

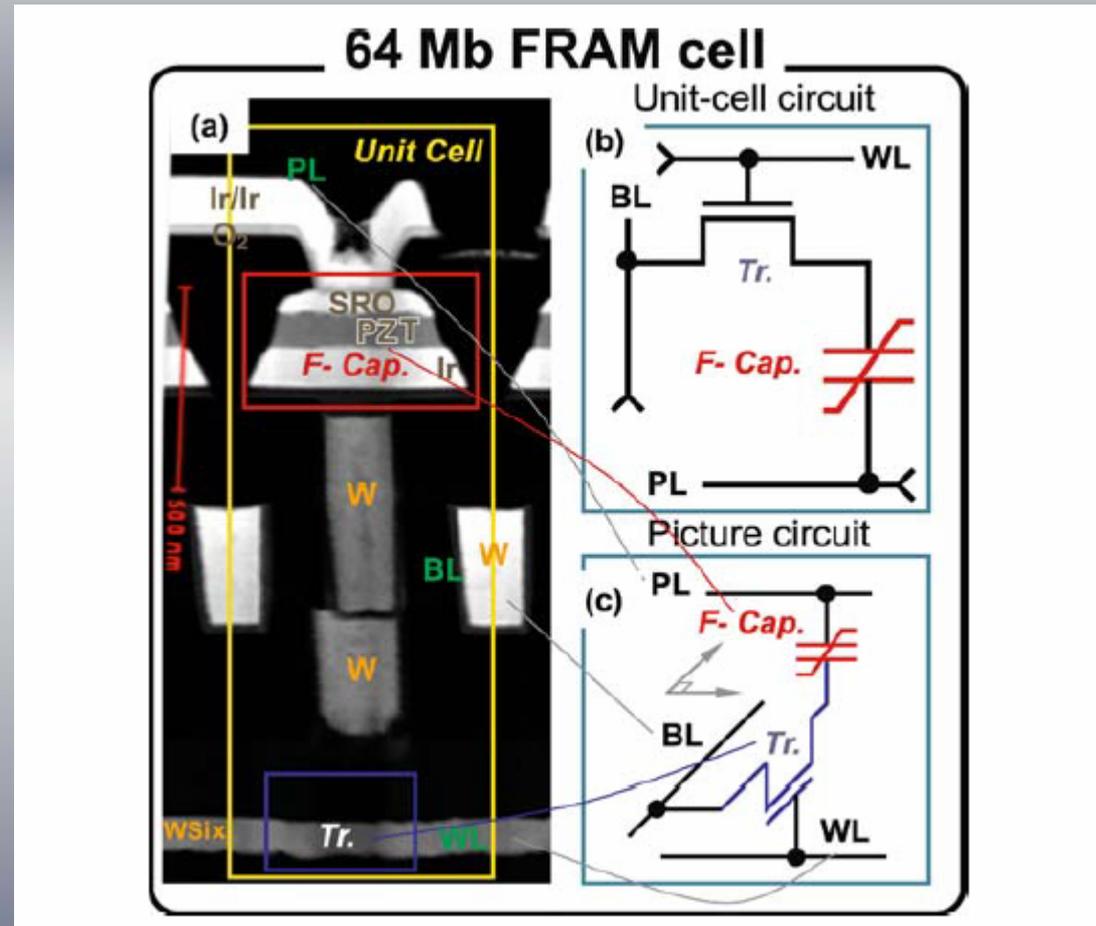
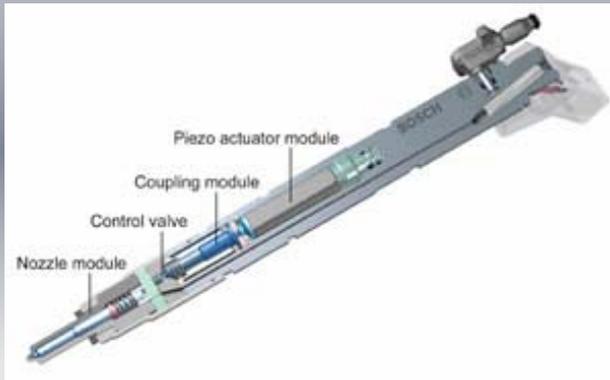
СТРУКТУРА СЕГНЕТОЭЛЕКТРИКОВ

