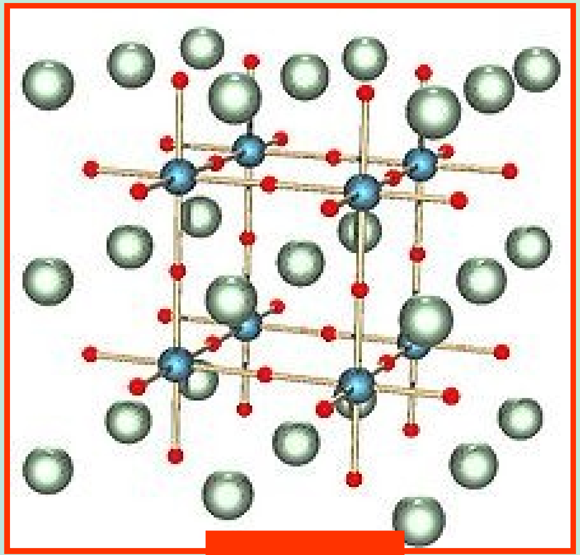
The question – why does STO16 have no low-temperature ferroelectric phase but STO18 does? We would be happy just to determine the structure!

Phase transitions

Strontium titanate (STO) is a classic perovskite ABO_3

Sr as the A-cation with 12-fold cuboctahedral coordination

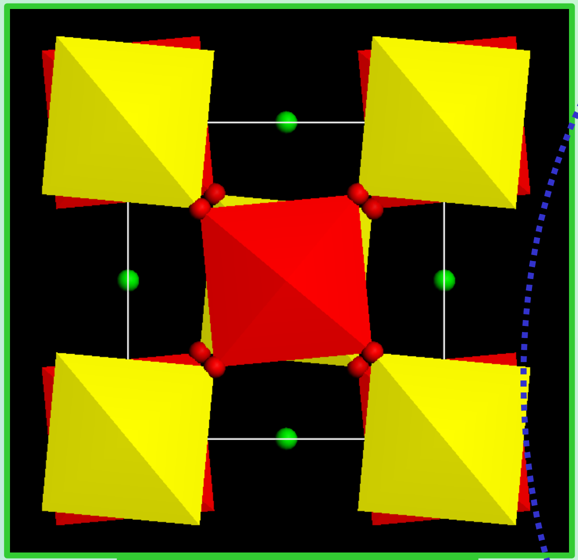
Ti as the B-cation with 8-fold octahedral coordonation



Cubic

110K →

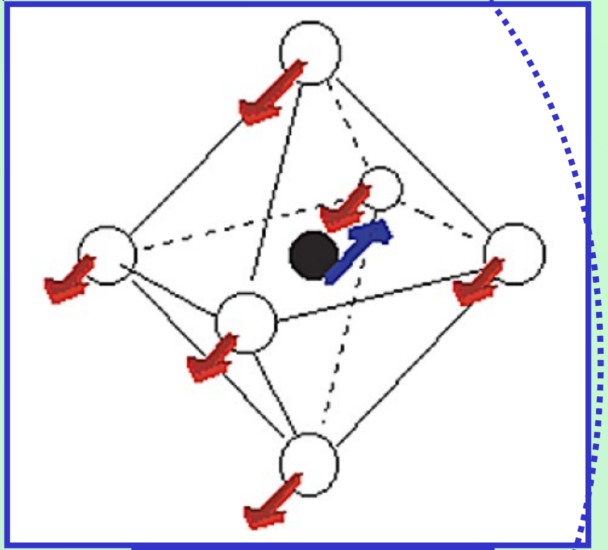
Rotation of octahedra



Tetragonal (Multidomain)

~35K →

Slater mode



Orthorhombic

Overview of talk

Existing crystallographic information

Sample preparation –

Our crystallographic failures

Did it actually work? Raman

Calculation of soft modes in tetragonal phase of STO, where do they lead?

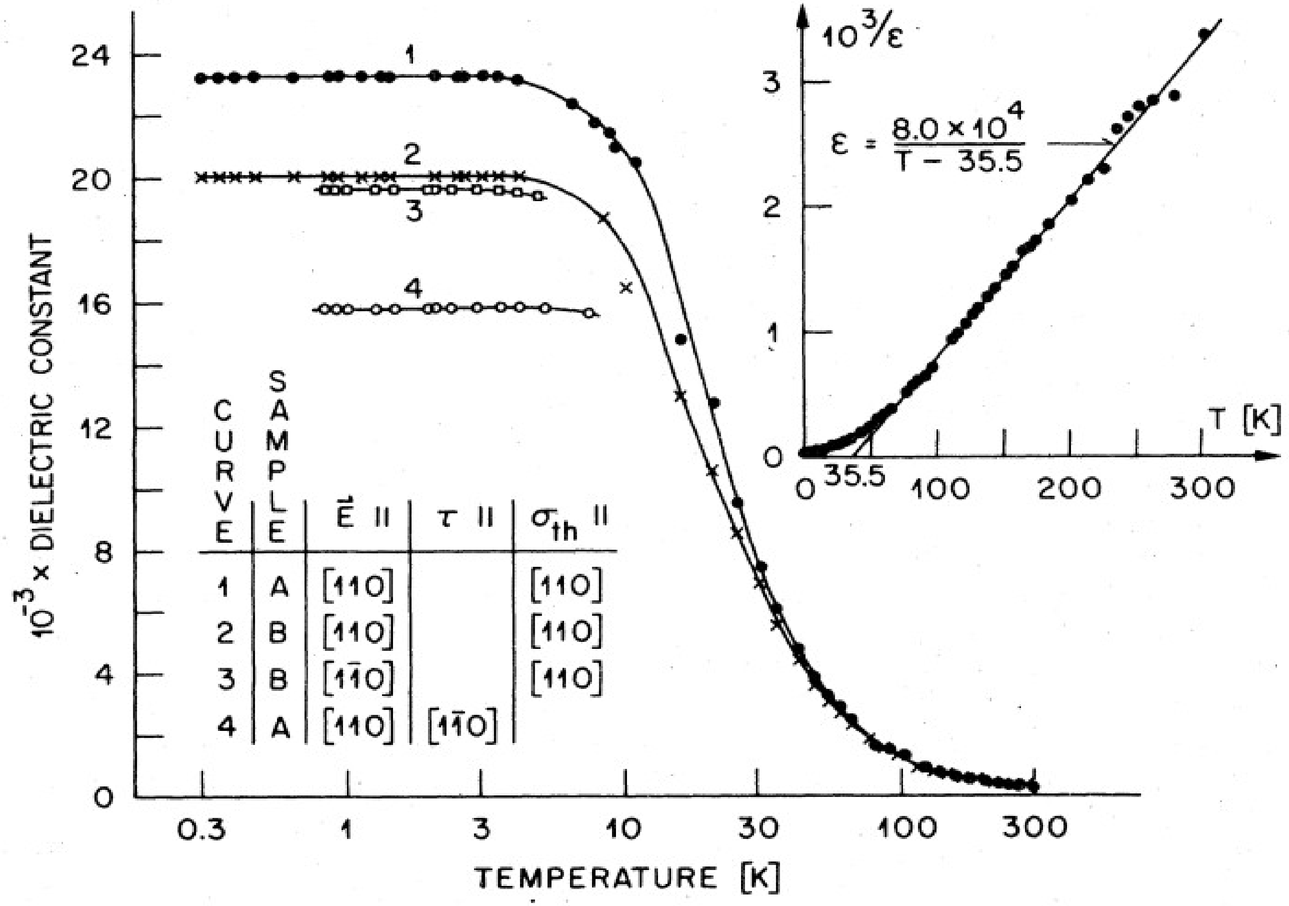
Optimise the resulting structure – does it make sense.

Can we measure phonons in STO18?

Can we say anything about the quantum paraelectric behaviour?

Is a quantum paraelectric

K. A. Muller and H. Burkard, Phys.Rev. B 19, 3593 (1979)



CURVE	SAMPLE	$\vec{E}$ ∥	τ ∥	σ_{th} ∥
1	A	[110]		[110]
2	B	[110]		[110]
3	B	$[1\bar{1}0]$		[110]
4	A	[110]	$[1\bar{1}0]$	

FIG. 2. Dielectric constants ϵ_{110} and $\epsilon_{1\bar{1}0}$ of the monodomain $SrTiO_3$ samples *A* and *B* (σ_{th} is the stress applied by thermal treatment). Inset: $10^3/\epsilon$ vs *T*.

Becomes ferroelectric if the content of ^{18}O isotope exceeds 33%

M. Itoh, R. Wang, Y. Inaguma, T. Yamaguchi, Y-J. Shan, and T. Nakamura, Phys. Rev. Lett., 82, 3540 (1999)

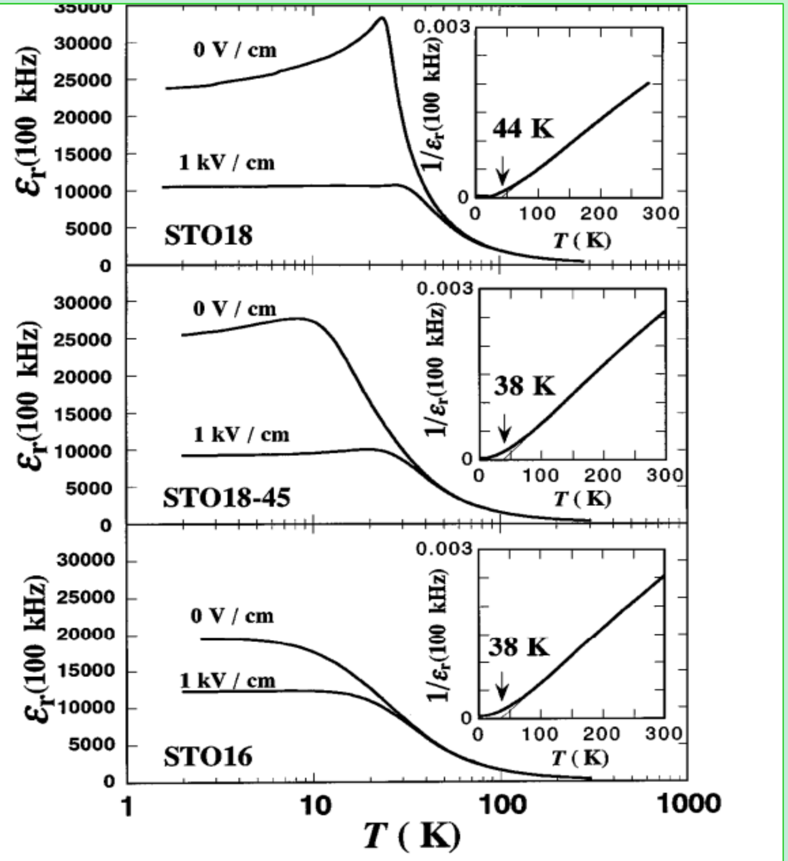


FIG. 1. Comparison of temperature dependence of ε_r and tan δ for STO16, STO45-18, and STO18. Insets show the temperature dependence of $1/\varepsilon_r$ for zero bias. Temperatures in the insets show θ obtained by the least squares fitting by Curie-Weiss law, $\varepsilon_r = C/(T - \theta)$, for the data between 100 and 200 K.

