

司



部

Manipulation of quantum fluctuations and ferroelectricity in quantum paraelectrics

J. –M. Liu (刘俊明)

Laboratory of Solid State Microstructures, Nanjing University

International Center for Materials Physics, Institute of Materials Research

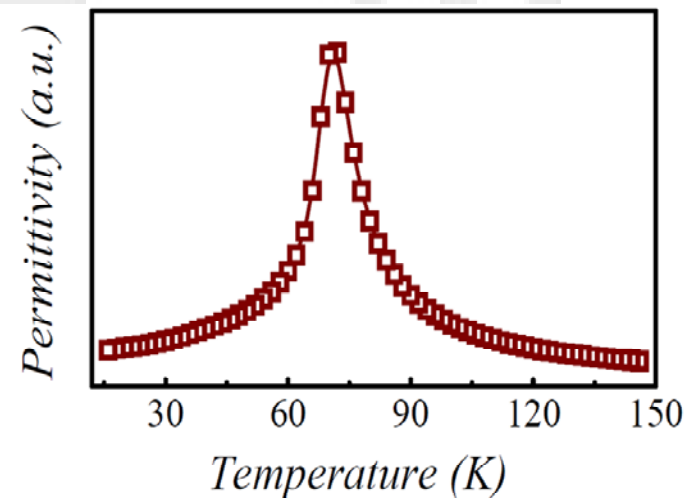
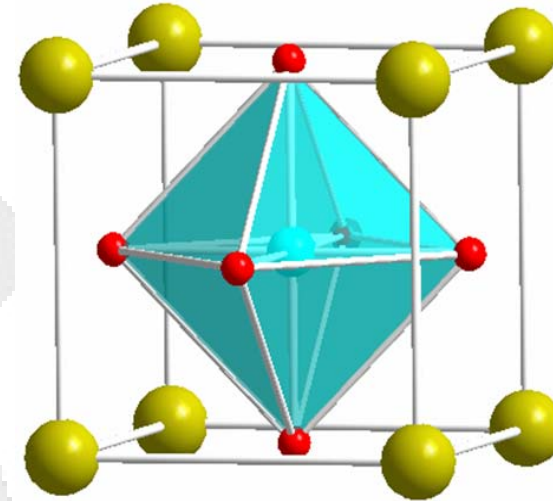
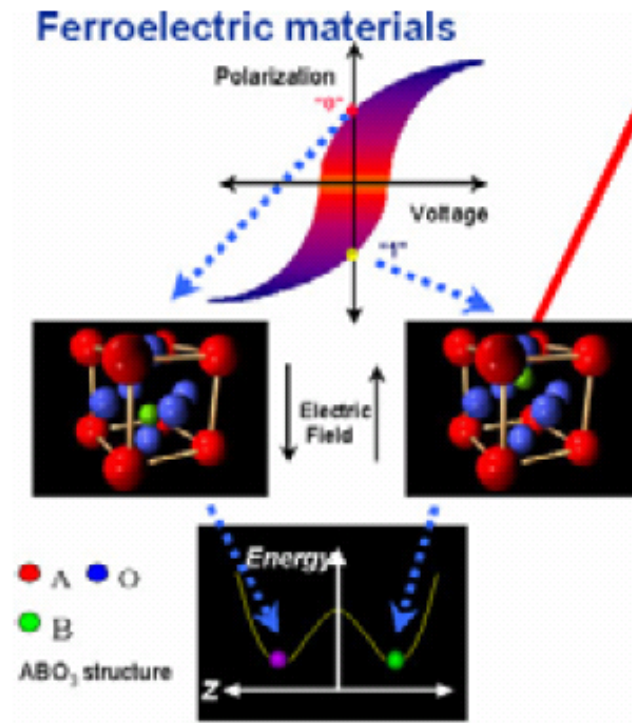
Content

- **Background and Motivation**
- **A-site disorder: symmetry scenario**
- **Enhancement of QFs**
- **Magnetoelectric effect in EuTiO_3**
- **Summary**



Background & motivation

What is ferroelectricity?

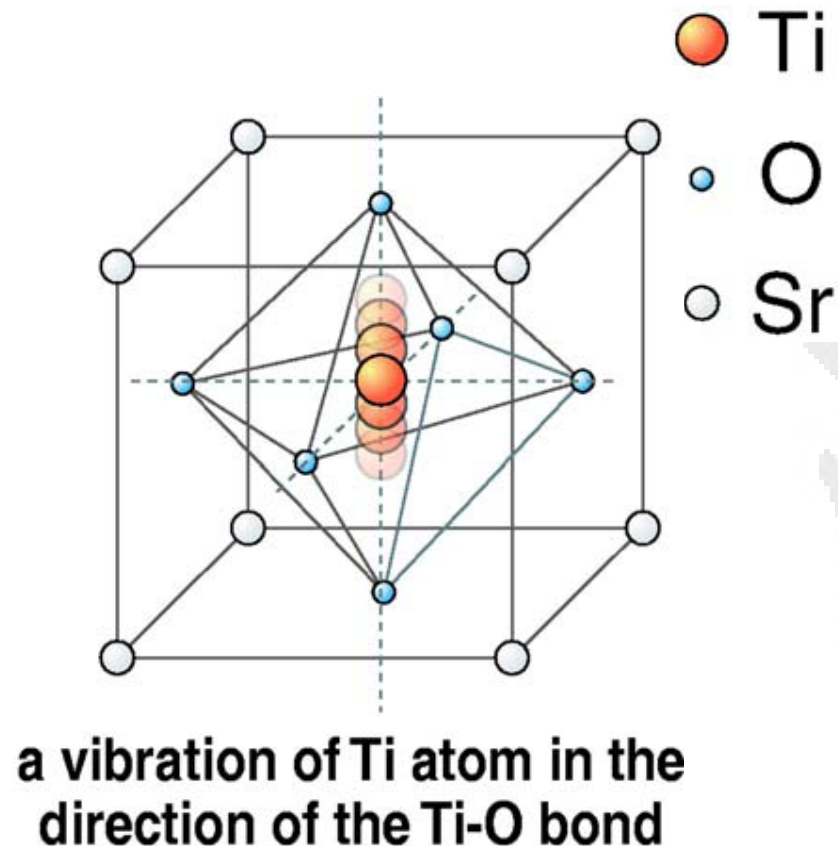


- Typical perovskite structure with lattice distortion

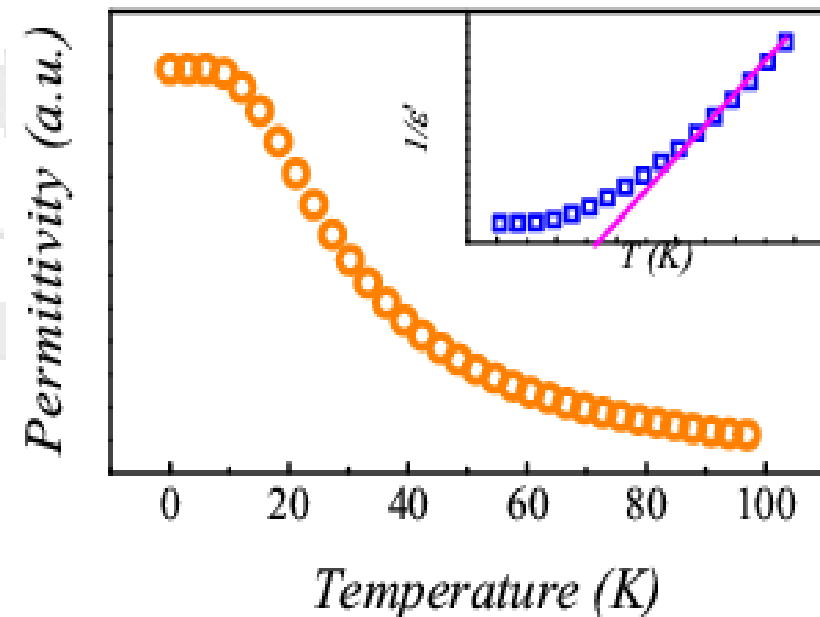


Background & motivation

What is quantum paraelectricity (QPE)?



PRB 72, 121101(R); PRB 19, 3593; PRL 52, 2289



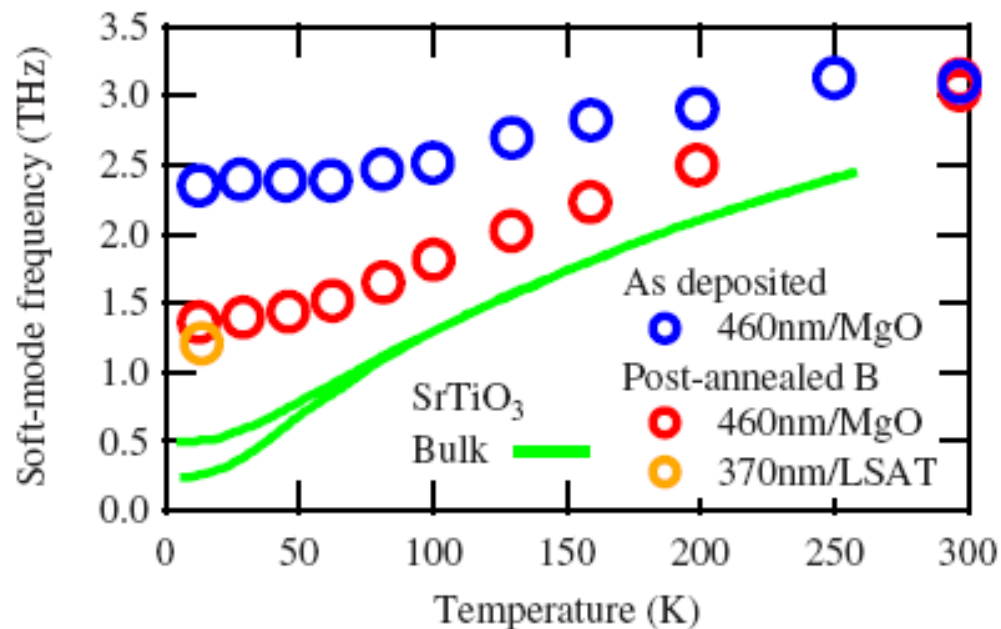
➤ Typical perovskite structure without much lattice distortion



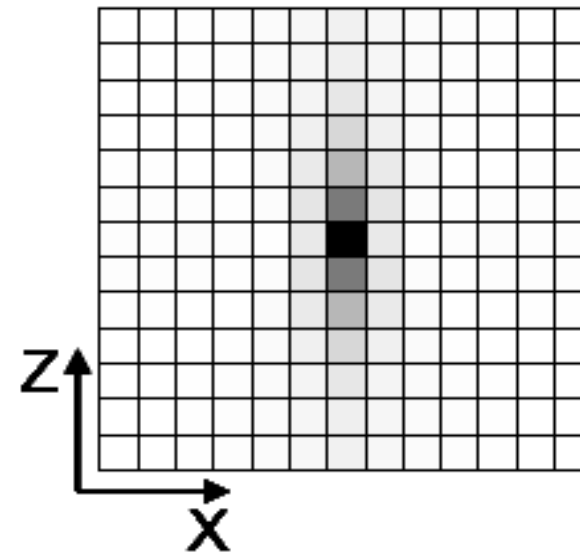
Background & motivation

Simple mechanism for quantum fluctuations (QFs)

APL 93, 132903; PRL 74, 2587



Soft mode



No symmetry break



Background & motivation

Simple theory on QPE

PRB 72, 121101(R); PRB 19, 3593; PRL 52, 2289

$$H = \sum_1^N \frac{p_i^2}{2m_i} + V(\mu_1, \mu_2, \dots, \mu_i, \dots, \mu_N) \quad [p_i, \mu_i] = -i\hbar\delta_{ij} \Rightarrow \Delta Z$$

$$kT_C = 1/2\kappa\Delta z^2(0) \Rightarrow \Delta Z > \Delta z(0)$$

$$\varepsilon' = \frac{C}{(T_1/2)\coth(T_1/2T) - T_0}$$

$$C = \frac{2a^3\varepsilon_0\nu B}{q^2(3b_1 + 2b_2)kD} \quad T_1 = \frac{h\nu}{k}$$

$$T_0 = \frac{2a^3\varepsilon_0\nu}{q^2(3b_1 + 2b_2)kD} \left(\frac{Dq^2}{2a\varepsilon_0\nu} - 1 \right)$$

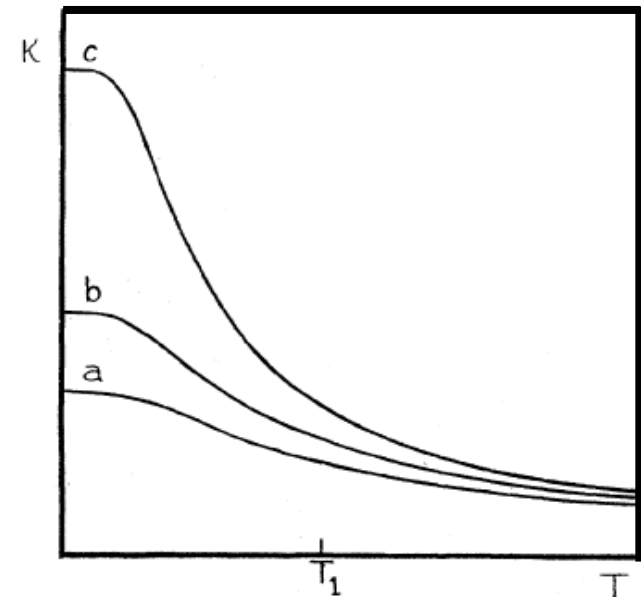


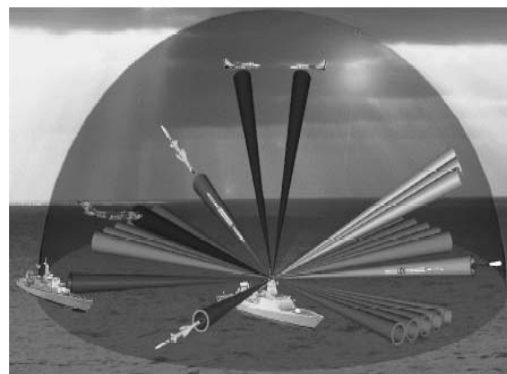
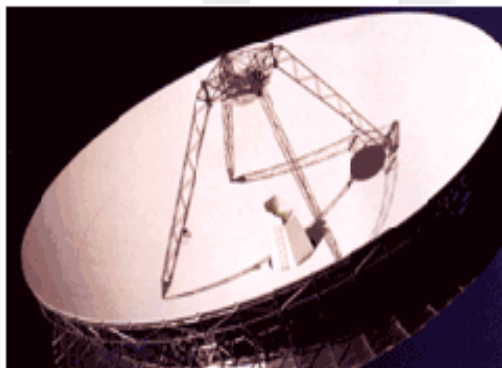
FIG. 1. Curve *a*: $T_0 = -0.25T_1$; Curve *b*: $T_0 = 0$; Curve *c*: $T_0 = 0.25T_1$.