Сложные проблемы простых структур

С.Б. Вахрушев

ФКС 2014

Функциональные сегнето и пьезоэлектрики



Heckmann Diagramm

- Пьезоэлектрический коэффициент:

$$d_{i\mu} = \frac{\partial \mathcal{D}_i}{\partial T_\mu}$$

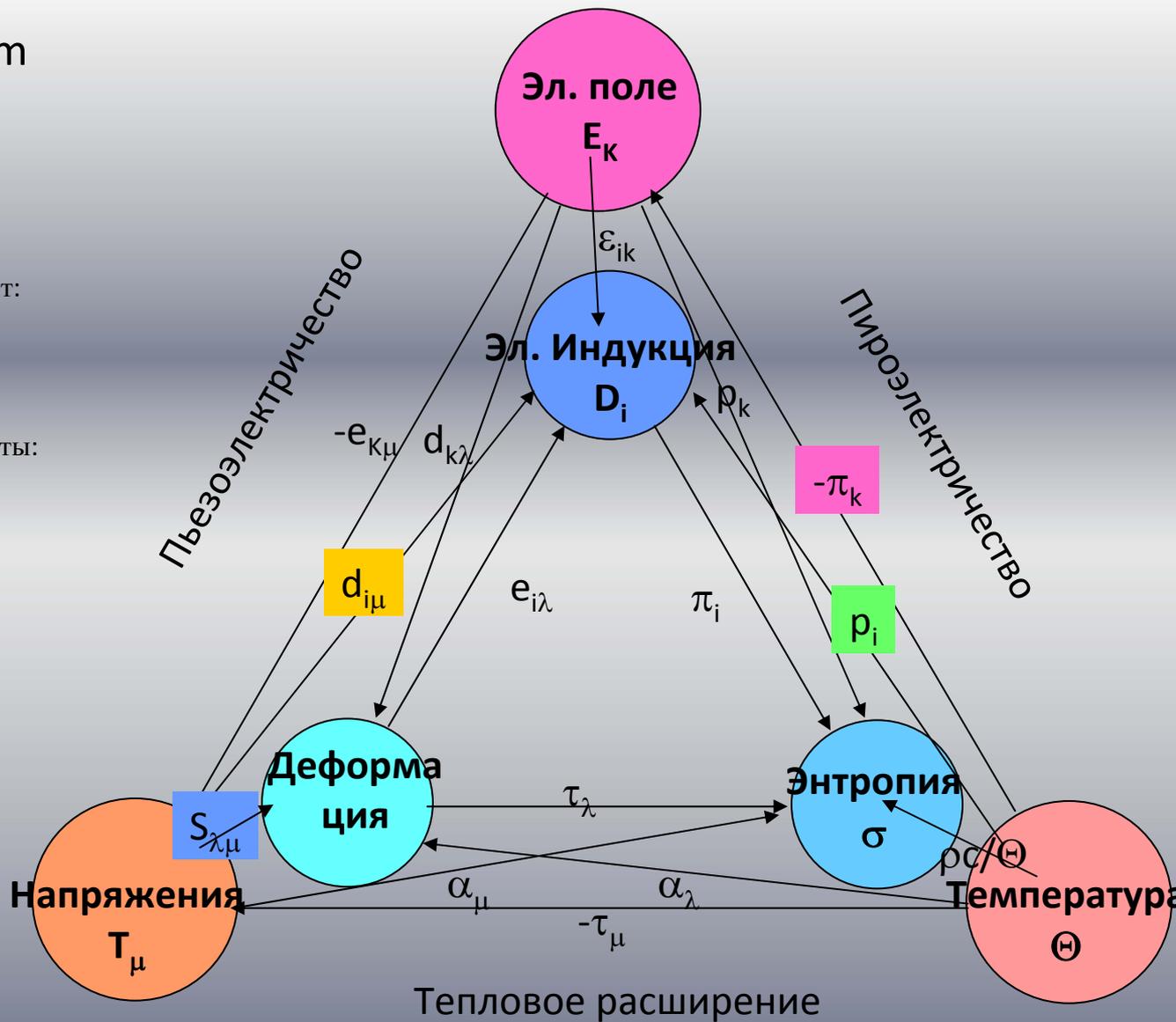
- Пироэлектрические коэффициенты:

$$p_i = \frac{\partial \mathcal{D}_i}{\partial \theta} = \frac{\partial \sigma}{\partial E_i}$$

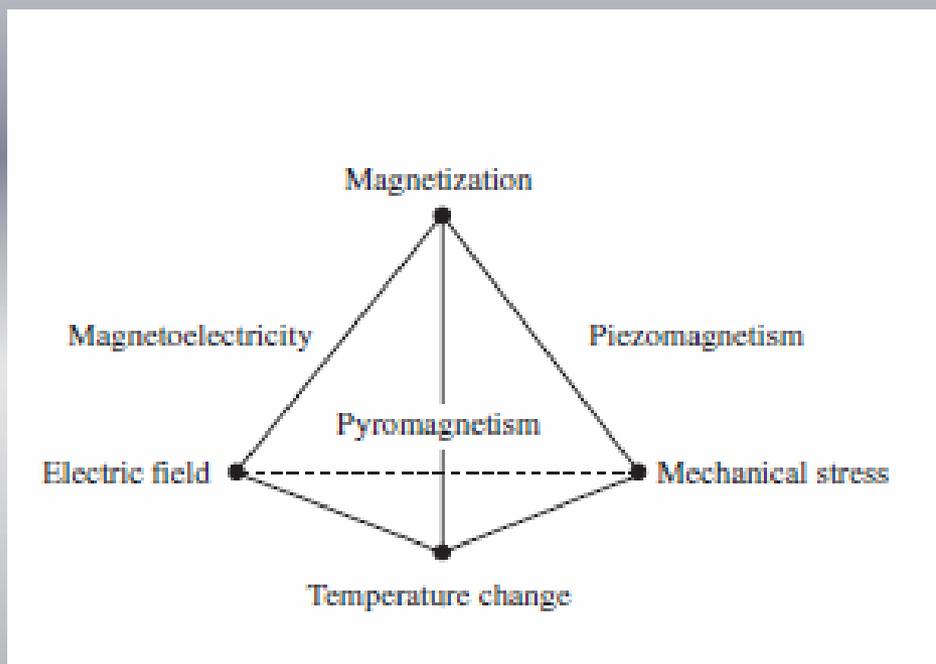
$$\pi_k = -\frac{\partial E_k}{\partial \theta} = \frac{\partial \sigma}{\partial \mathcal{D}_k}$$

- Упругий модуль:

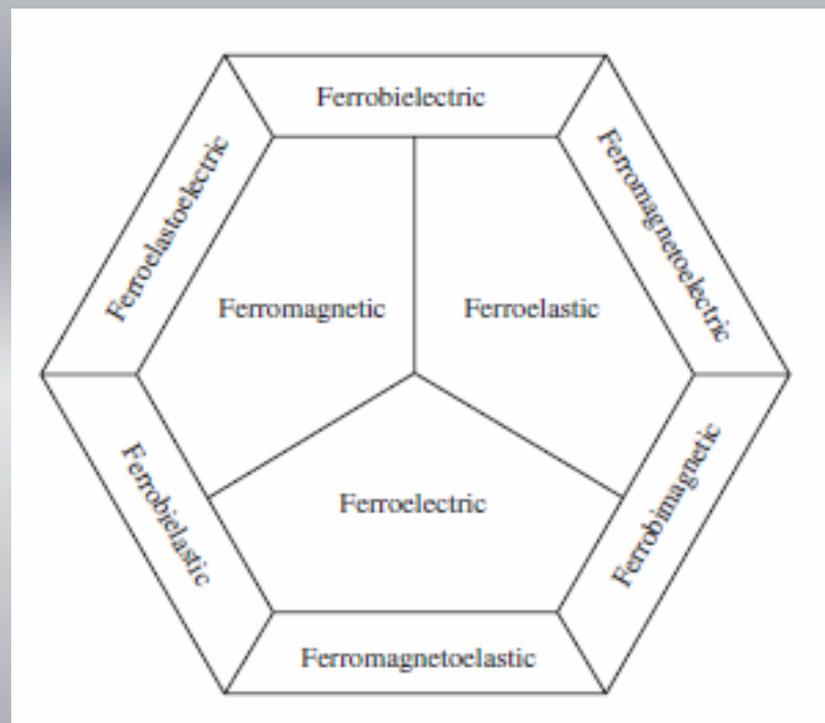
$$C_{\lambda\mu} = \frac{\partial T_\mu}{\partial S_\lambda} = S_{\lambda\mu}^{-1}$$



Добавление магнетизма



9 типов ферроиков Из них 6 мультиферроиков



Пьезо- пиро- сегнетоэлектрики



Электреты

Начиная с древнего мира (трибоэлектреты)

пьезоэлектрики

→ 1880 Жолио и Пьер Кюри

пироэлектрики

сегнетоэлектрики

Немного истории

- 1920 – 1930 – Эра Сегнетовой соли
Э Сеньет (E. Seignette) 1655, Валашек - 1920
- 1930 – 1940 – период KDP
- 1940 – 1950 – Титанат Бария, PZT
- 1950 – 1960 – бурное развитие, открытие релаксоров
- 1960 – 1970 – развитая наука (*представление о мягких модах, критические явления*)
- 1970 – 1980 – Диверсификация (*ферроики, электрооптика ...*)
- 1980 – 1990 – Интегральные сегнетоэлектрики
- 1990 – 2000 – миниатюризация (*пленки, нанокompозиты*)
- 2000 – 2010 – внутренне неоднородные сегнетоэлектрики (*доменная инженерия, доменные стенки*)
- 2010 - ... Мультиферроики...

Пьезо- пиро- сегнетоэлектрики



Электреты



Начиная с древнего мира (трибоэлектреты)

пьезоэлектрики

→ 1880 Жолио и Пьер Кюри



пироэлектрики



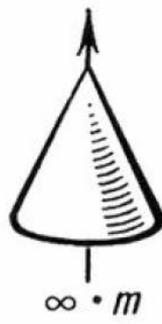
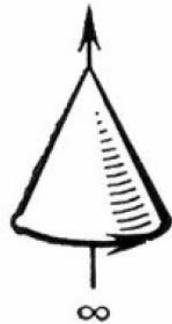
сегнетоэлектрики

Симметрия макроскопических свойств (немагнитных)

- При рассмотрении макроскопических физических свойств материала мы должны учитывать только его точечную группу – 32 точечных группы
- В случае поликристаллических, аморфных, стеклообразных материалов, жидких кристаллов и, в ряде случаев, жидкостей необходимо включать в рассмотрение группы Кюри

Группы Кюри

ПРЕДЕЛЬНЫЕ ГРУППЫ СИММЕТРИИ



Принципы Неймана и Кюри

- Группа симметрии любого физического свойства кристалла должна включать в себя элементы симметрии точечной группы кристалла
- Если не монокристалл, то + предельная группа

- Кристалл под внешним воздействием изменяет свою точечную симметрию так, что сохраняет лишь элементы симметрии, общие с элементами симметрии воздействия

$$T'_{ijk\dots} = a_{il} a_{jm} a_{kn} \dots T_{lmn\dots} = T_{ijk\dots}$$

Простейший случай. Поляризация (индукция) – тензор 1-го ранга (вектор)

- $P'_i = \alpha_{ij} P_j = P_i$

Центр инверсии

$$(p') = \begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1 \\ -p_2 \\ -p_3 \end{pmatrix} = -(p).$$

Очевидный вывод: в центросимметричных группах поляризация запрещена.