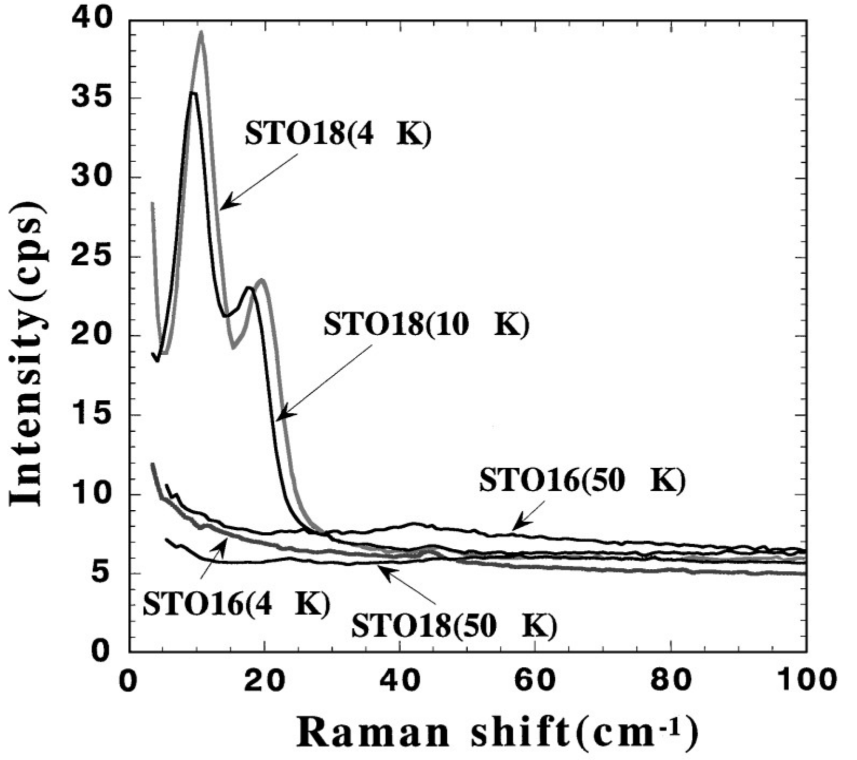
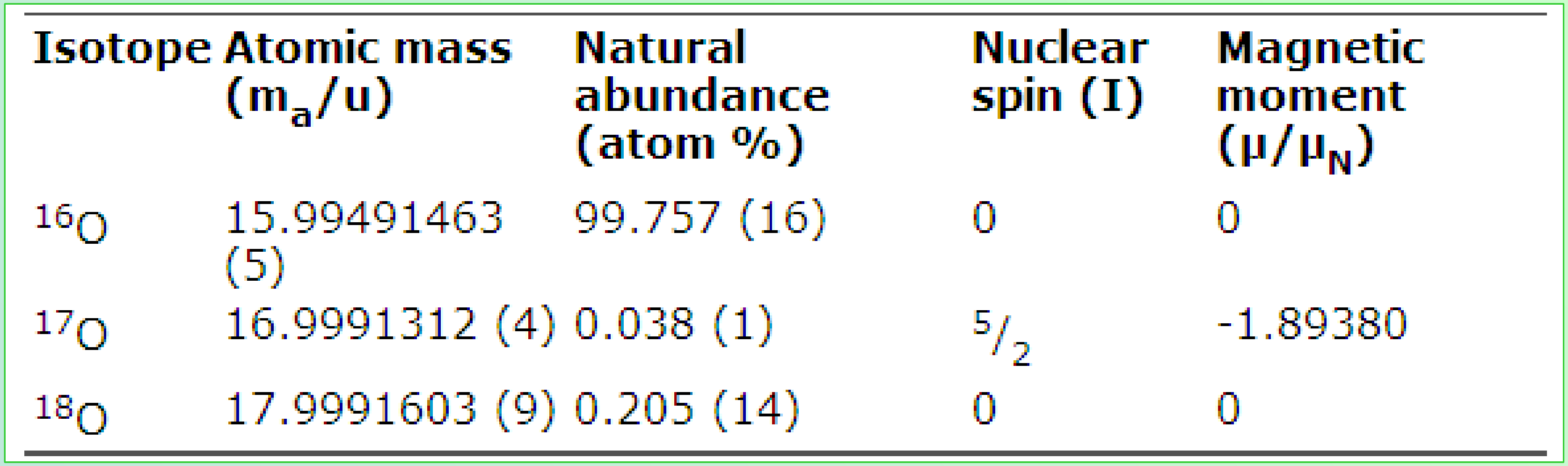


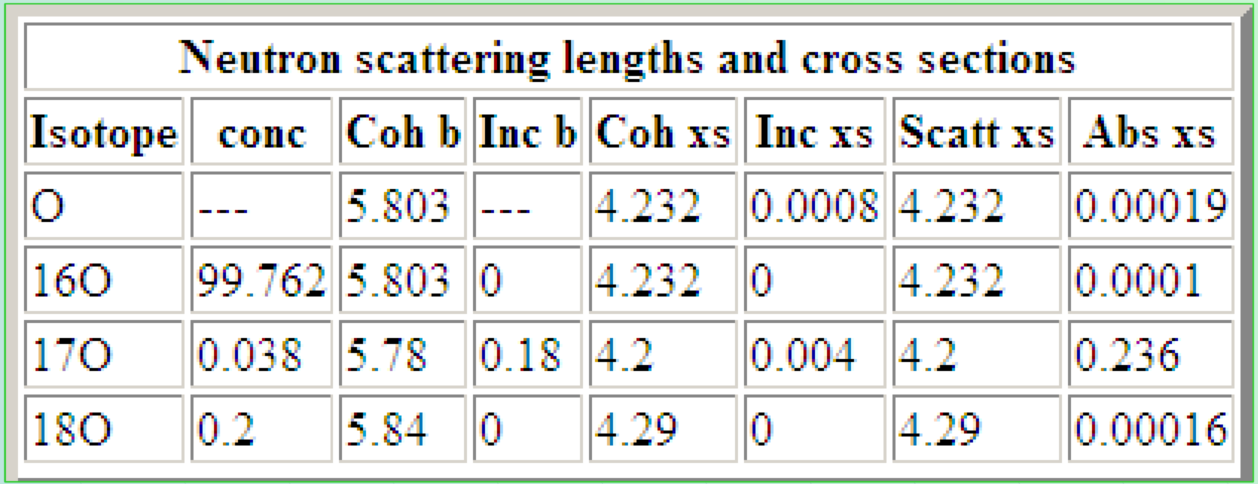
FIG. 4. Raman spectra for STO16 and STO18 at 4, 10, and 50 K.

Not particularly easy, ^{18}O not abundant



Isotope	Atomic mass (m_a/u)	Natural abundance (atom %)	Nuclear spin (I)	Magnetic moment (μ/μ_N)
^{16}O	15.99491463 (5)	99.757 (16)	0	0
^{17}O	16.9991312 (4)	0.038 (1)	$^5/_2$	-1.89380
^{18}O	17.9991603 (9)	0.205 (14)	0	0

Good neutron scattering cross-section (can see against heavier elements) but no difference in coherent scattering between ^{18}O and ^{16}O)



Neutron scattering lengths and cross sections

Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
O	---	5.803	---	4.232	0.0008	4.232	0.00019
16O	99.762	5.803	0	4.232	0	4.232	0.0001
17O	0.038	5.78	0.18	4.2	0.004	4.2	0.236
18O	0.2	5.84	0	4.29	0	4.29	0.00016

Structural information on ferroelectric phase is limited:

Single-crystal (multidomain) neutron diffraction Y. Noda, K. Mochizuki, H. Kimura, M. Itoh, T. Kyomen,and R. Wang, Journal of the Korean Physical Society 46, 69 (2005)

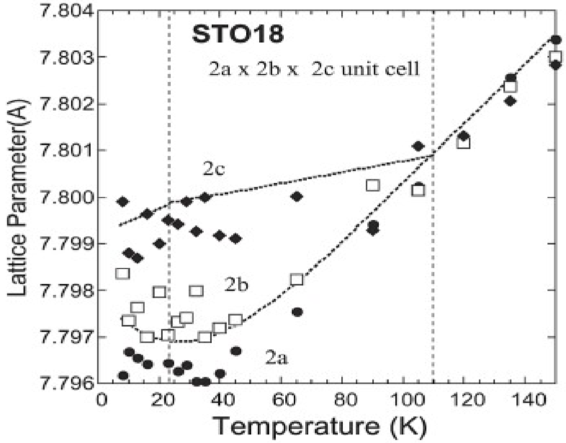


Fig. 1. Lattice parameters referred to *fct* unit cell.

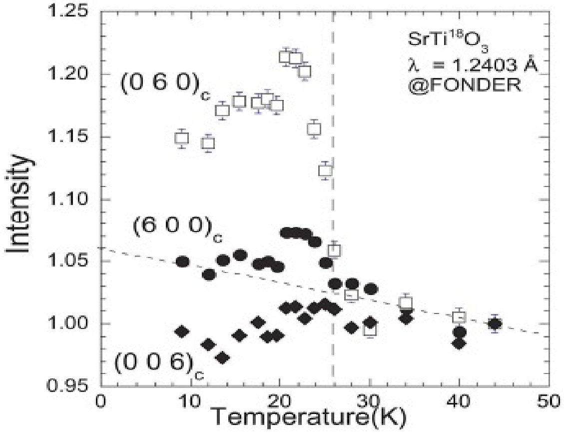


Fig. 2. Intensity of {6 0 0}$_c$ Bragg reflection as a function of temperature.