PR 86, 118; PRB 18, 2394; PRB 8, 1256

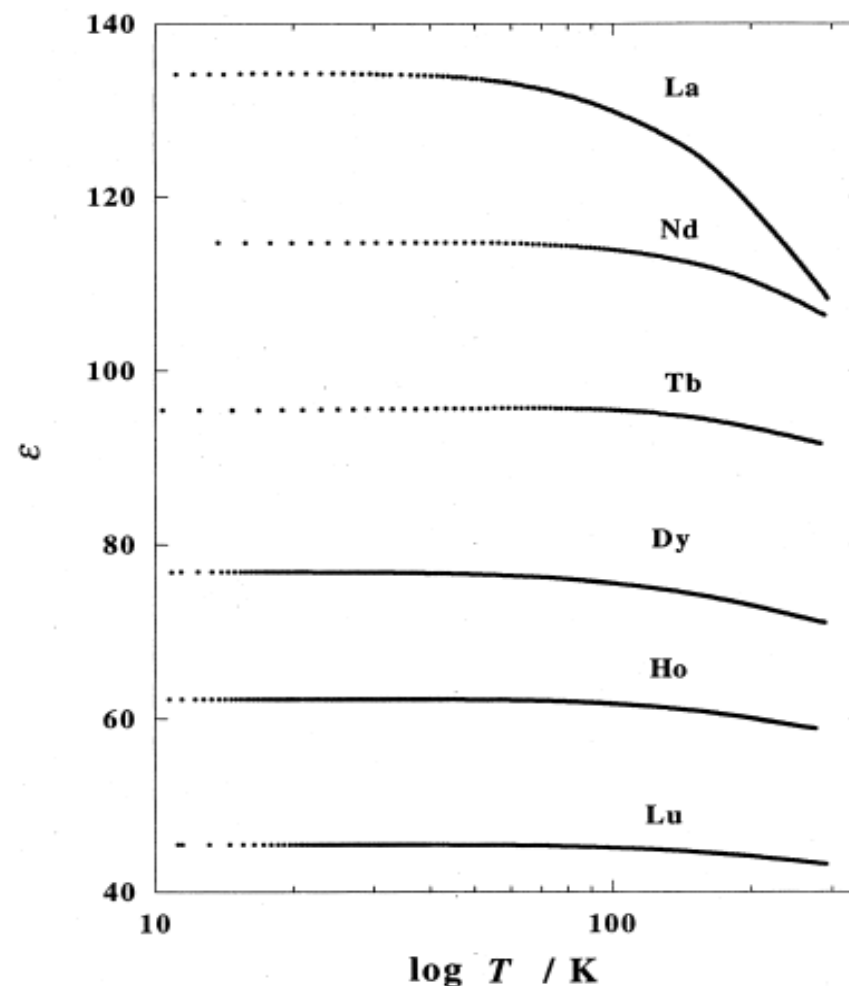
Background & motivation

Other quantum paraelectrics

- Not only STO but also other titanates show QPE: $(\text{Ln}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (Ln=Dy, Ho, Er, Tm, Yb, Lu)
- High dielectric susceptibility & low loss: potential applications

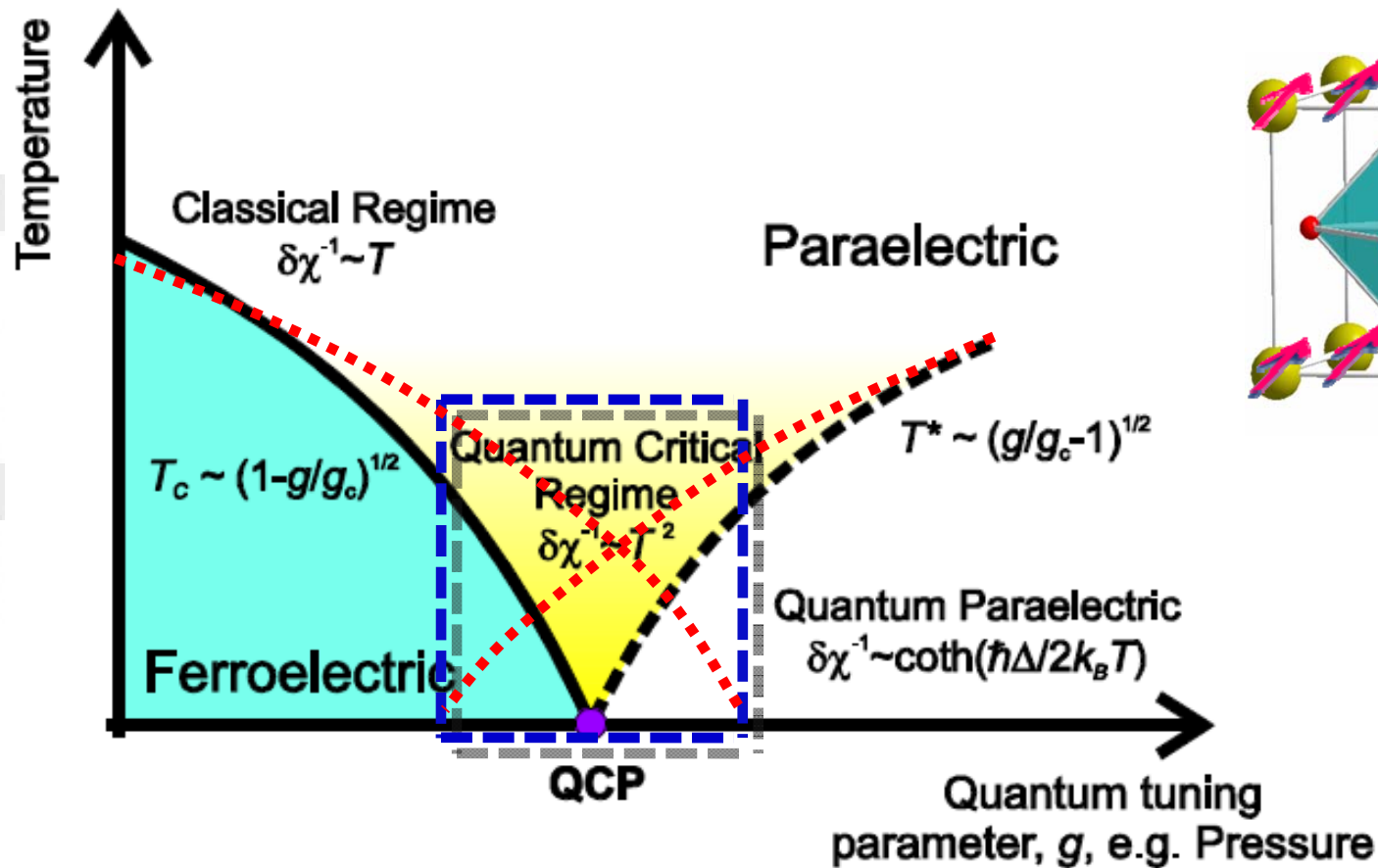


PRB 77,052106



Background & motivation

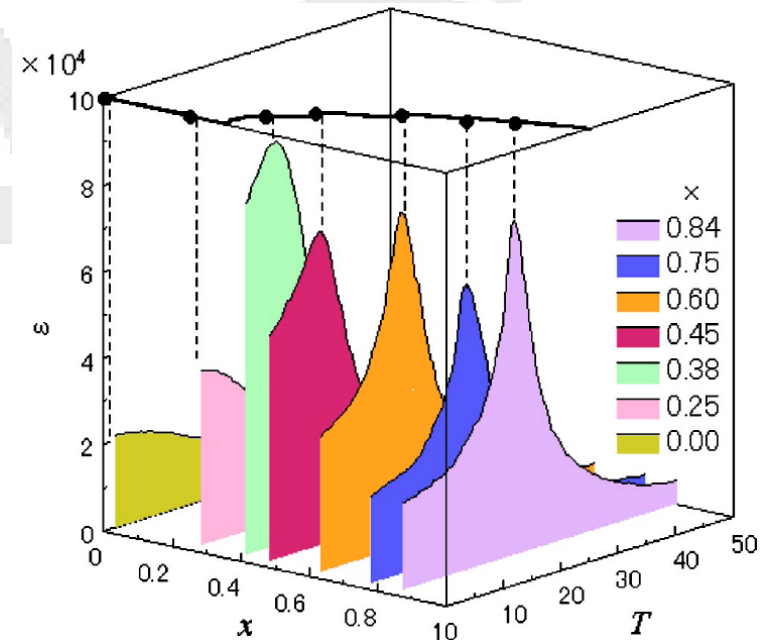
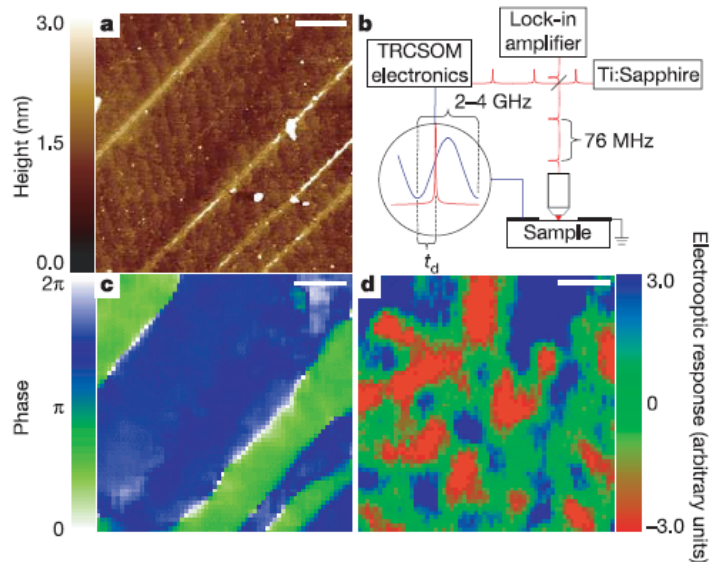
Manipulate the QFs?



A-site disorder: symmetry scenario

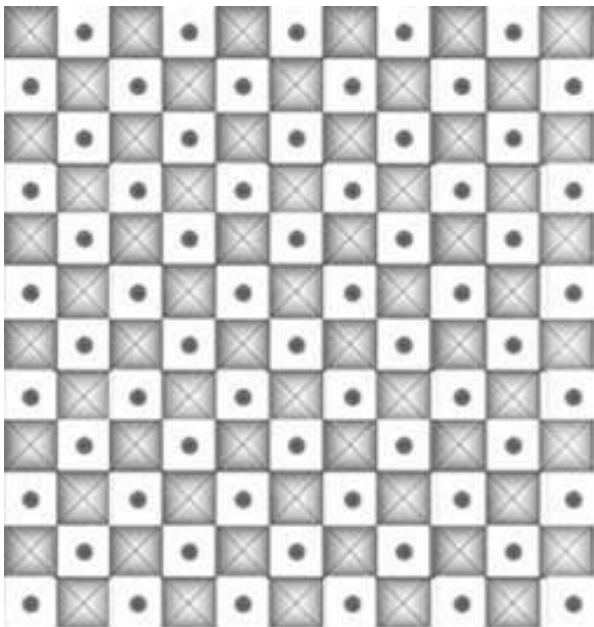
Symmetry scenario: SrTiO_3

- Tolerance factor $t=1.01$ (STO, cubic), 1.07 (BTO, tetragonal), 0.97 (CTO, tetragonal). SrTiO_3 : a marginal system
- Oxygen isotope effect (right)
- Strain effect (bottom)

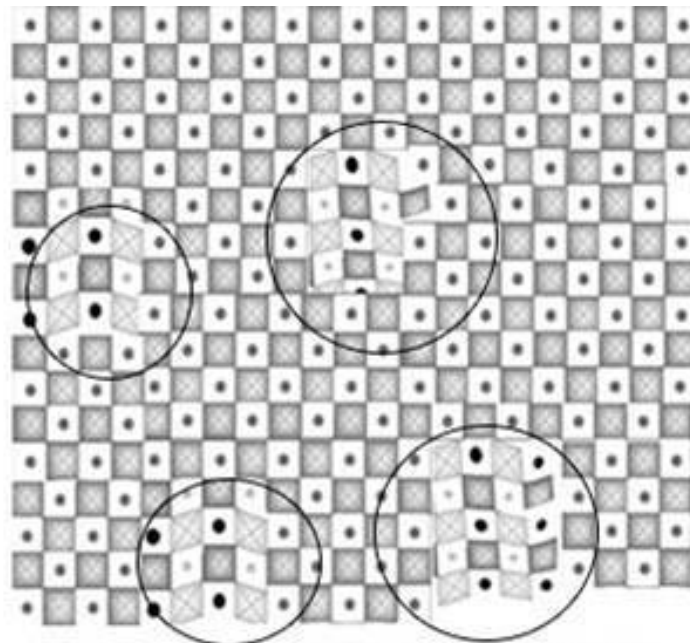


A-site disorder: symmetry scenario

A-site structural disorder, without symmetry breaking



(a) 理想的结构



(b) 存在随机畸变的结构

$$\sigma^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$$

Keep macroscopic symmetry but modulating local disorder
degree of freedom



A-site disorder: symmetry scenario

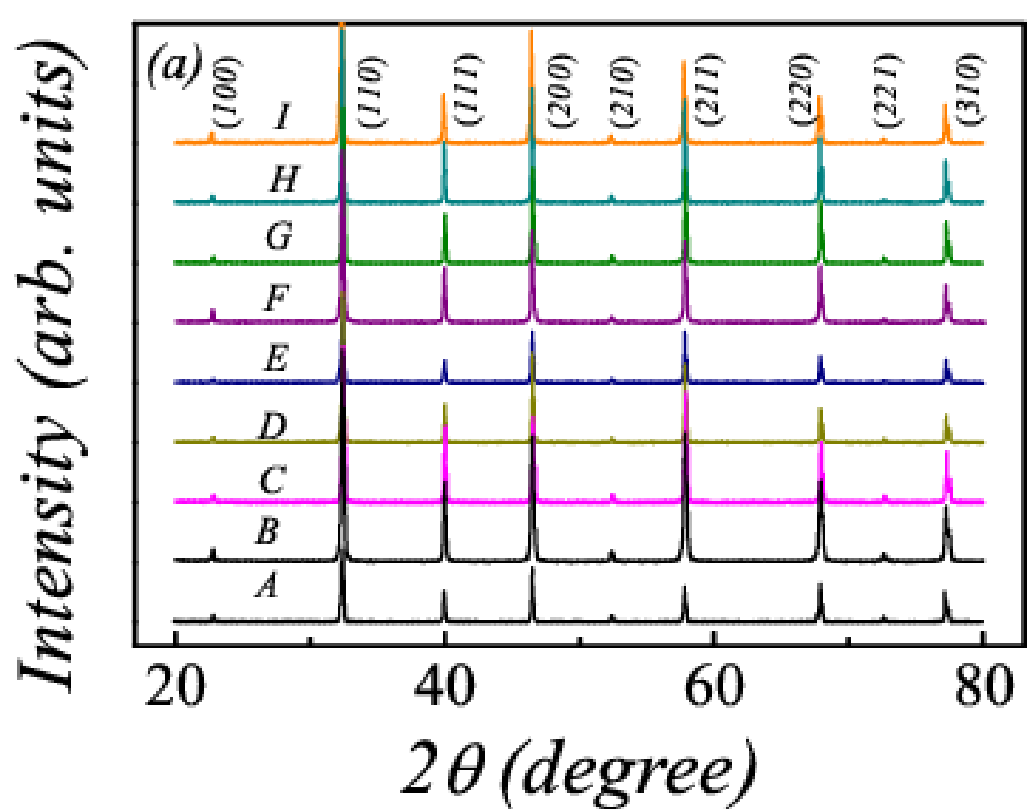
Pure A-site structural disorder

$$\sigma^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2$$

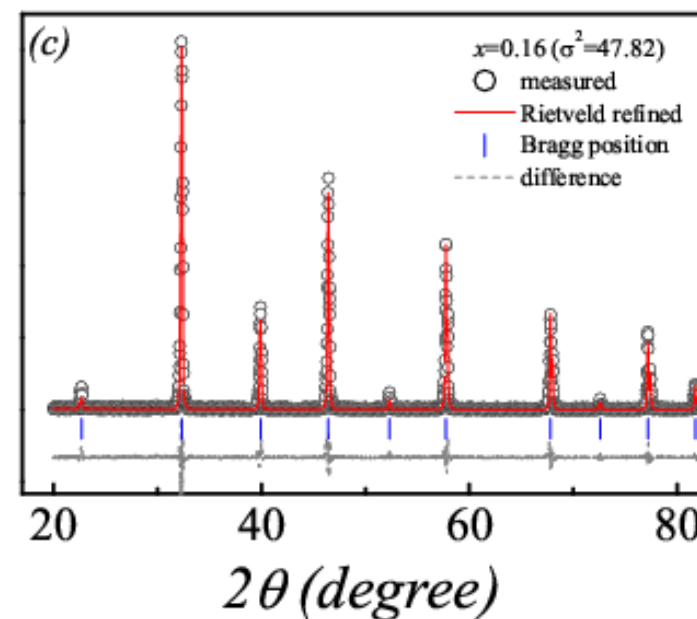
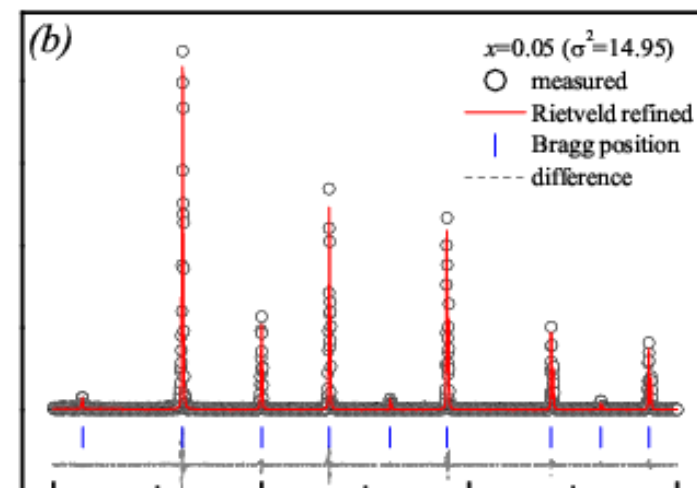
Sample (SrCaBaTiO ₃)	<i>x</i>	σ^2 (10 ⁻⁶ nm ²)	lattice parameters (nm)	error (x10 ⁻⁵)
SrTiO ₃	0	0	0.3905	
Sr _{0.98} Ca _{0.012778} Ba _{0.007222} TiO ₃	0.02	5.978	0.390289	7
Sr _{0.97} Ca _{0.019167} Ba _{0.010833} TiO ₃	0.03	8.967	0.390421	9
Sr _{0.95} Ca _{0.031945} Ba _{0.018055} TiO ₃	0.05	14.95	0.390624	14
Sr _{0.92} Ca _{0.051112} Ba _{0.028888} TiO ₃	0.08	23.91	0.390467	4
Sr _{0.90} Ca _{0.063890} Ba _{0.036110} TiO ₃	0.10	29.89	0.390269	3
Sr _{0.88} Ca _{0.076668} Ba _{0.043332} TiO ₃	0.12	35.97	0.390256	4
Sr _{0.86} Ca _{0.089446} Ba _{0.050554} TiO ₃	0.14	41.58	0.390461	3
Sr _{0.84} Ca _{0.102224} Ba _{0.057776} TiO ₃	0.16	47.82	0.390421	4

A-site disorder: symmetry scenario

Structural identification

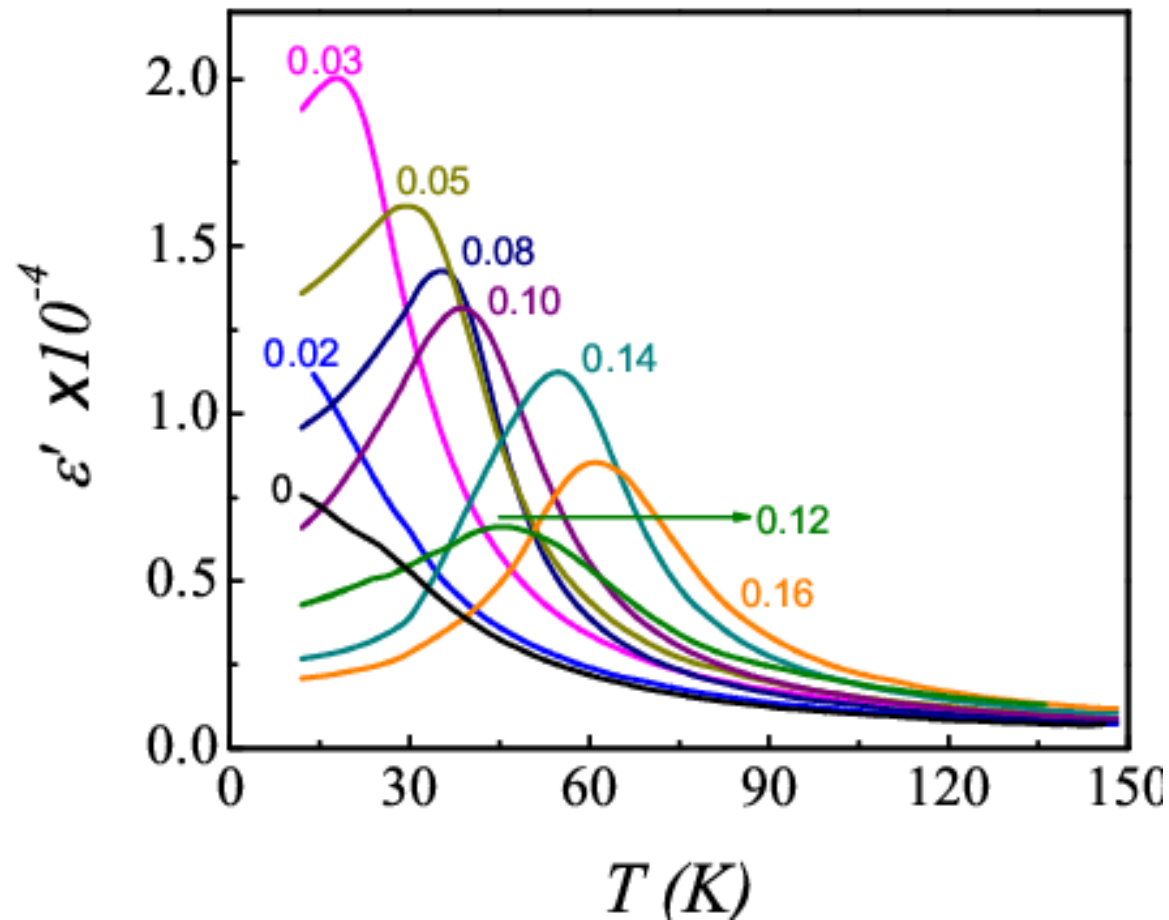


Intensity (arb. units)



A-site disorder: symmetry scenario

Dielectric evidence of FE state

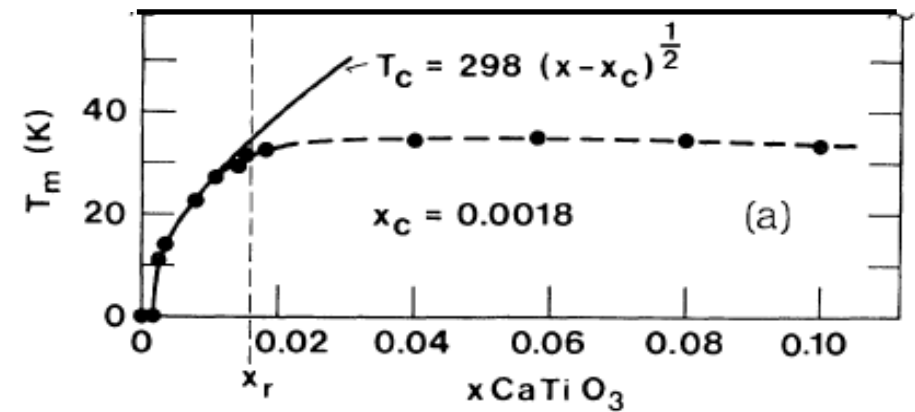
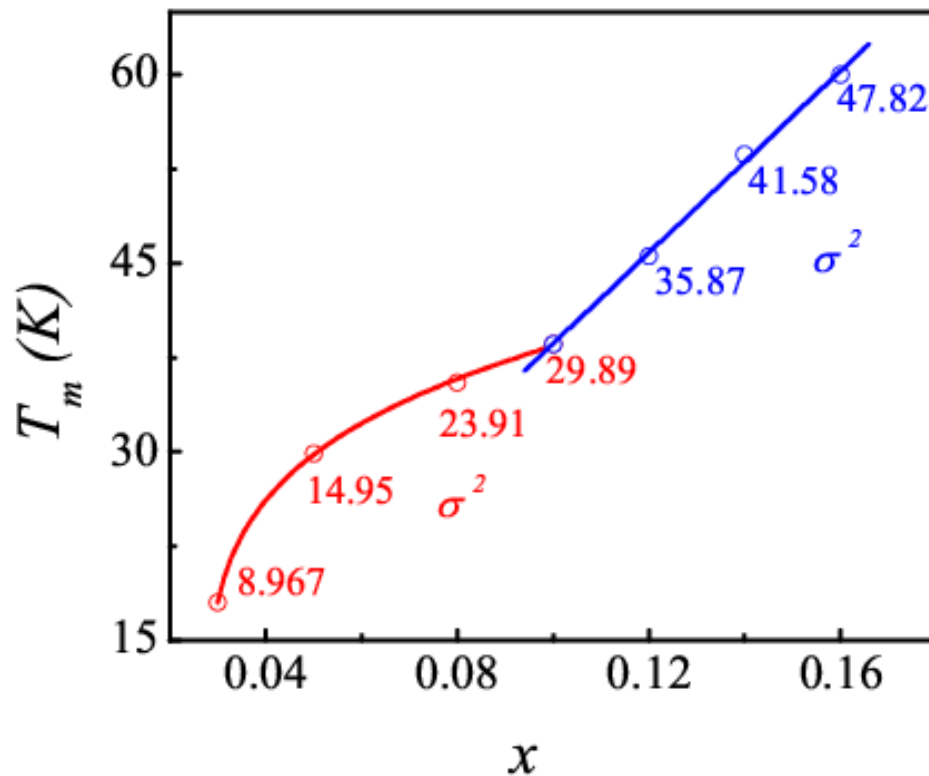