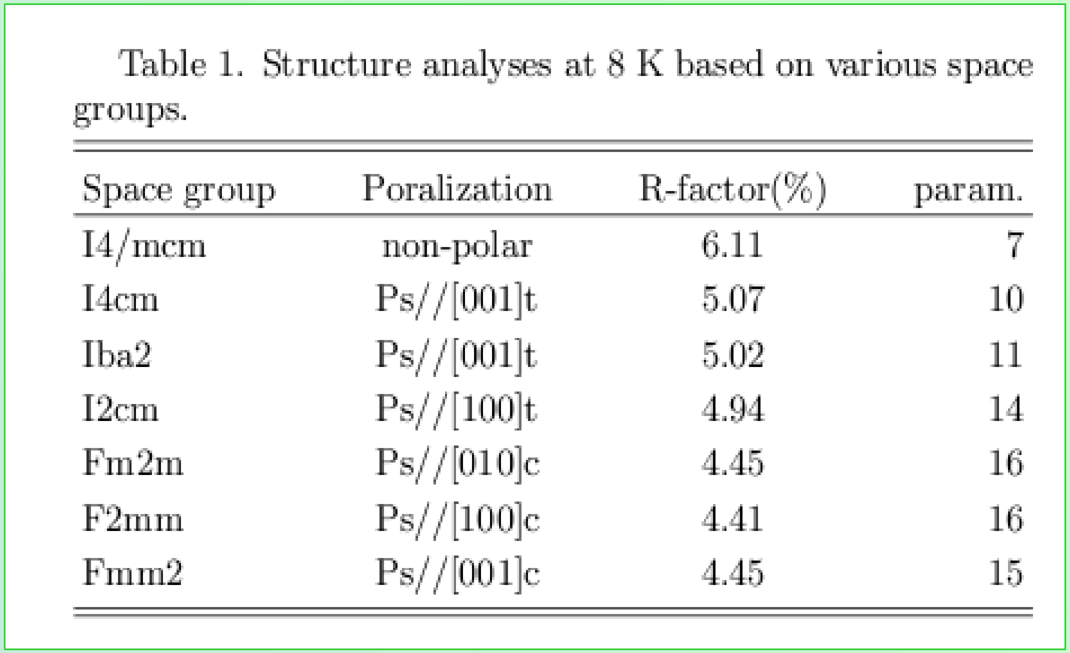


Table 1. Structure analyses at 8 K based on various space groups.

Space group	Poralization	R-factor(%)	param.
I4/mcm	non-polar	6.11	7
I4cm	Ps//[001]t	5.07	10
Iba2	Ps//[001]t	5.02	11
I2cm	Ps//[100]t	4.94	14
Fm2m	Ps//[010]c	4.45	16
F2mm	Ps//[100]c	4.41	16
Fmm2	Ps//[001]c	4.45	15

Definite evidence of transition at ~35K, fairly certain tetragonal → orthorhombic, but space-group not certain.

Situation overview

Paraelectric phase:

I 4/mcm symmetry

Known structure

Phase transition

Ferroelectric phase:
Unknown structure

Based on results published so far

Must have:
- Dipole moment
- Raman peaks below 50 cm^{-1}

Our objectives:

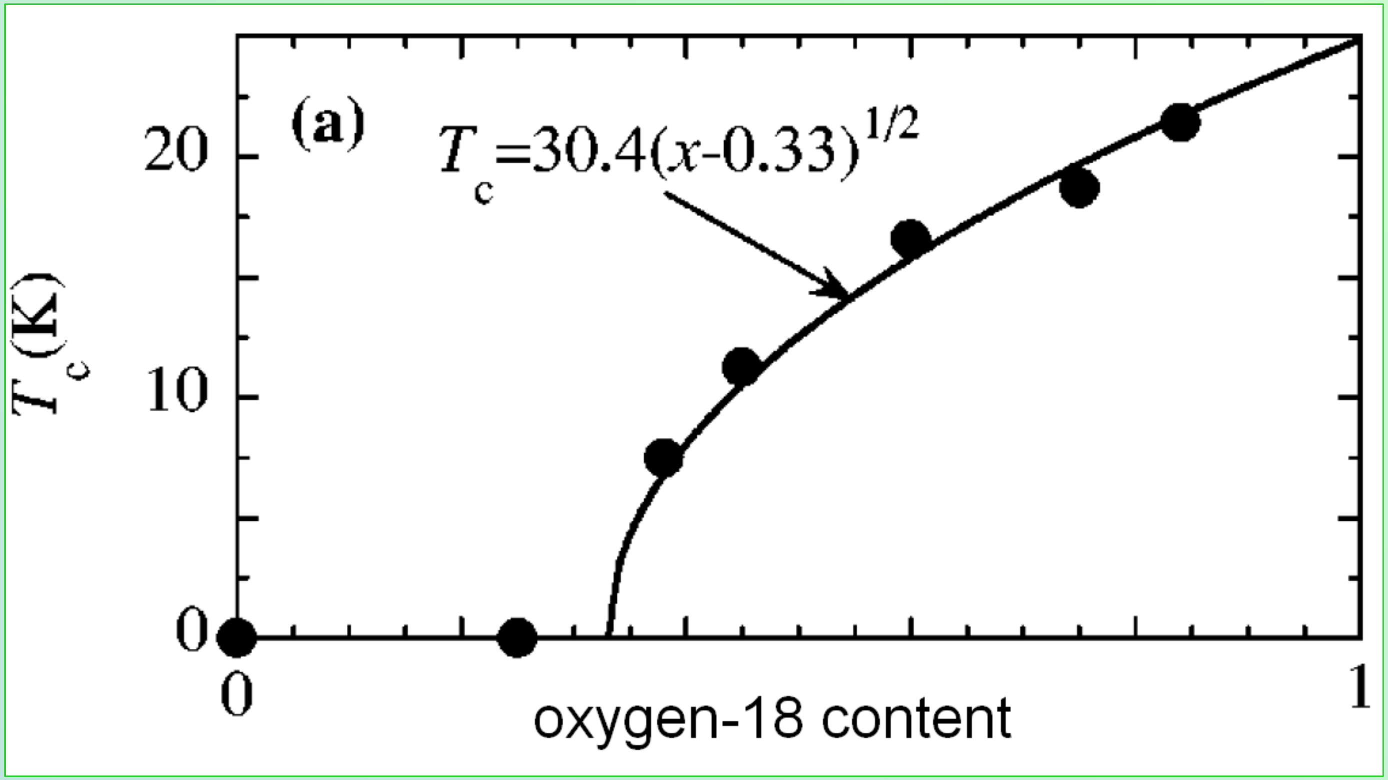
1. Determine the **structure** of the ferroelectric phase.
2. Determine the **mechanism** of the phase transition from paraelectric into ferroelectric phase.
3. Analyse the **dynamics** of both structures.

Sample preparation

We tried to make the stuff by solid-state exchange: ^{18}O for ^{16}O then weigh to see what we got.

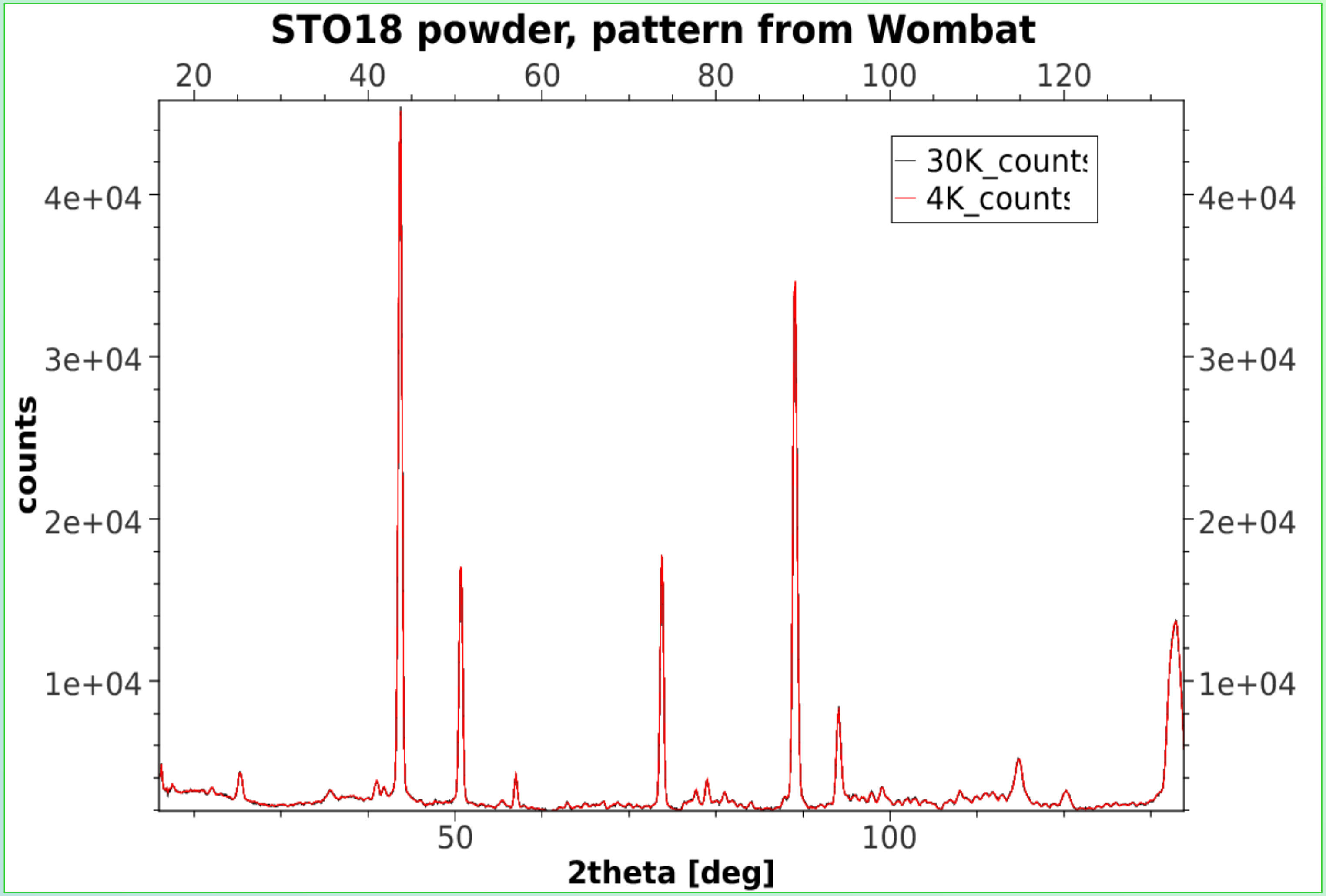
Ferroelectric phase transition varies with amount of oxygen-18

(R. Wang and M. Itoh, Phys. Rev. B, 2001)