1. Clear deviation from QPE state into FE-like state
2. It is really a FE state?



A-site disorder: symmetry scenario

FE state at high disorder degree



$$T_m(x) = A(x - x_c)^r$$

$$A = 67.7$$

$$r = 0.2158$$

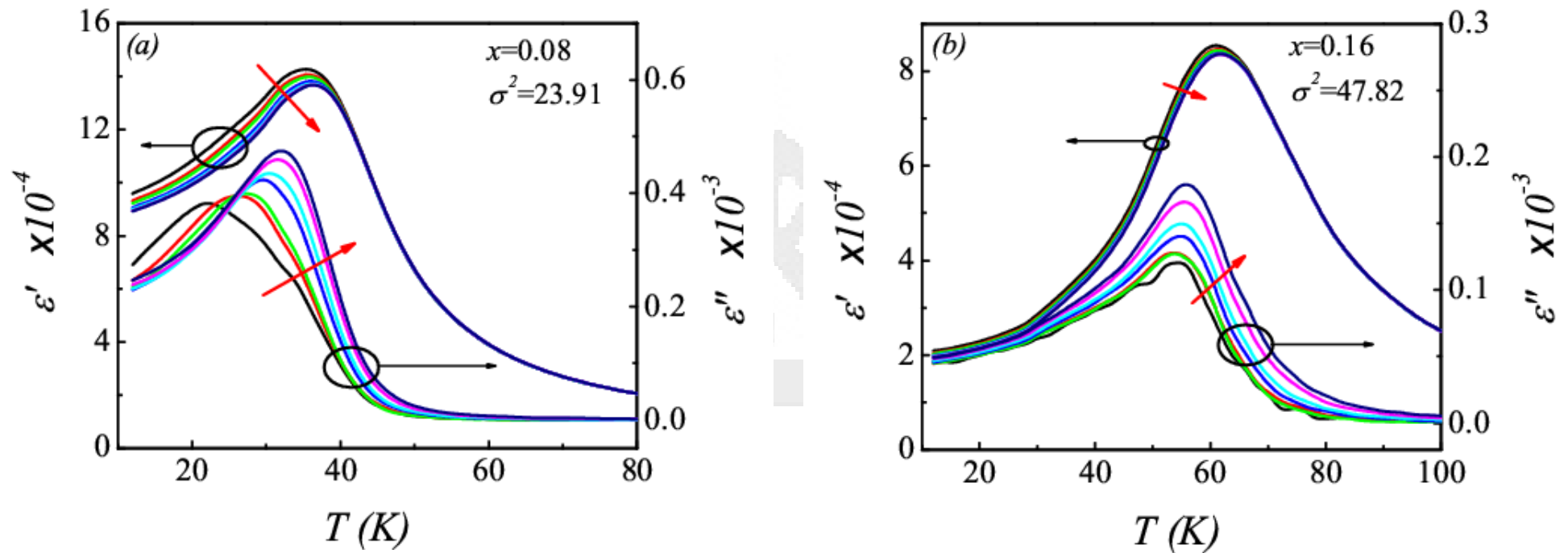
$$x_c = 0.02758$$

Clear deviation from the pure QPE system



A-site disorder: symmetry scenario

Dielectric dispersion at low and high degrees of disorder



Clear relaxor ferroelectric behavior given by the dielectric dispersion

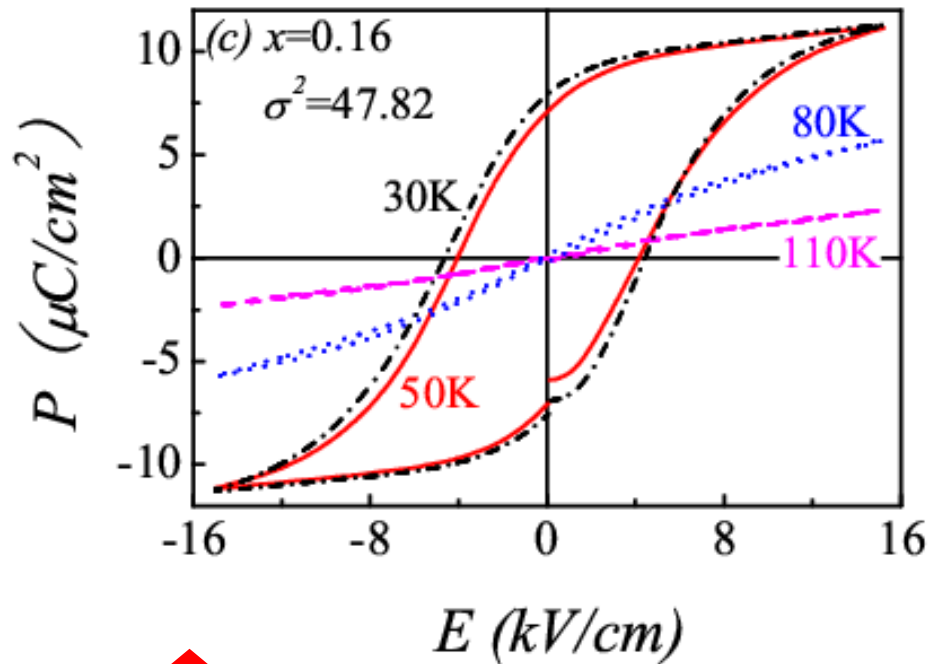


A-site disorder: symmetry scenario

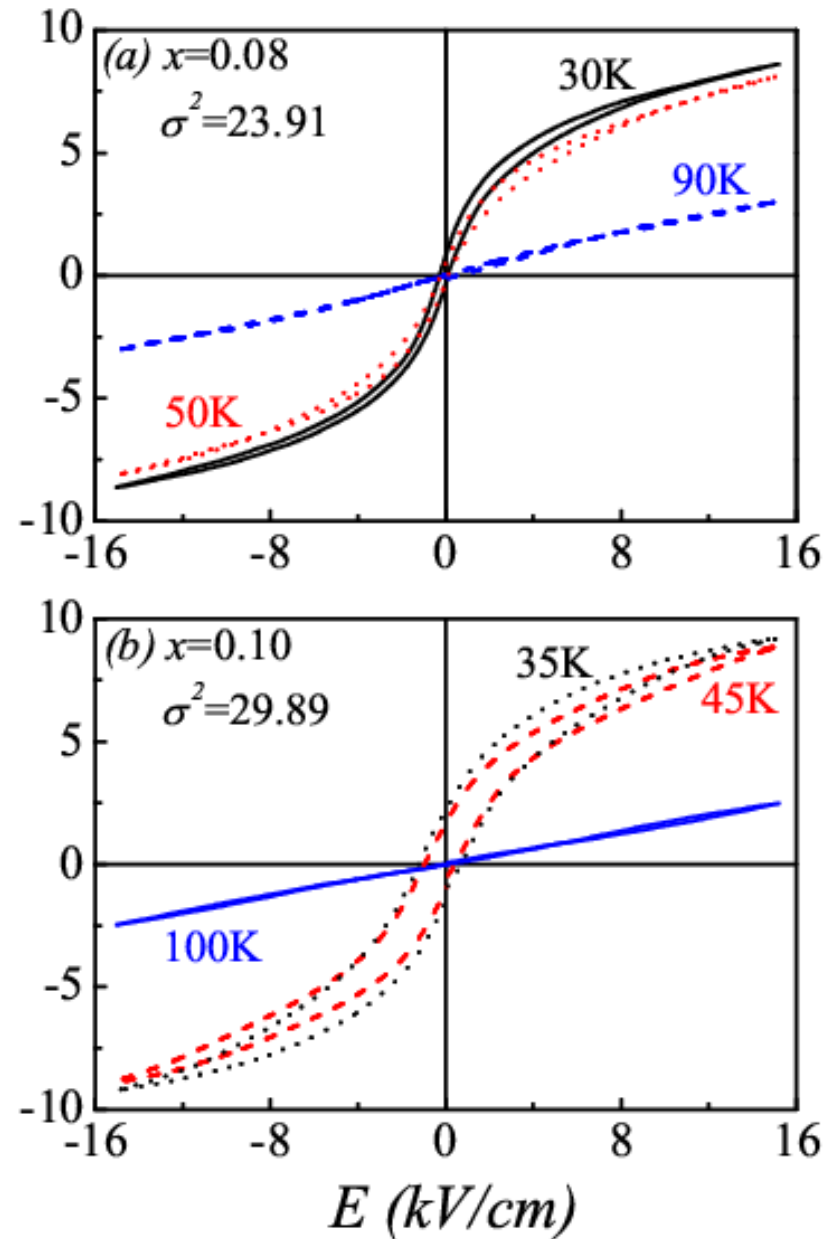
ferroelectricity



Loop for RFE

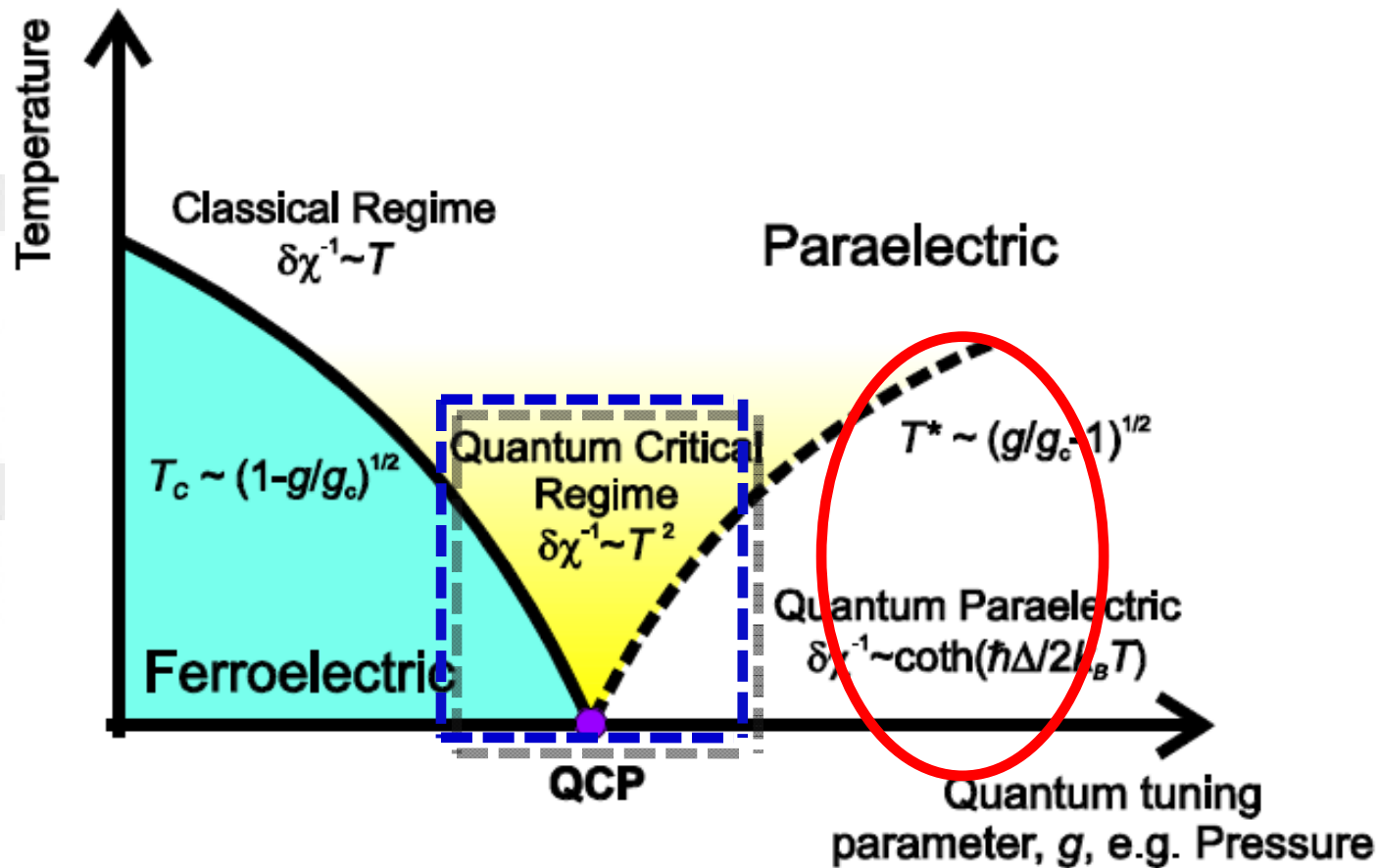


Loop for FE



Background & motivation

Manipulate the QFs?

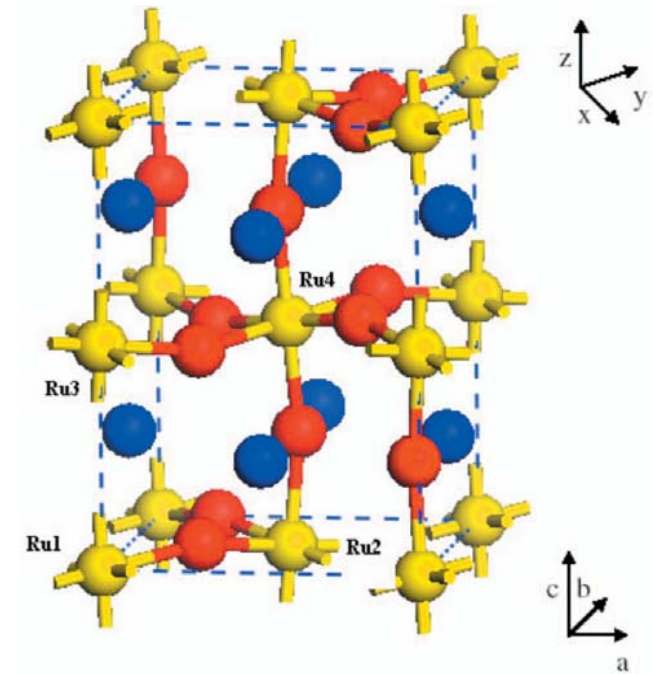
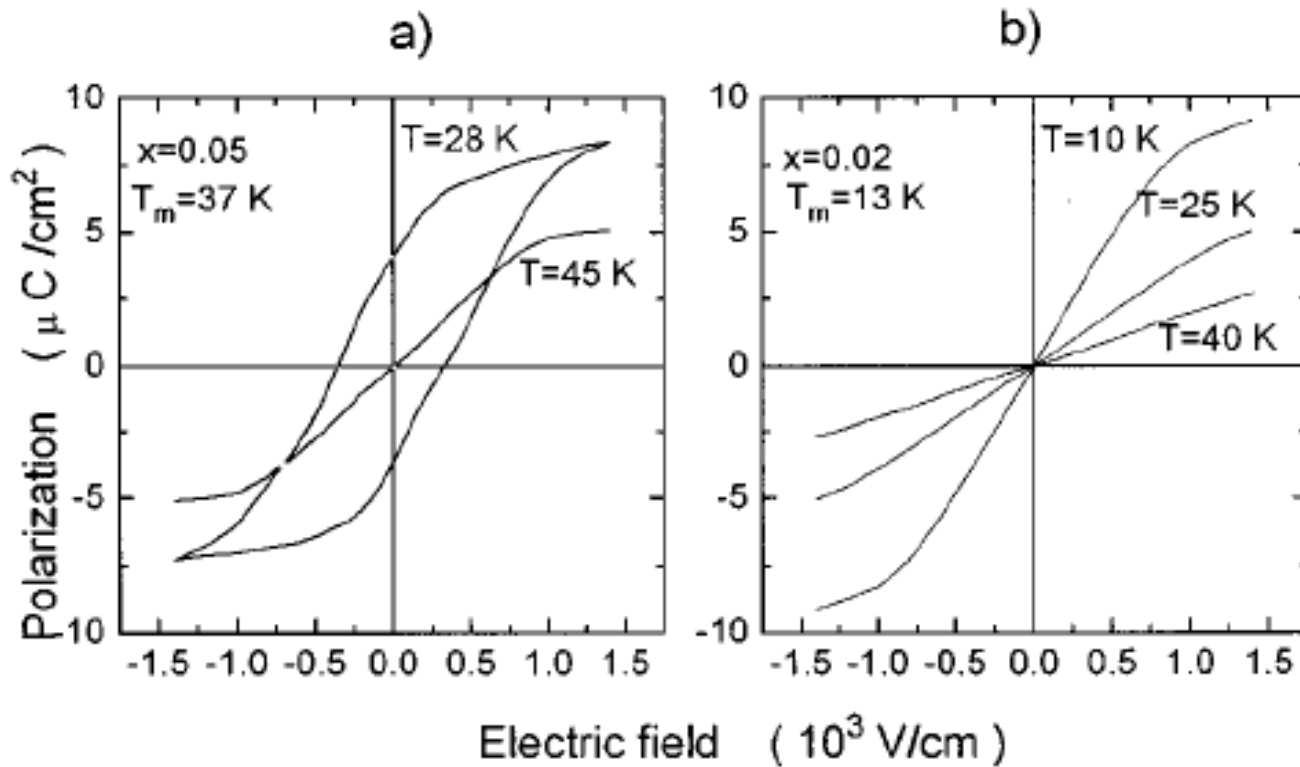


Enhancement of QFs

Problem II: how to enhance local quantum fluctuation?

PRB 54, 3151

$\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$

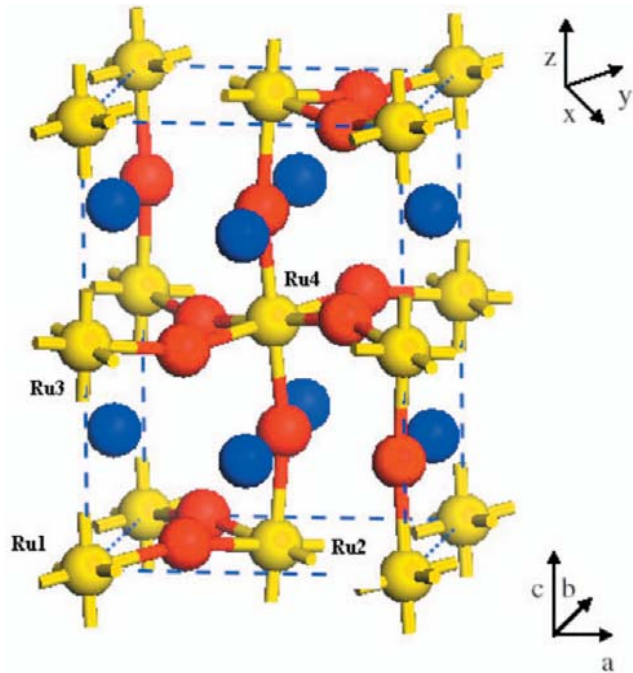


**SrRuO_3 FM metal
with $T_c=160 \text{ K}$**



Enhancement of QFs

Problem II: how to enhance local quantum fluctuation?



1. e_g (doublet), t_{2g} (triplet) low-spin ($t_{2g}^3 \uparrow t_{2g} \downarrow$)
2. High conductivity results from the π overlap between cation t_{2g} and anion p orbitals

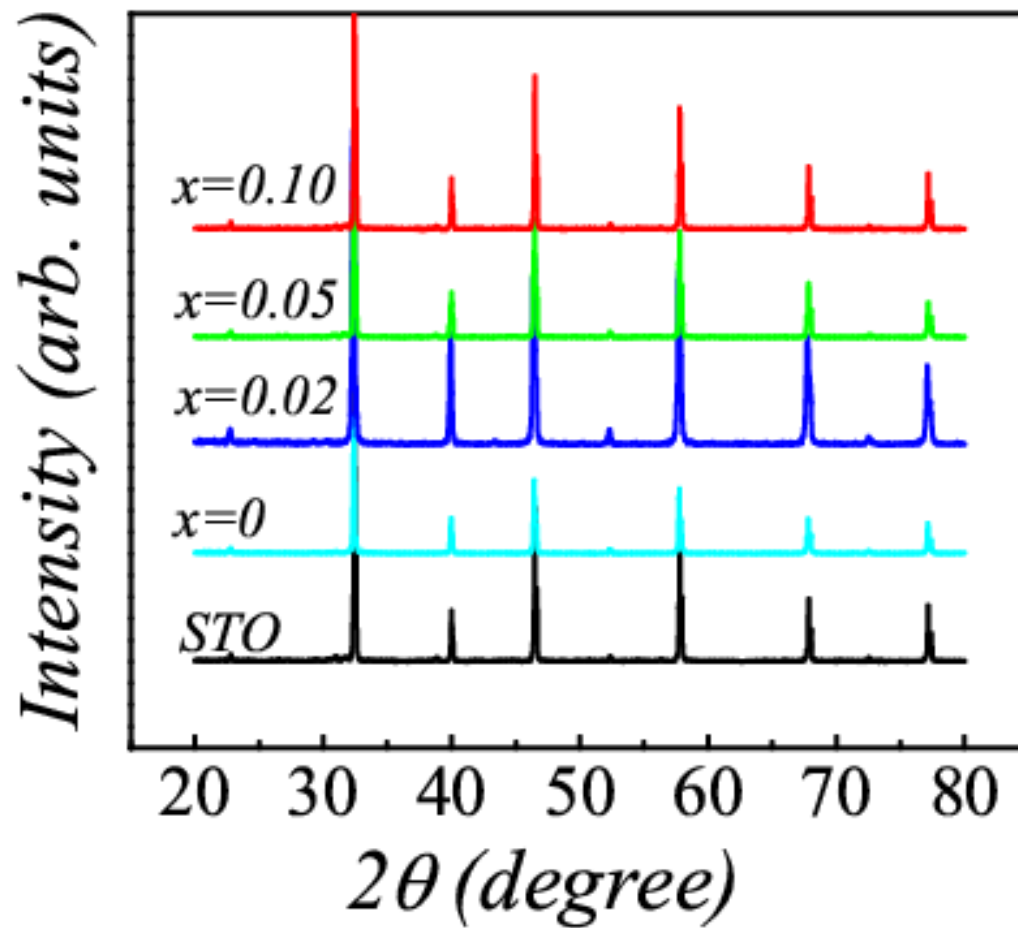
$\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ (SBT)