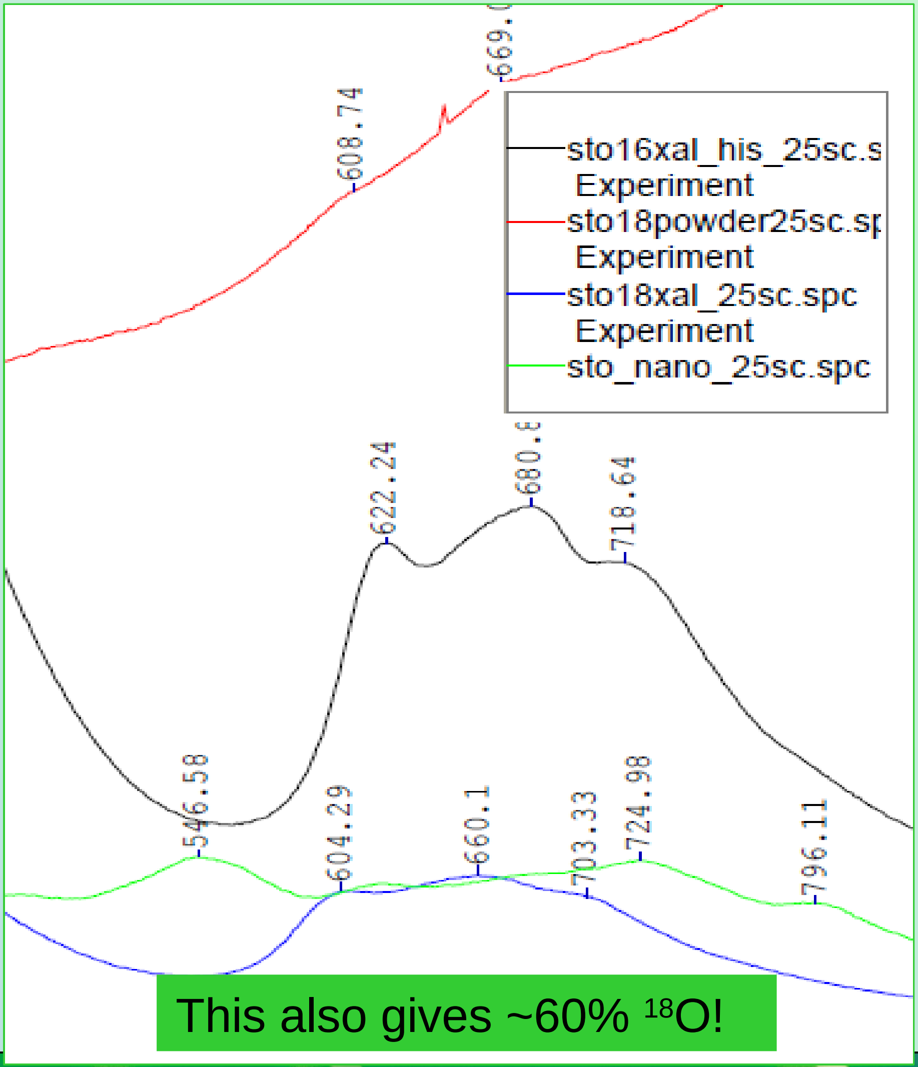


We estimate our exchange (from weight) to be ~60%
This would give the transition at ~17K

From neutron powder diffraction we see no transition between 30 and 4K! Did the oxygen really exchange?



Room-temperature Raman is complex – no fundamentals are Raman-active. Can sort out multiphonons (from PHONON) and assign oxygen participation.



This also gives ~60% ^{18}O!

shift [cm^{-1}] O18	shift [cm^{-1}] O16	Main contributions
69.3	71.8	O, Ti
109.3	116	O only
141.7	141.8	Sr
147.7	147.7	Sr
164.2	165	all
172.6	173.6	all
231.06	245	O
245.27	260.1	O only
407	426.3	O
410	431.5	O
426.2	433.8	Ti
433.8	434.8	Ti
451.8	479.2	O only
452.65	480.1	O only
498.6	528.8	O
508.85	539.7	O
780.8	828.2	O only

In the regular STO crystal the sum of the yellow rows gives the peak at 622 cm^{-1} and the sum of the green rows gives the peak at 681 cm^{-1}.

Maciej Bartkowiak

“What can I do without a sample?”

M. Takesada, M. Itoh, and T. Yagi, PRL **96,** 227602 (2006)

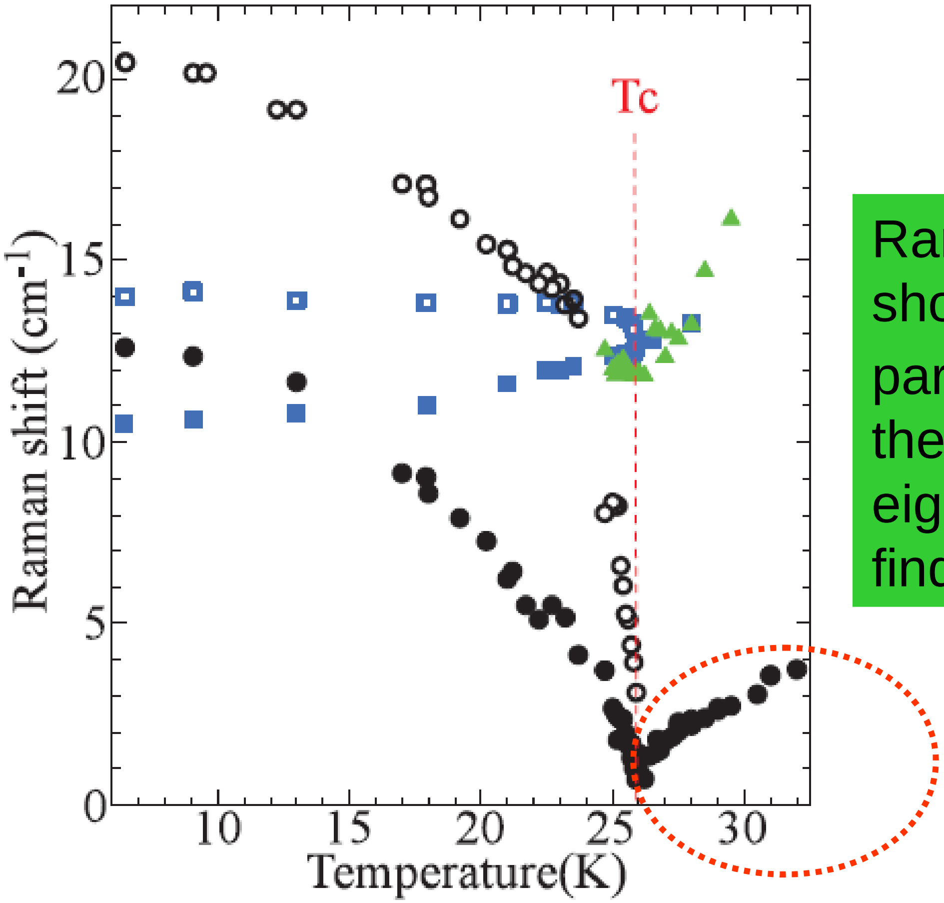
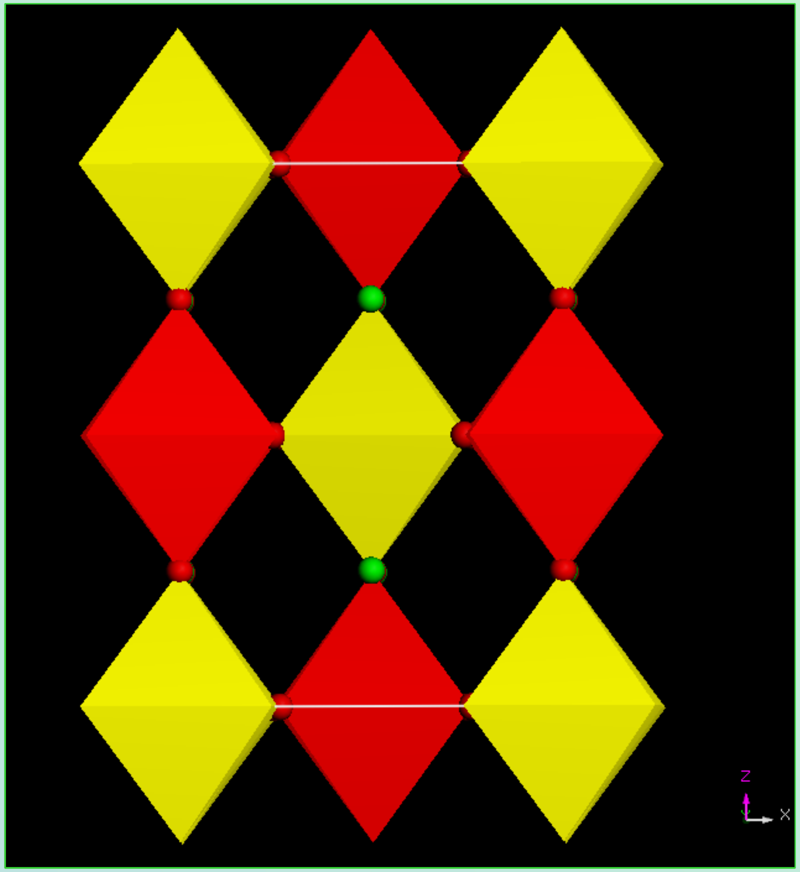


FIG. 2 (color). The temperature dependence of E_u (●), A_{2u} (▲), and E_g (■) modes above T_c, and $A_1(E_{u1})$ (●), $B_2(E_{u2})$ (○), $B_1(E_{g1})$ (■), $A_2(E_{g2})$ (□), and $B_1(A_{2u})$ (▲) modes below T_c in $SrTi^{18}O_3$. The E_g, $B_1(E_{g1})$, and $A_2(E_{g2})$ modes are observed in the VH geometry (see Fig. 3).