Ru-doping enhances the quantum fluctuation & draws SBT back to QPE



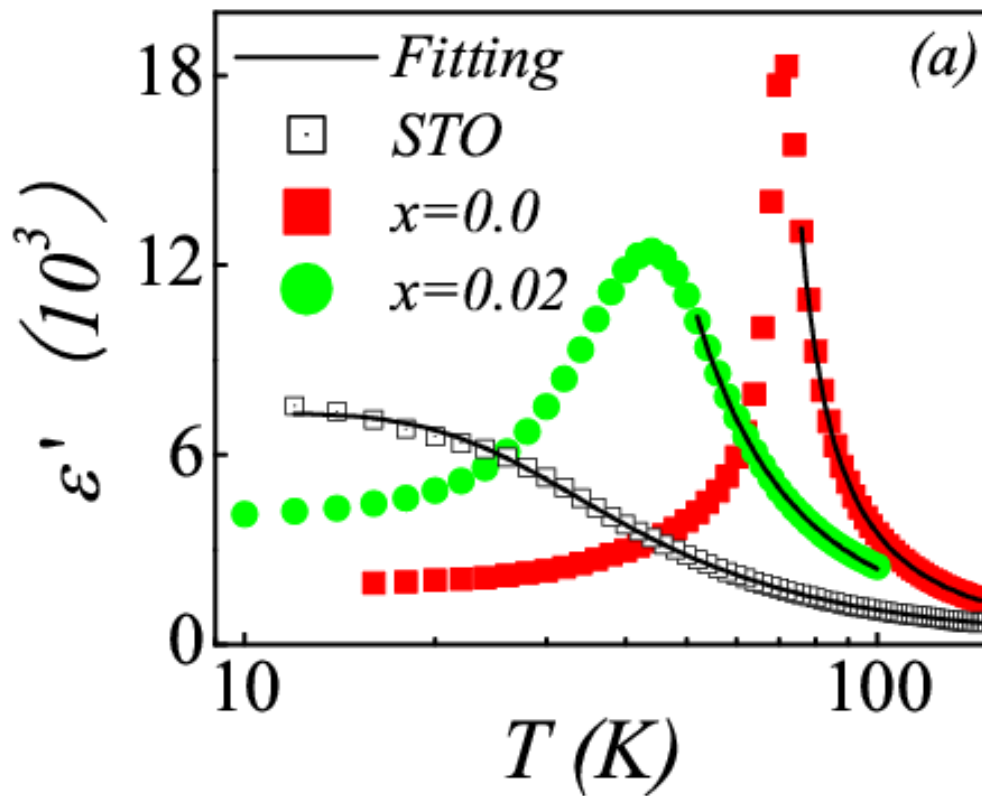
Enhancement of QFs

Ru-doping: no symmetry breaking



Enhancement of QFs

Suppression of FE state into QFE and QPE

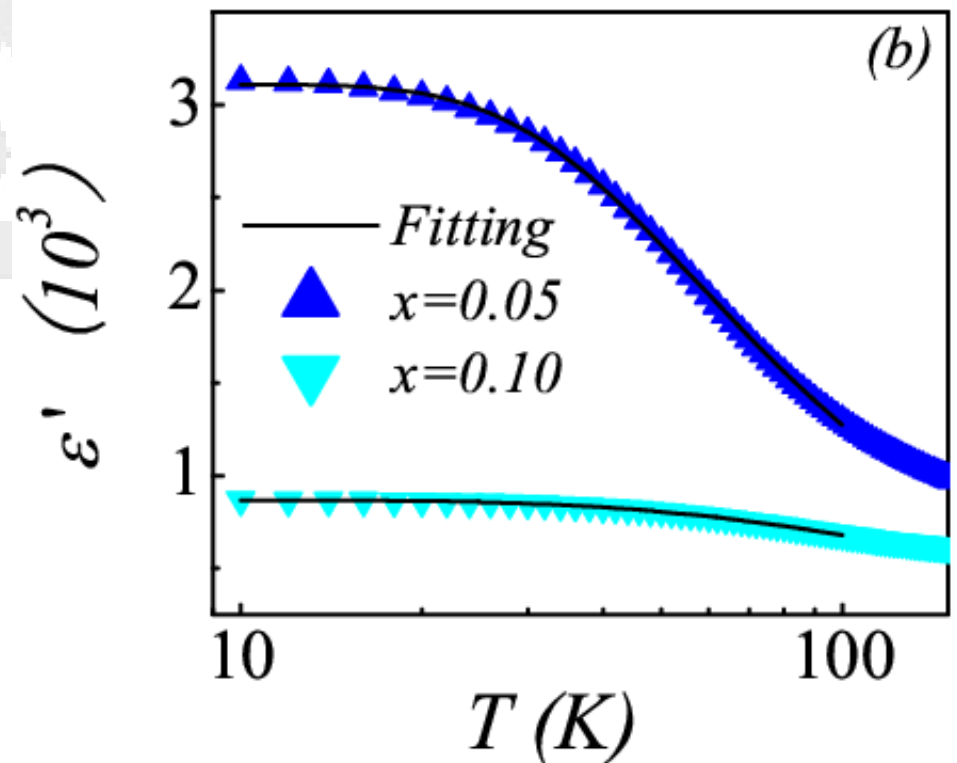


SBTR ($x=0$) $T_C=72K$

SBTR ($x=0.02$) $T_C=45K$



$$\varepsilon' = \frac{C}{(T_1 / 2) \coth(T_1 / 2T) - T_0}$$



Enhancement of QFs

Suppression of FE state into QFE and QPE

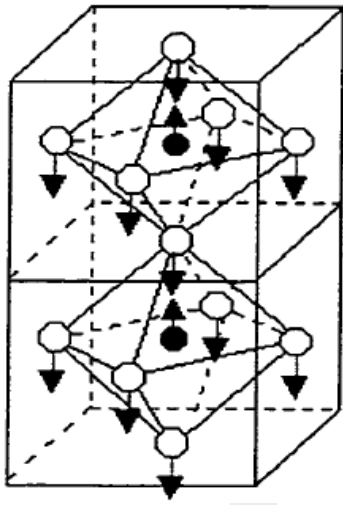
	$C(10^5)$	$T_1(K)$	$T_0(K)$	$T_1-2T_0(K)$
<i>STO</i>	<i>0.8</i>	<i>92</i>	<i>35.3</i>	<i>19.4</i>
<i>x=0.0</i>	<i>1.0</i>	<i>141</i>	<i>89.3</i>	<i>-37.6</i>
<i>x=0.02</i>	<i>1.15</i>	<i>131</i>	<i>67.7</i>	<i>-4.4</i>
<i>x=0.05</i>	<i>1.24</i>	<i>101</i>	<i>10.7</i>	<i>79.6</i>
<i>x=0.10</i>	<i>1.9</i>	<i>94</i>	<i>-172.9</i>	<i>439.8</i>

$$\varepsilon' = \frac{C}{(T_1 / 2) \coth(T_1 / 2T) - T_0}$$



Enhancement of QFs

Raman evidence



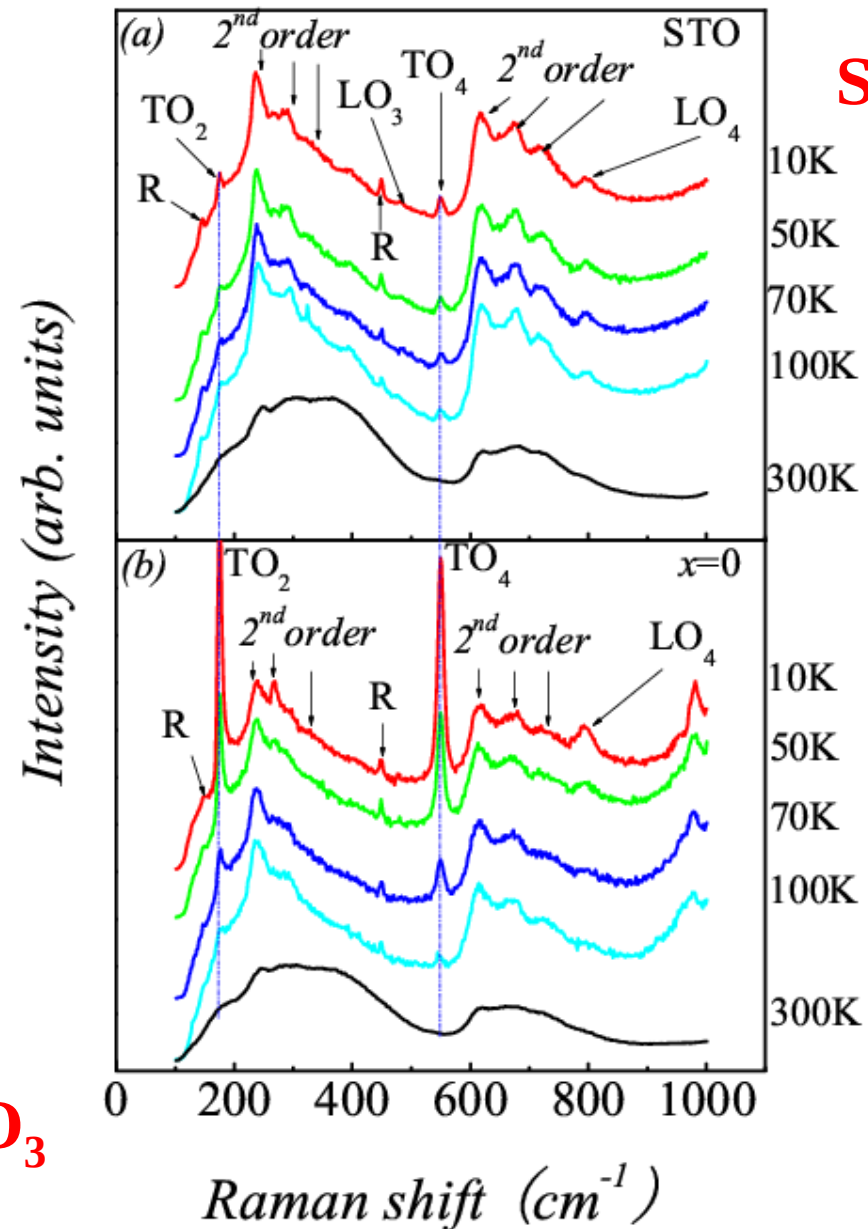
FE modes

$\text{TO}_2 = 174 \text{ cm}^{-1}$

$\text{TO}_4 = 549 \text{ cm}^{-1}$



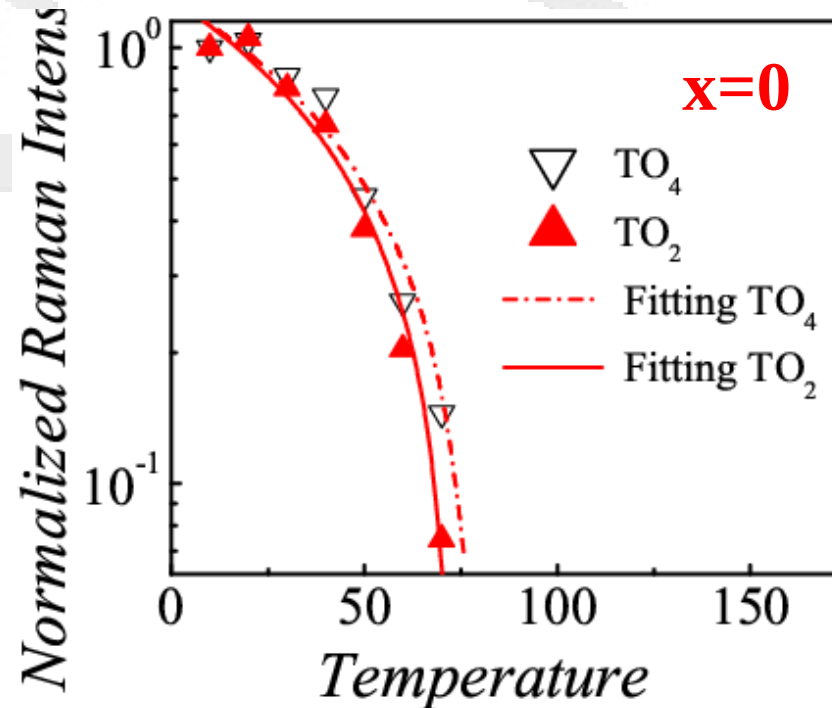
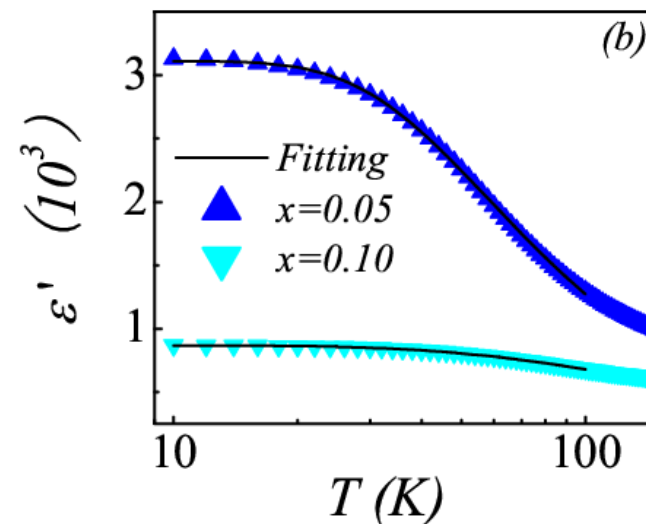
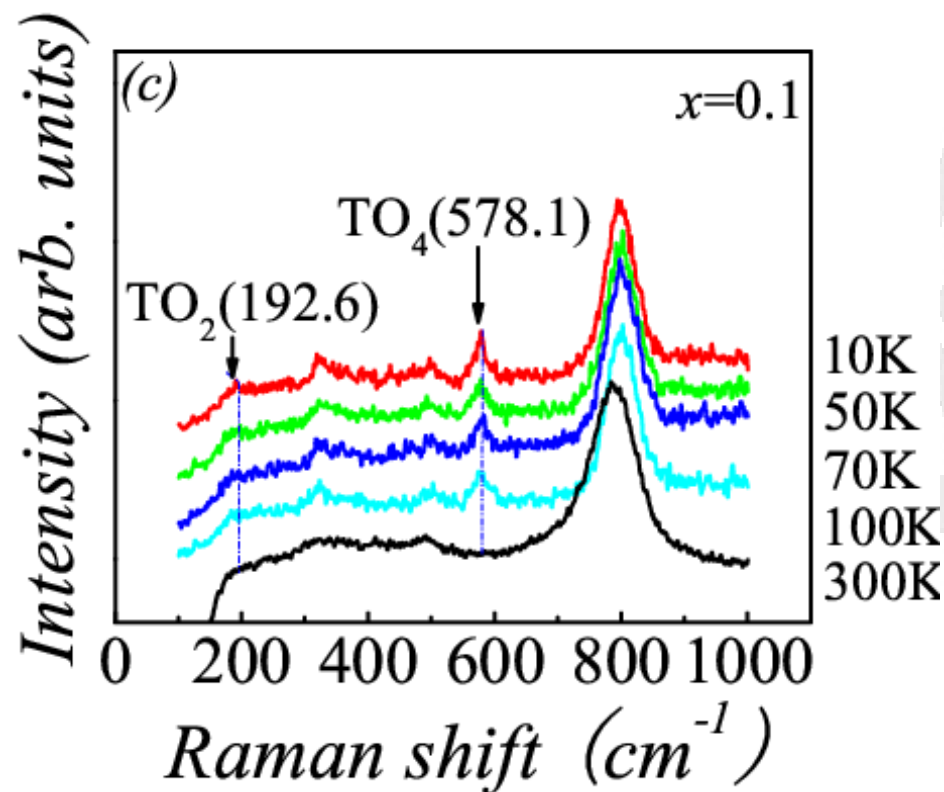
$\text{Sr}_{0.9}\text{Ba}_{0.1}\text{TiO}_3$



SrTiO_3

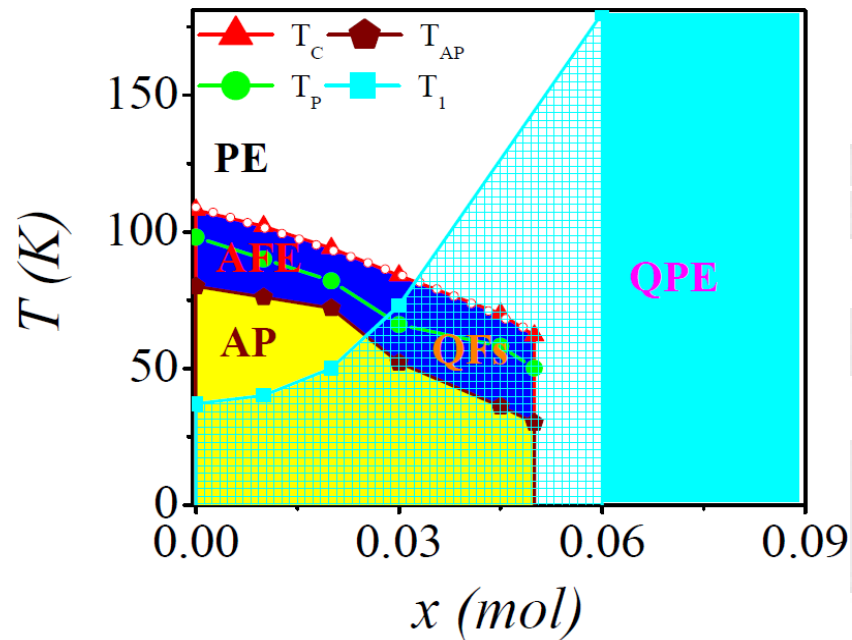
Enhancement of QFs

Raman evidence



Enhancement of QFs

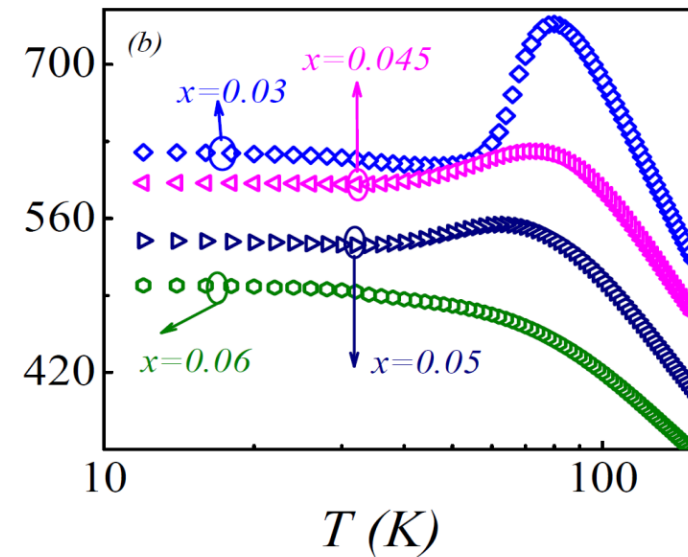
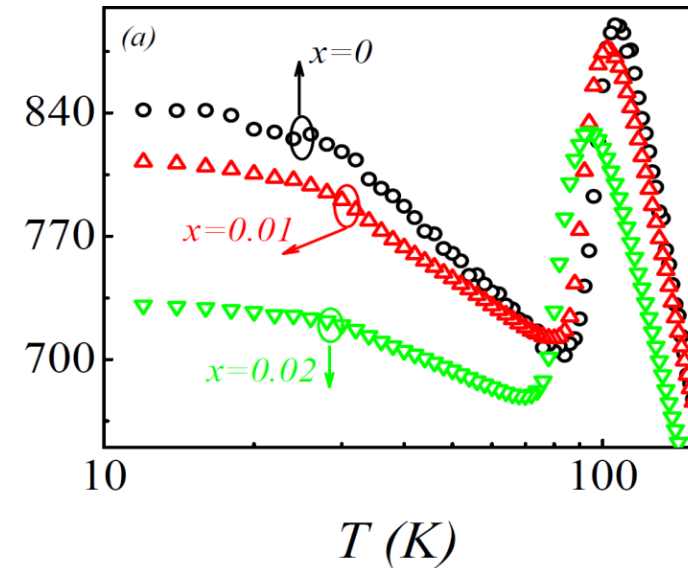
Raman evidence



$$T_c = 397.6x(0.07-x)^{1/2}$$

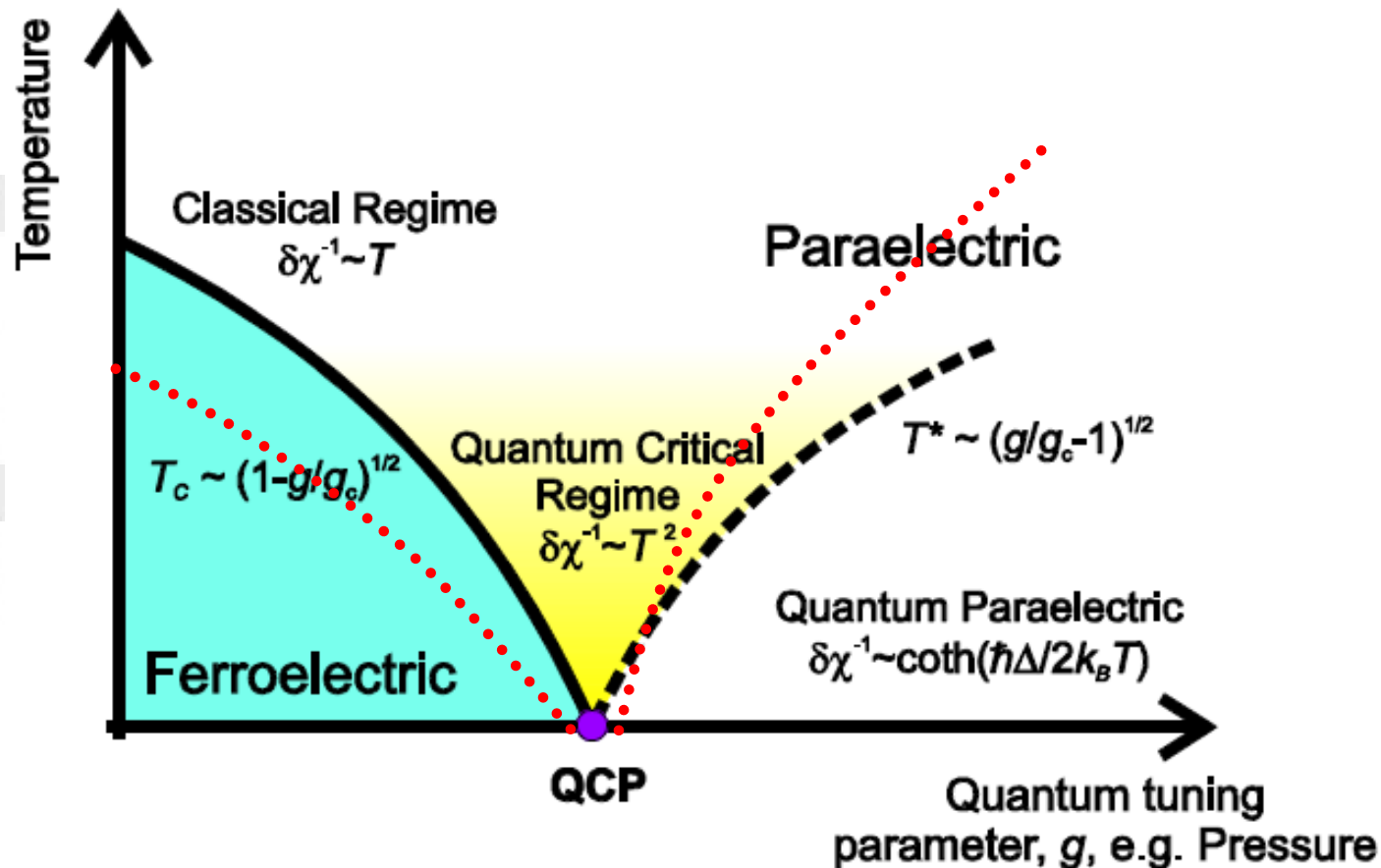
β

β



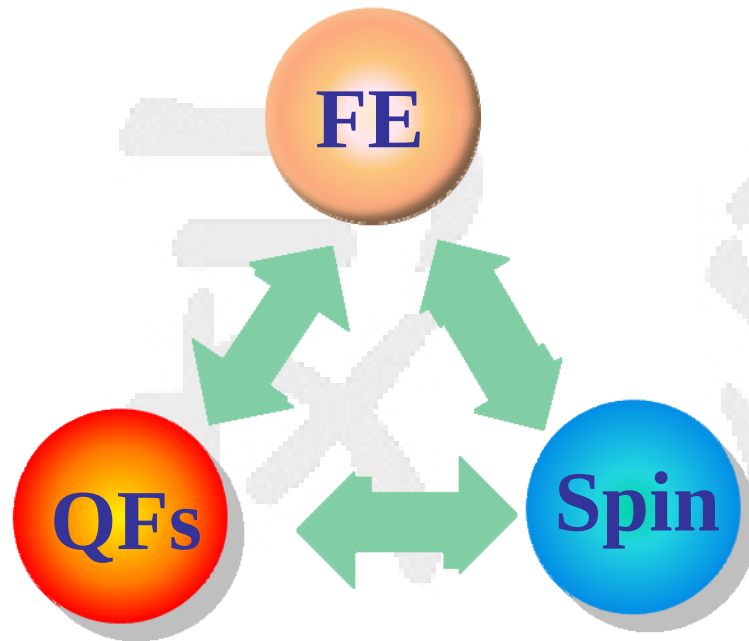
Background & motivation

Effect of spin order?



Magnetoelectric effect in EuTiO_3

Motivation



EuTiO_3

$Pm3m$, $a=0.3905\text{nm}$

Quantum paraelectric

$T_S=30\text{K}$

QFs vs FE

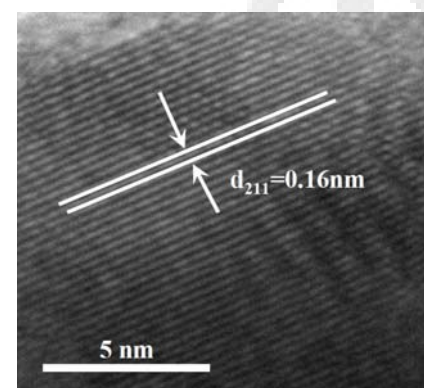
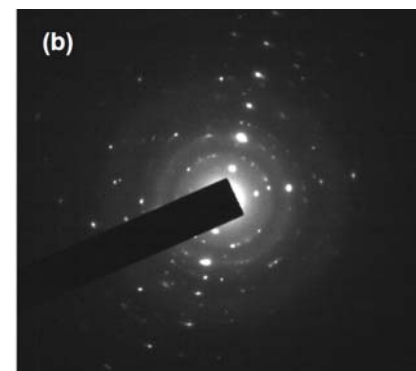
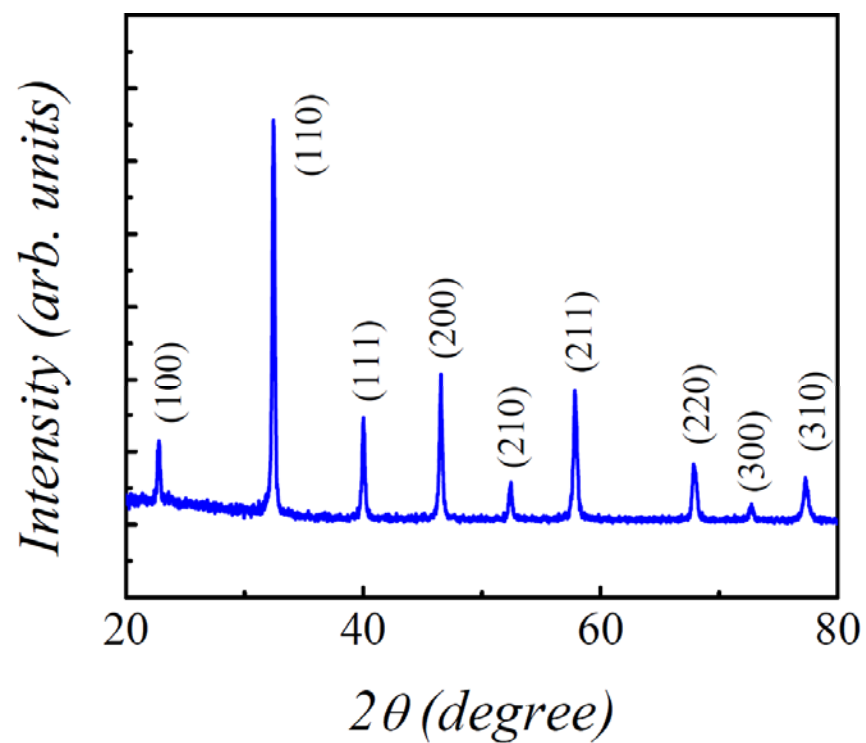
$\text{Eu}^{2+}(S=7/2)$, G-AFM