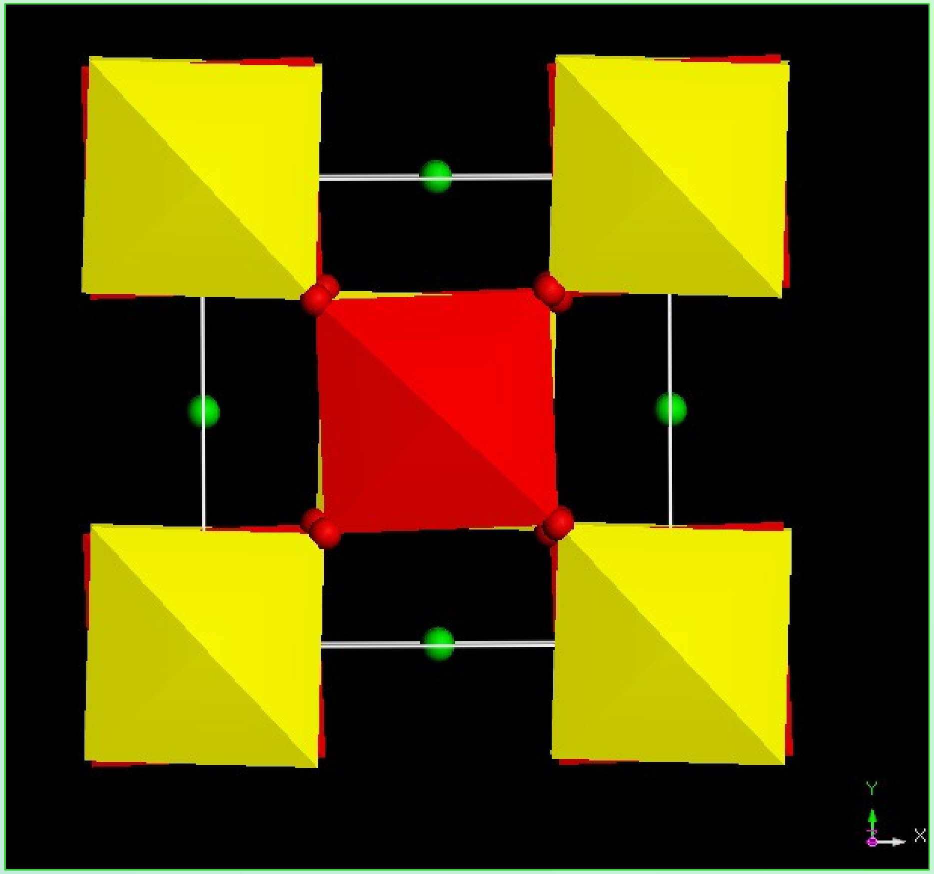
Raman spectra of STO18 show a soft mode (E_u) in the paraelectric phase. We need to do the lattice dynamics to get the eigenvectors of this mode (if we find it!)

A reasonable starting point:

experimental structure of the paraelectric phase at **1.5 K** (Kiat et al., J. Phys.: Cond. Matt., 1996)



SIDE VIEW

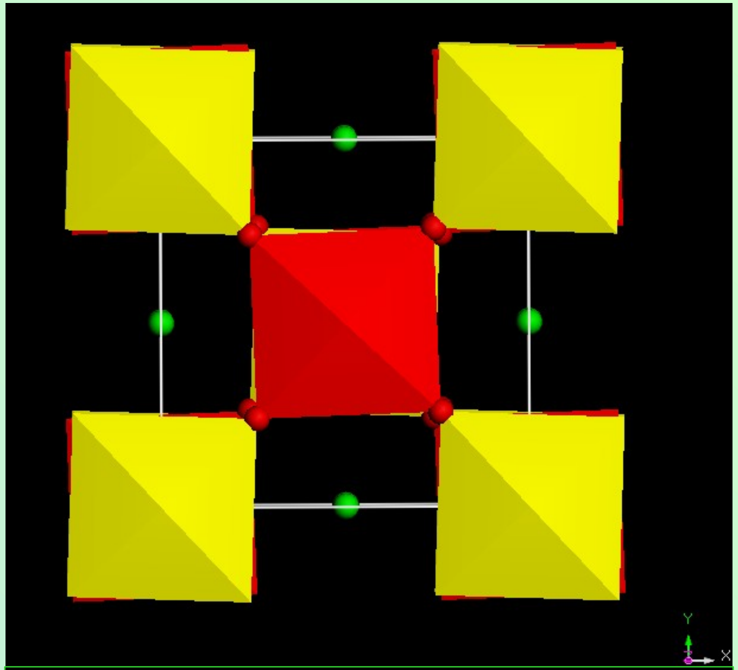


TOP VIEW

The energy minimization: our first step

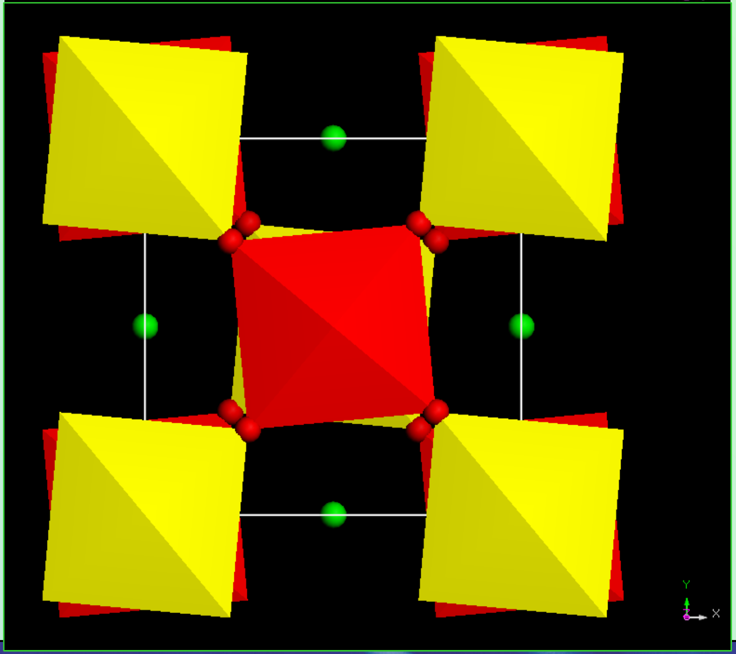
Crystallographic structure
cell energy (free energy)

-160.573019 eV



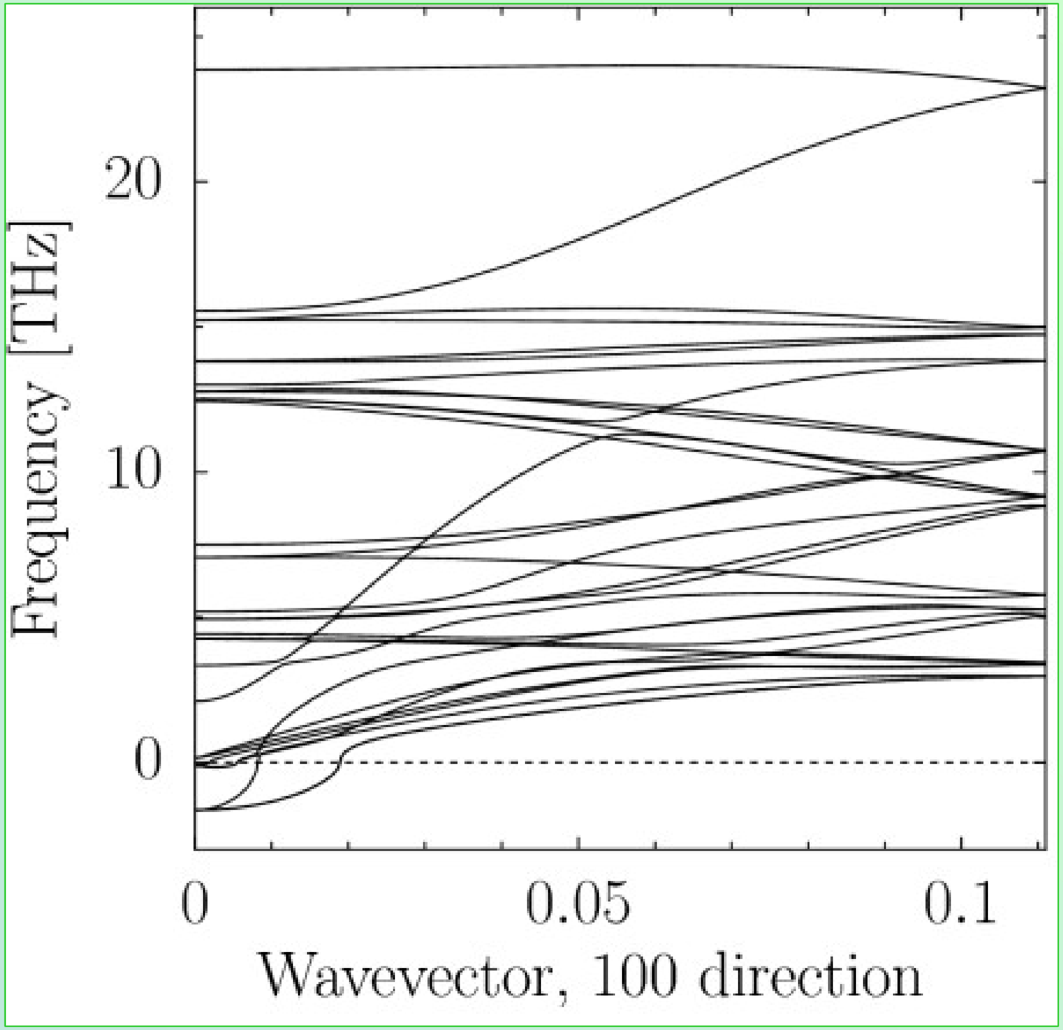
Relaxed structure
cell energy (free energy)

-160.597644 eV

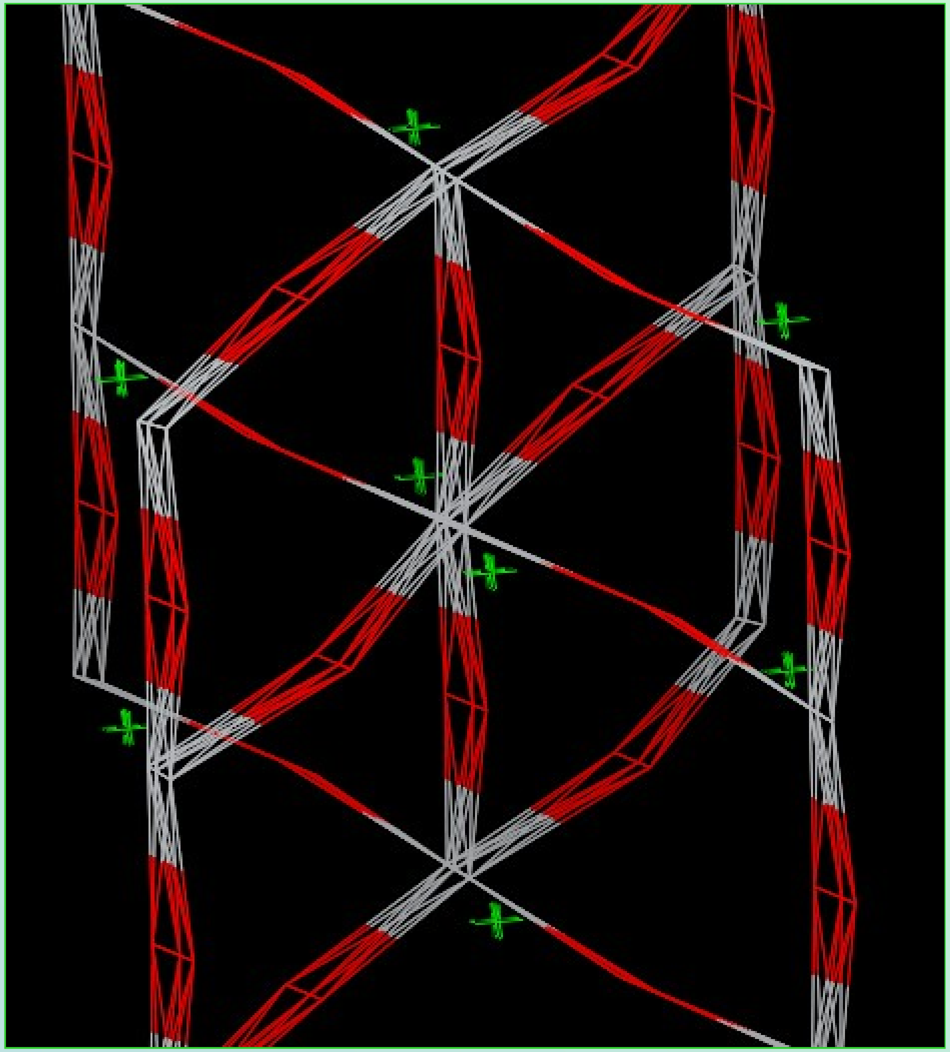


Calculated Dispersion curves of paraelectric (tetragonal) $SrTiO_3$

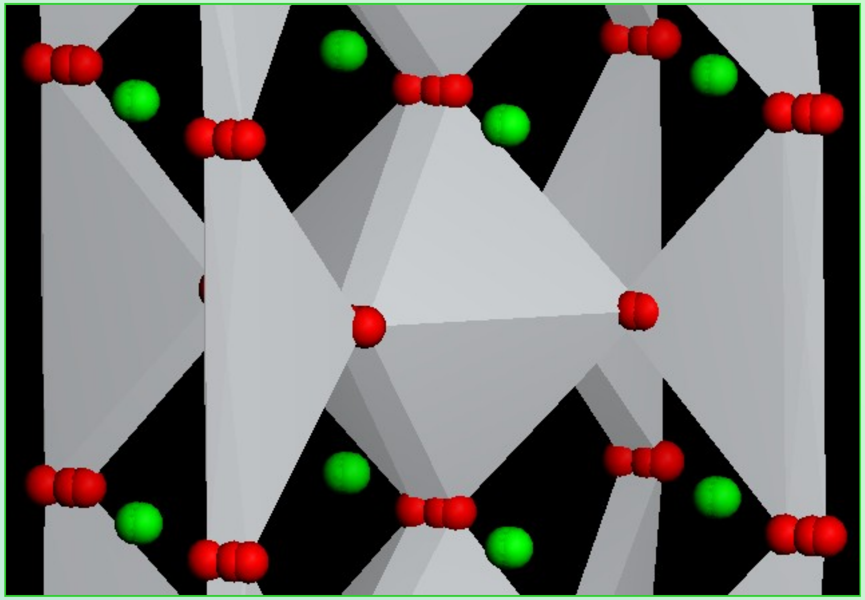
The presence of soft-modes is clear, and it is Eu (at the gamma-point)



What does displacement lead to?



It is the expected Slater mode, but there is also a slight displacement of the strontium



Leads to Ima2, identical to I2cm with permutation of axes

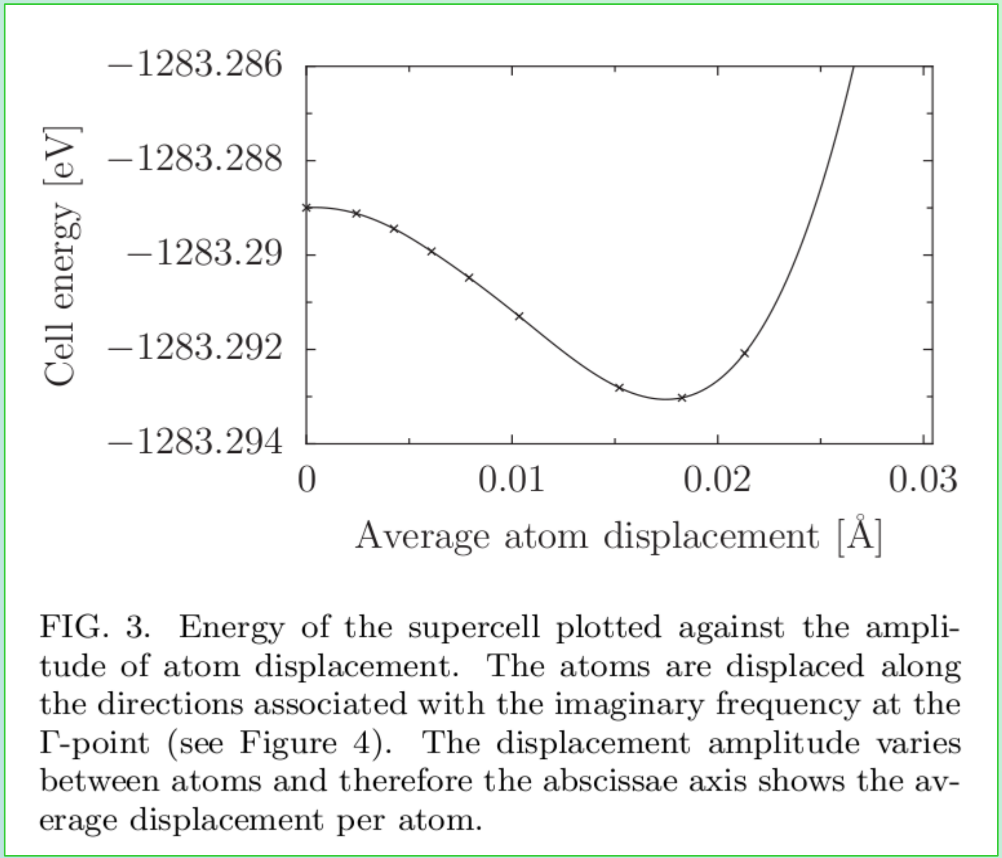
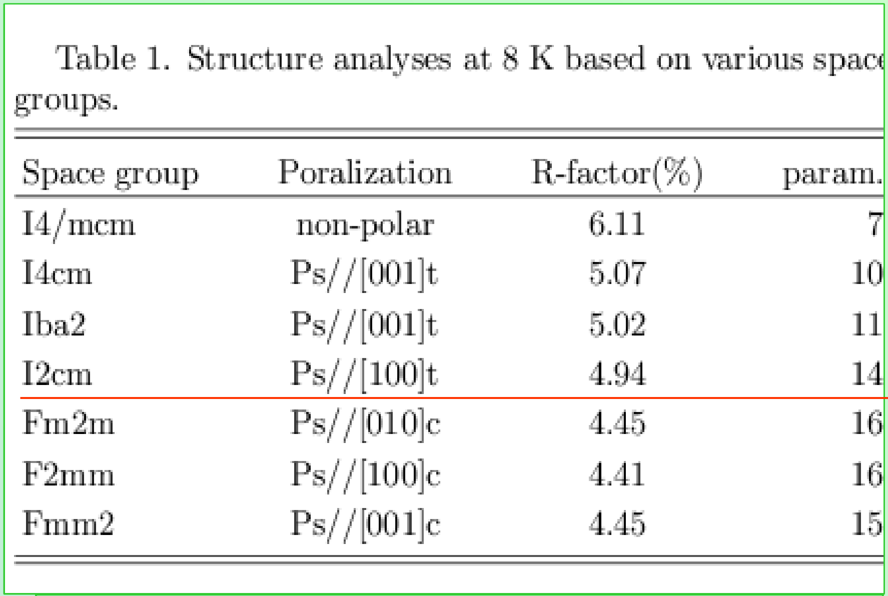


FIG. 3. Energy of the supercell plotted against the amplitude of atom displacement. The atoms are displaced along the directions associated with the imaginary frequency at the Γ-point (see Figure 4). The displacement amplitude varies between atoms and therefore the abscissae axis shows the average displacement per atom.



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Single-crystal (multidomain) neutron diffraction Y. Noda, K. Mochizuki, H. Kimura, M. Itoh, T. Kyomen,and R. Wang, Journal of the Korean Physical Society 46, 69 (2005)

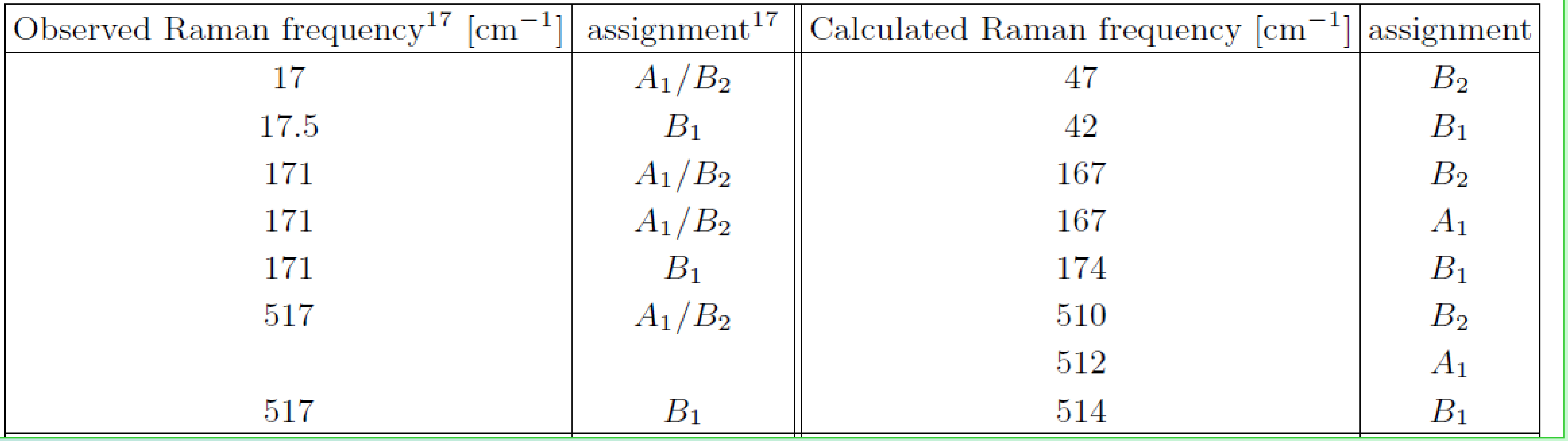
Is our result reasonable?