Soft mode 10meV



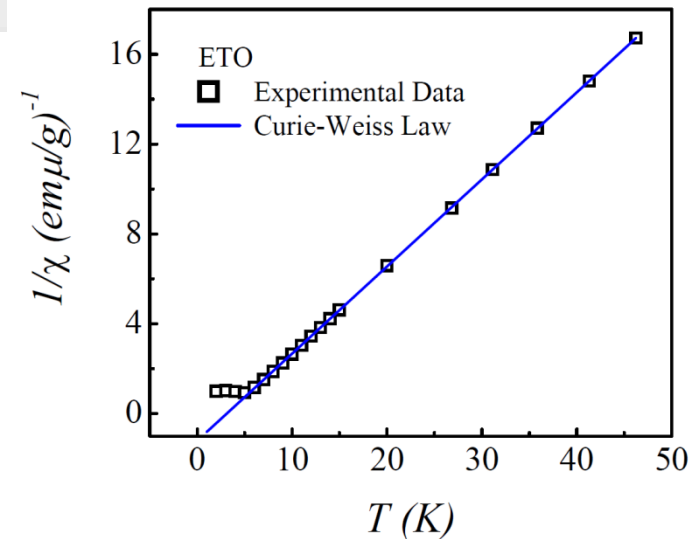
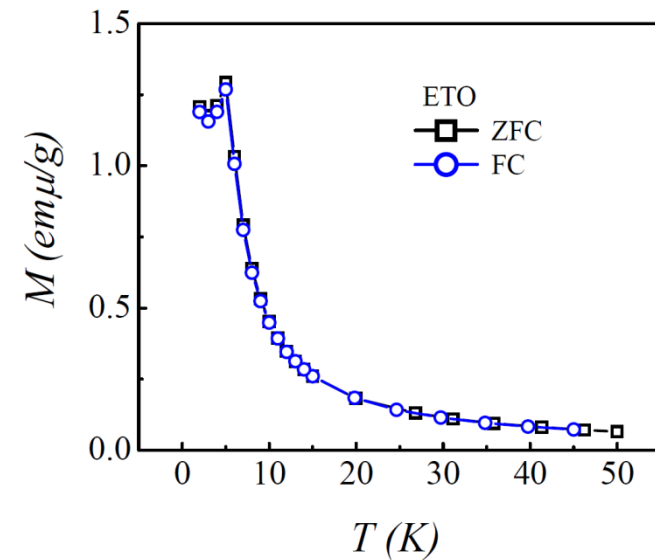
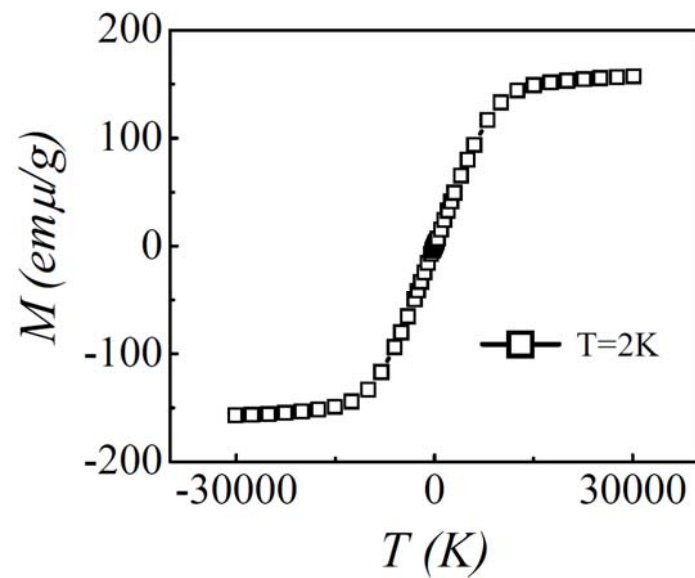
Magnetoelectric effect in EuTiO_3

Preparation



Magnetoelectric effect in EuTiO_3

Magnetic behaviors

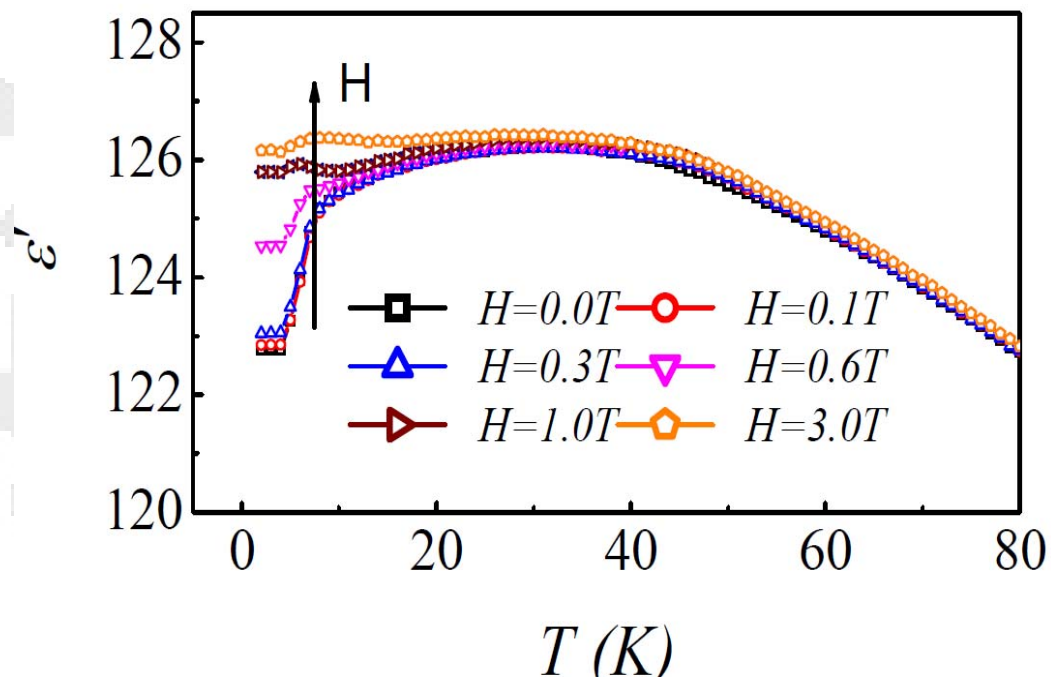


$T_N=5\text{K}$, G-AFM
High H , G-AFM to FM



Magnetoelectric effect in EuTiO_3

Magnetic field induced QPE



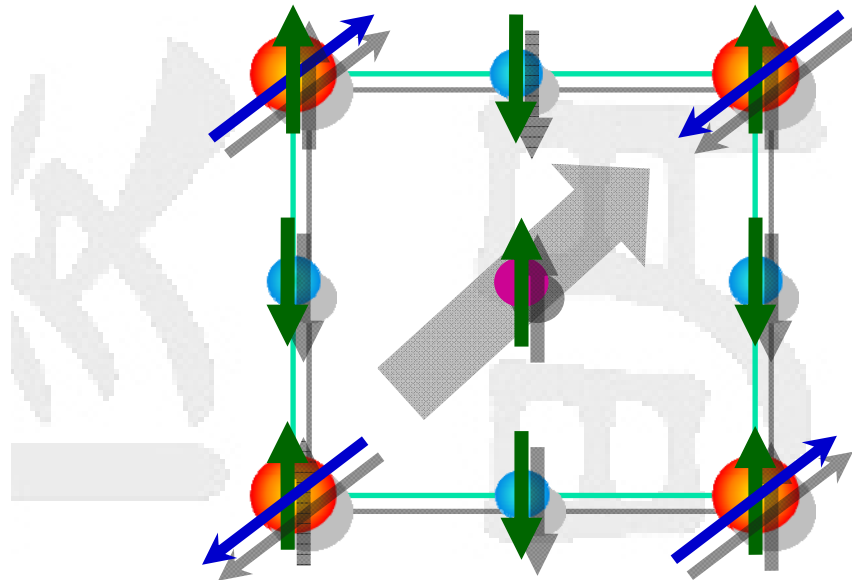
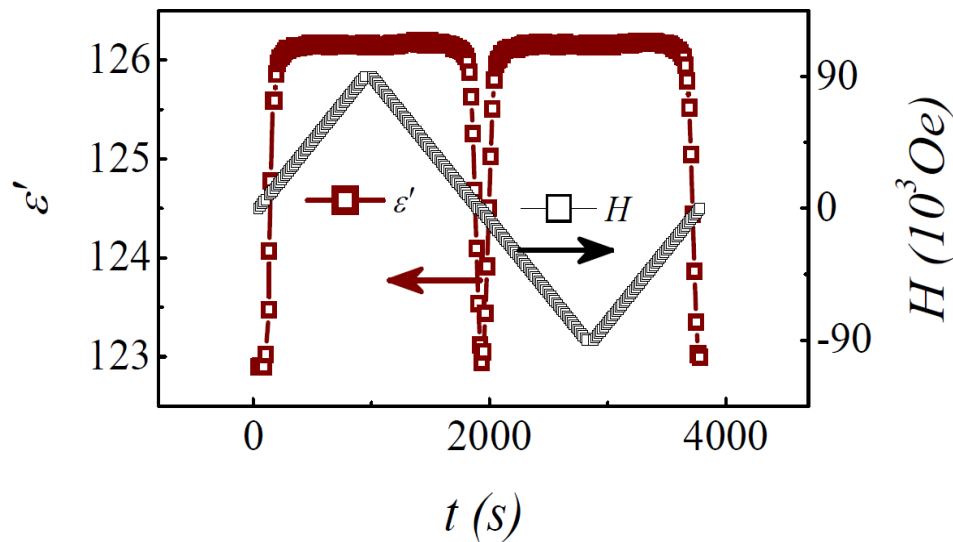
$T_S \sim 40\text{K}$, quantum saturation temperature

$T_N \sim 5\text{K}$, sharp drop of dielectric constant



Magnetoelectric effect in EuTiO_3

Magnetic field induced QPE



$H \rightarrow \text{Eu}^{2+} (S=7/2)$ rotation

Spin (Eu^{2+}) - phonon (T_{1u}) coupling

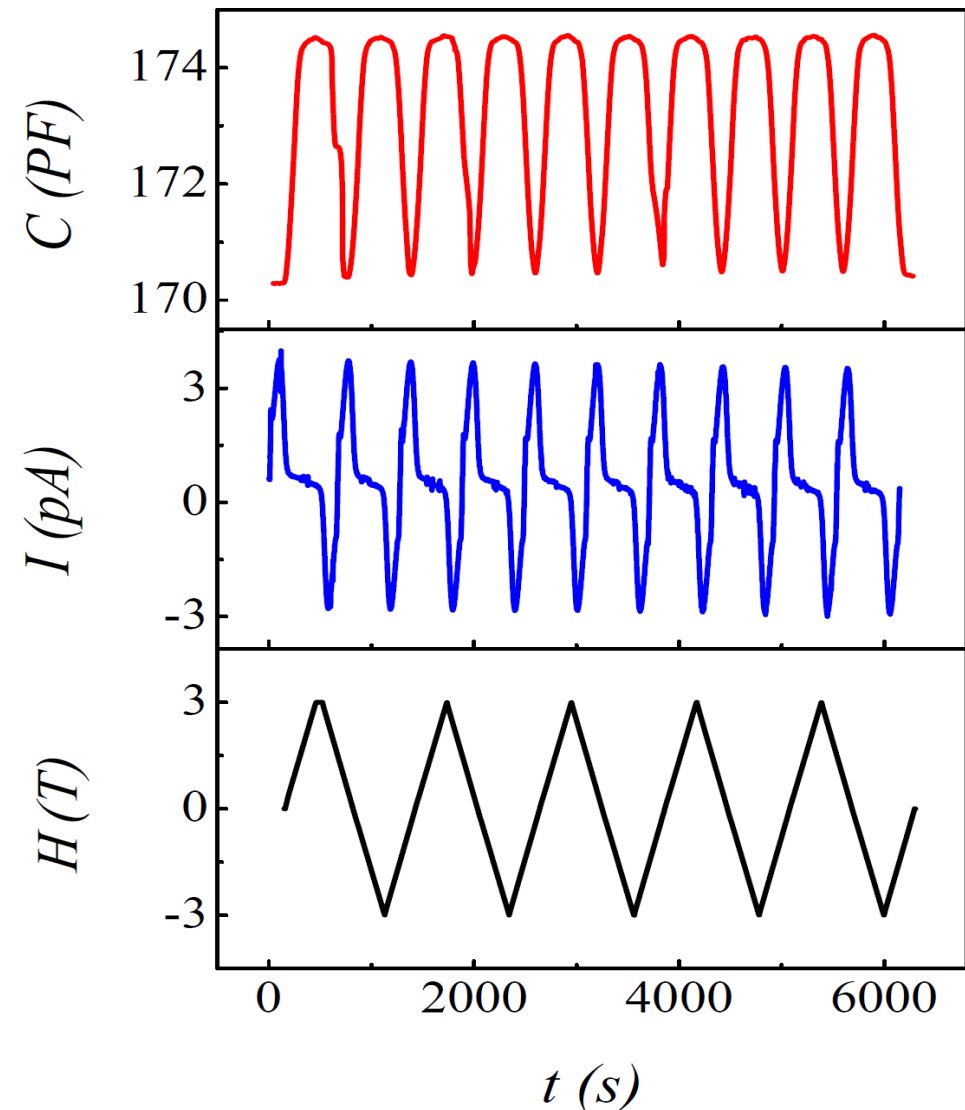
$$\epsilon = \epsilon_0 [1 + \alpha (S_i \cdot S_j)]$$



Magnetoelectric effect in EuTiO_3

Magnetic field induced QPE

Magnetic field enhances the quantum fluctuations, and thus induces the magnetoelectric response



Summary

- A-site disorder and B-site Ru^{4+} substitution can obviously modulate the QFs.
- QFs can be respectively suppressed by the A-site disorder and enhanced by the Ru^{4+} substitution.
- Excellent magnetoelectric effects in quantum paraelectric EuTiO_3 .



Thank you for your attentions!