Starting point		Result
I 4/mcm tetragonal centrosymmetric	Symmetry	I ma2 orthorhombic non-centrosymmetric
Zero electronic dipole moment (from Berry phase calculations)	Ferroelectricity	Non-zero electronic dipole moment (from Berry phase calculations)
Total energy -160.597644 eV	Energy	Total energy -160.599194 eV

Calculated Raman-active modes for Ima2 cell

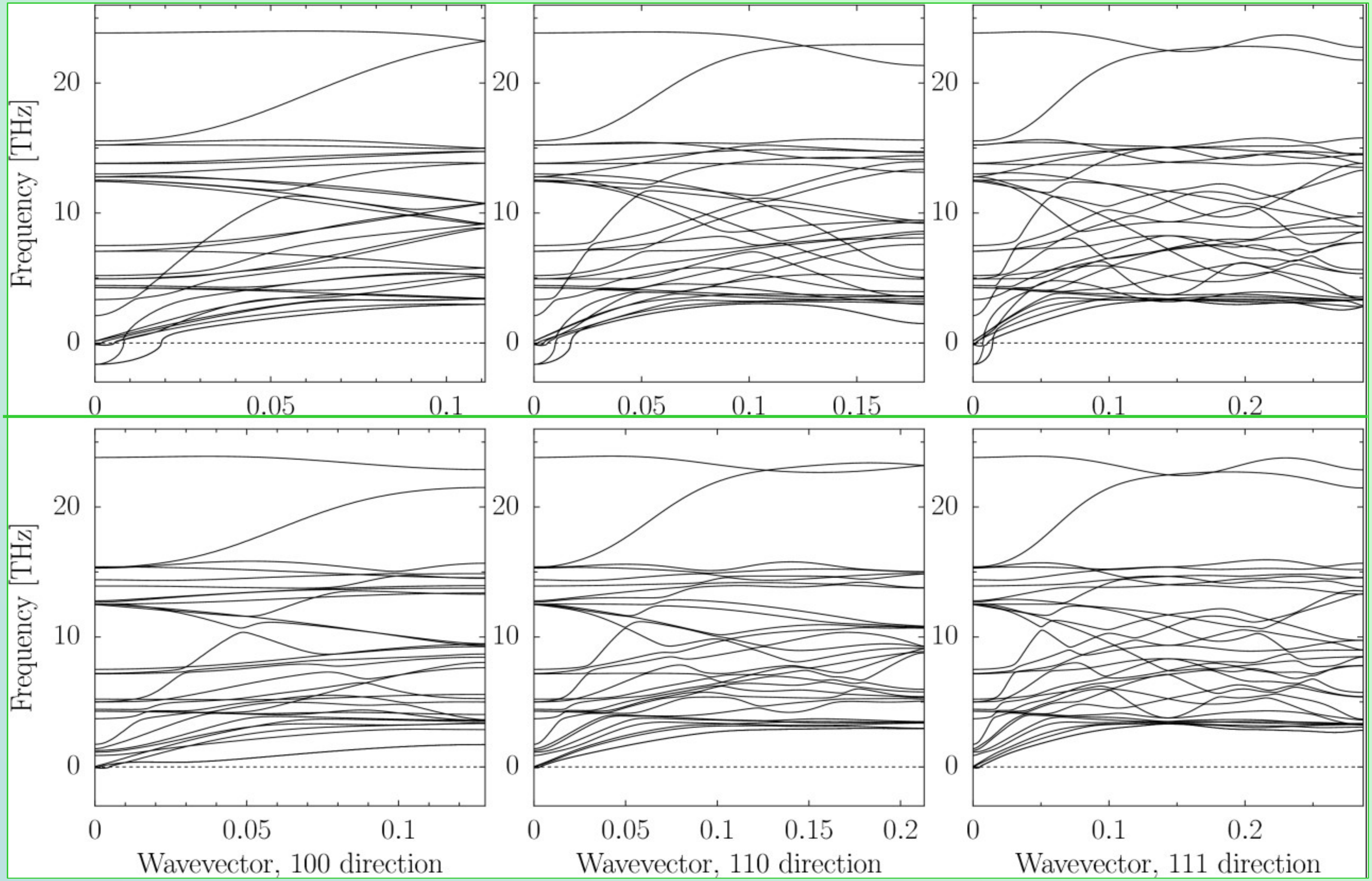
Shigenari et al., PRB 2006

Ours

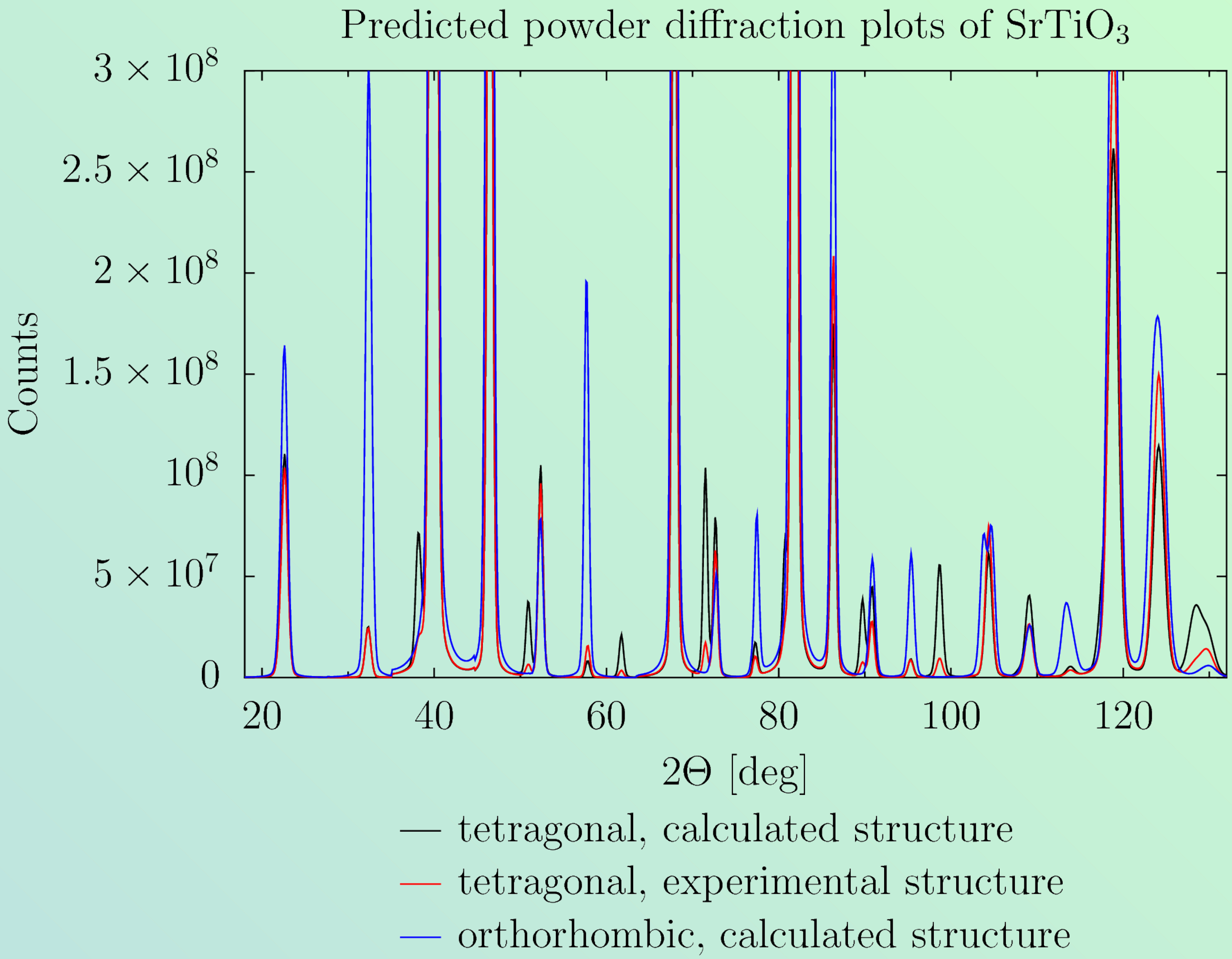


Observed Raman frequency[17] [cm^{-1}]	assignment[17]	Calculated Raman frequency [cm^{-1}]	assignment
17	A_1/B_2	47	B_2
17.5	B_1	42	B_1
171	A_1/B_2	167	B_2
171	A_1/B_2	167	A_1
171	B_1	174	B_1
517	A_1/B_2	510	B_2
		512	A_1
517	B_1	514	B_1

Is the new Ima2 structure stable?



Differences in neutron diffraction are small, but we should see them



Could we measure the phonons?

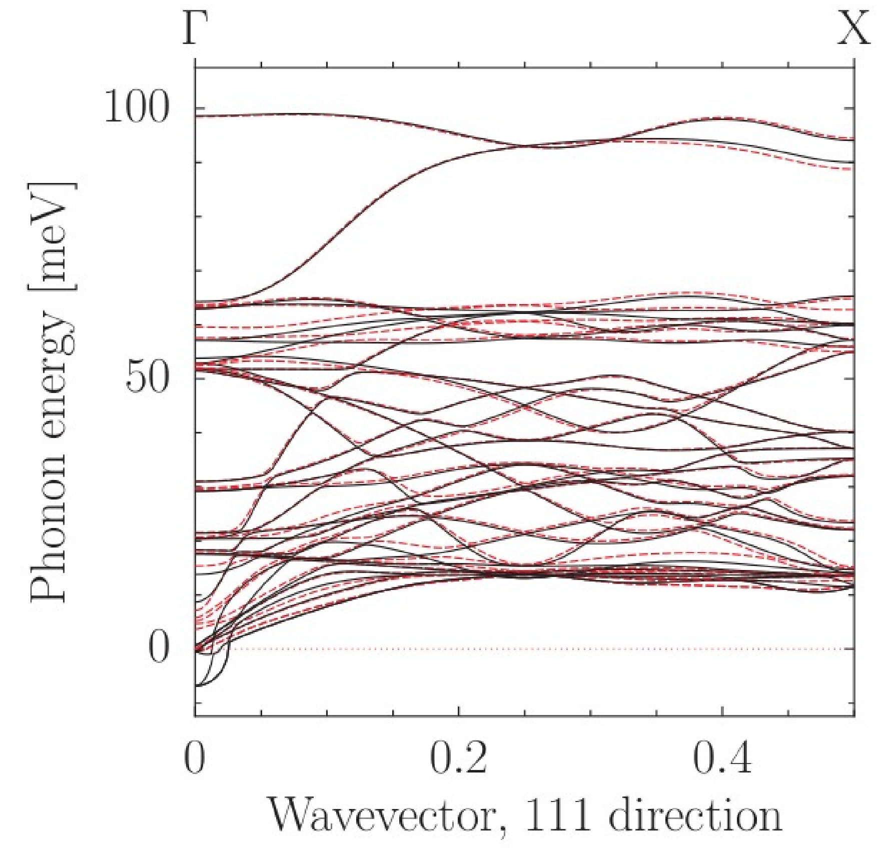


FIG. 2. Phonon dispersion curves calculated for structure B (black lines) and structure C (dashed red lines) from the centre of the Brillouin zone to the zone boundary along the [111] direction. The negative values correspond to calculated imaginary frequencies. Structure B is not stable, as indicated by the imaginary phonon frequencies at the Γ point.

It will be difficult to measure the differences in dispersion between the 2 phases as large single crystals are expensive to make.

Differences are very small.

Differences in VDOS are smaller but we have enough powder to try this.

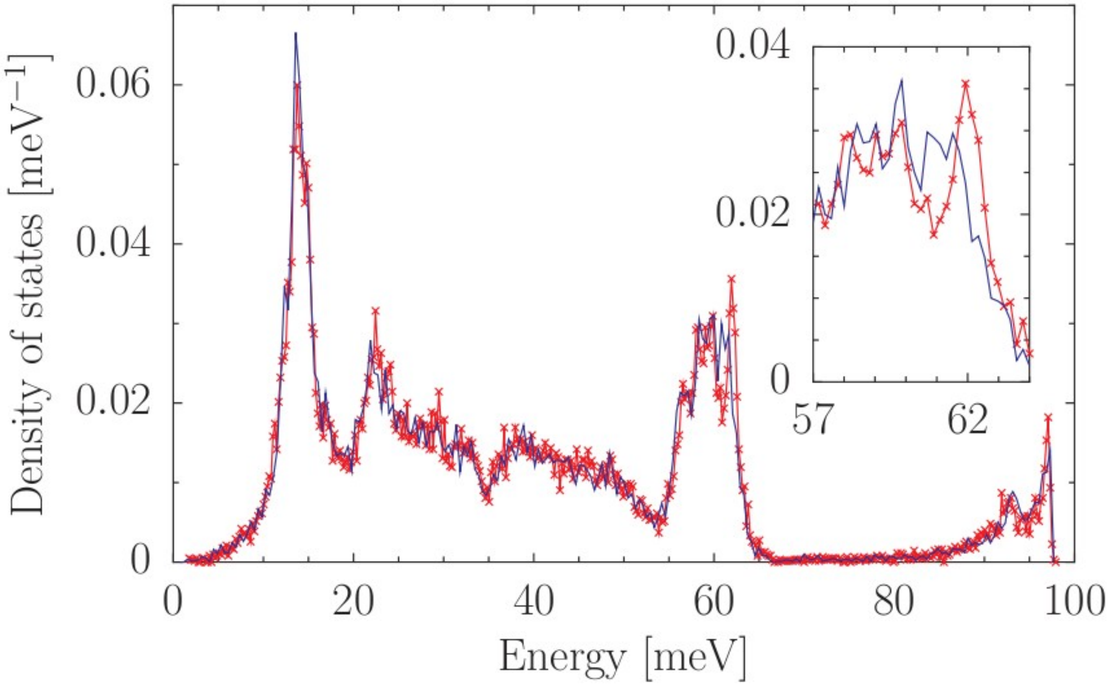


FIG. 5. The phonon density of states of $SrTi^{18}O_3$ calculated for (a) tetragonal structure B (blue line) and (b) orthorhombic structure C (red line with crosses). The inset shows the region around 60 meV where the difference between the two is most pronounced.

Why does the transition happen?

Mechanisms proposed so far:

NMR, EPR experiments -> order-disorder transition
(Blinc et al, PRL, 2005)

Raman experiments -> displacive transition,
softening of the Slater mode
(Takesada et al., PRL, 2006)

Raman experiments -> a mixed transition,
both order-disorder and displacive
(Shigenari et al., PRB, 2006)

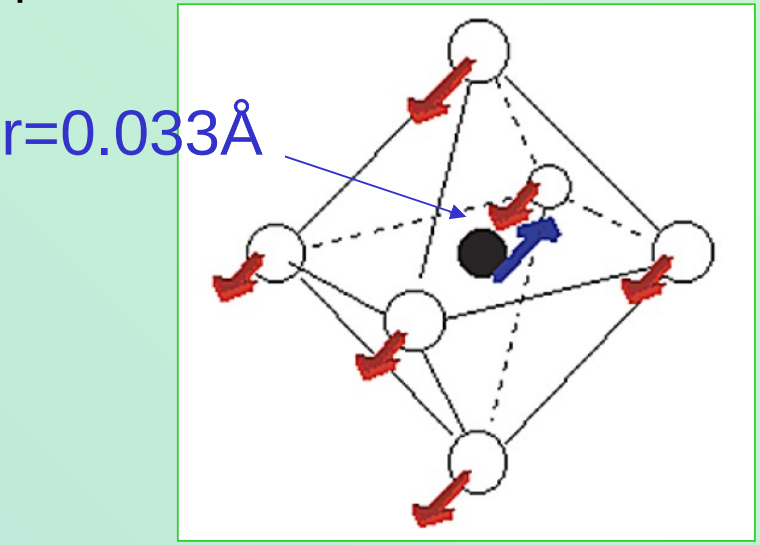
Raman experiments -> percolation of polar regions
(Shigenari and Abe, Ferroelectrics, 2008

What can we add?

The idea of the quantum paraelectric is that the classical displacement of the Ti (r) to reach the ferroelectric phase is less than its zero-point motion (z) .

It then becomes possible to adjust force-constants, and/or “phonon dressing” to get this condition at ~35K.

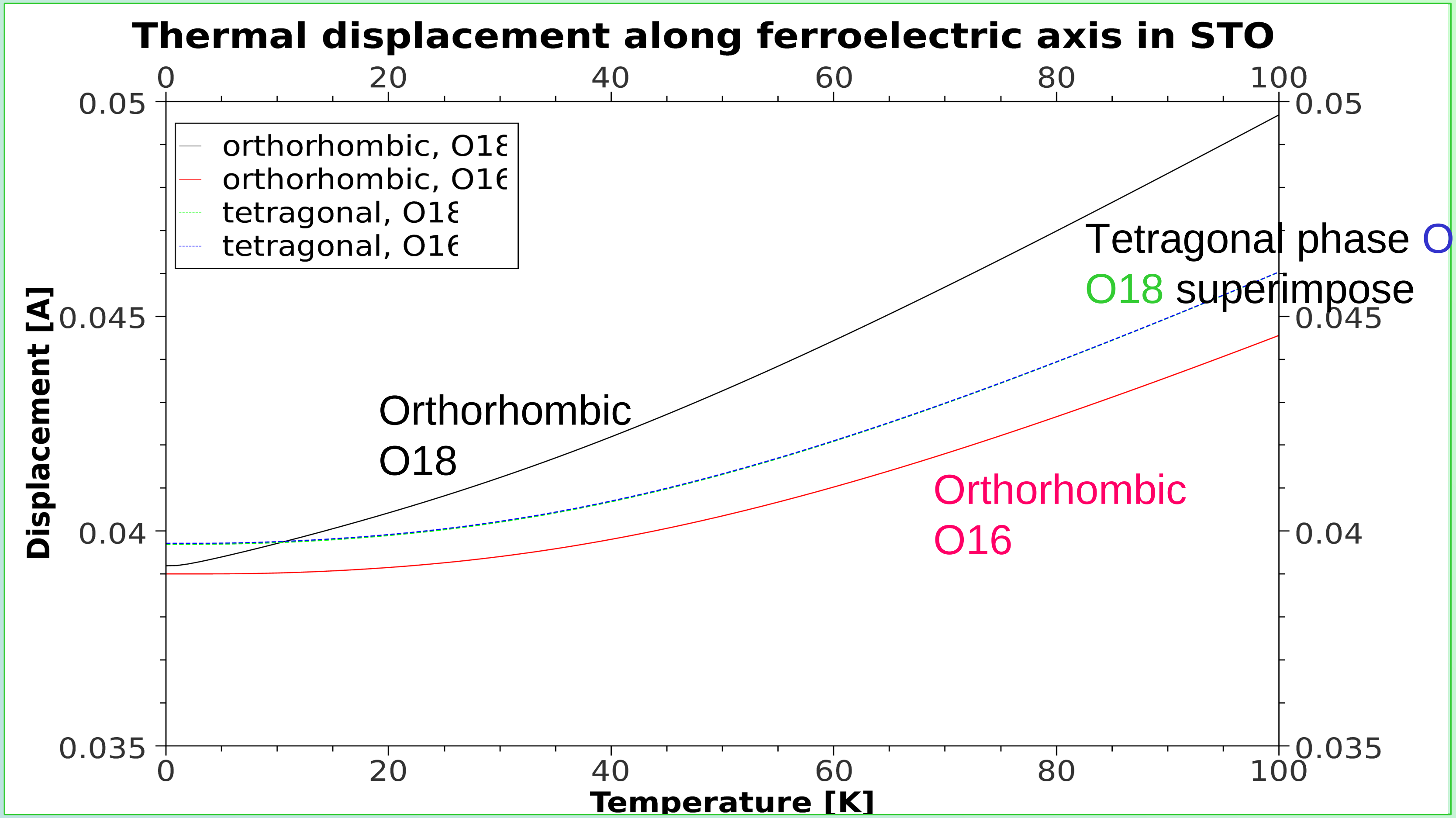
How do our results stack-up?



Zero-point from PHONON

r=0.033Å

z=0.039



Tetragonal phase O16, O18 superimpose

Orthorhombic O18

Orthorhombic O16

Where to now?

Calculation of Raman intensities
using DFPT approach implemented by Abinit package
or by CASTEP

Molecular dynamics simulation
in order to determine correlations between atomic positions

Experiment:
- specific heat measurements
- diffraction experiment with Wombat
- DOS measurements with Taipan

Appendix 3:
Calculation parameters

Energy cutoff: 650 eV

Supercell:
15.6144 x 11.0268 x 11.0268 Angstrom

K-points for the supercell:
2 x 4 x 4 shifted Monkhorst-Pack grid

PAW pseudopotentials, GGA treatment of exchange correlation

Where does the displacement lead to?