Группа 32 Ось 3-го порядка
Вдоль Z_3

$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1/2 + \sqrt{3}p_2/2 \\ -\sqrt{3}p_1/2 - p_2/2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

Ось 2-го порядка
Вдоль Z_1

$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ -p_2 \\ -p_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$$

Кварц – нецентросимметричный НЕПОЛЯРНЫЙ кристалл (пьезоэлектрик)

Поляризация продолжение

Турмалин – 3m

Ось 3-го порядка
Вдоль Z_3

$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1/2 + \sqrt{3}p_2/2 \\ -\sqrt{3}p_1/2 - p_2/2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

Плоскость
Перпендикулярна Z_1

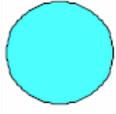
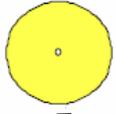
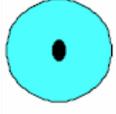
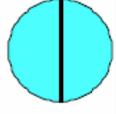
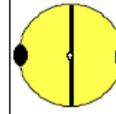
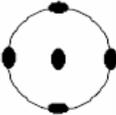
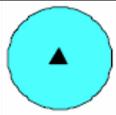
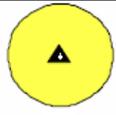
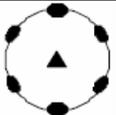
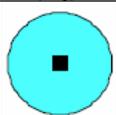
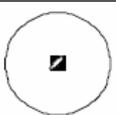
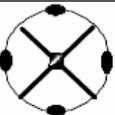
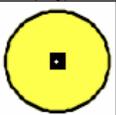
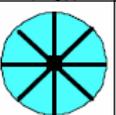
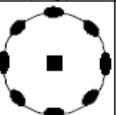
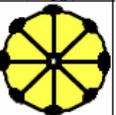
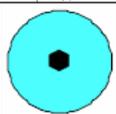
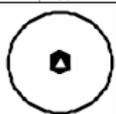
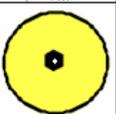
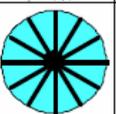
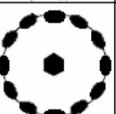
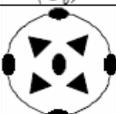
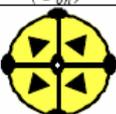
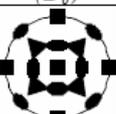
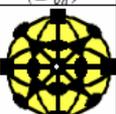
$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$$

Заполяризованная сегнетокерамика – ∞m

$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \cos \theta - p_2 \sin \theta \\ p_1 \sin \theta + p_2 \cos \theta \\ p_3 \end{pmatrix} = \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$$

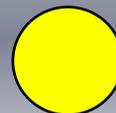
$$\begin{pmatrix} p'_1 \\ p'_2 \\ p'_3 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} -p_1 \\ p_2 \\ p_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$$

Ответ очевиден – поляризация
только по оси Z_3

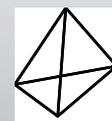
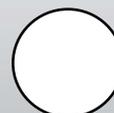
 1 (C_1)			 $\bar{1}$ (C_i)			
 2 (C_2)				 m (C_2)		 $2/m$ (C_{2h})
				 $mm2$ (C_{2v})	 222 (D_2)	 mmm (D_{2h})
 3 (C_3)			 $\bar{3}$ (S_6)	 $3m$ (C_{3v})	 32 (D_3)	 $\bar{3}m$ (D_{3d})
 4 (C_4)	 $\bar{4}$ (S_4)	 $\bar{4}2m$ (D_{2d})	 $4/m$ (C_{4h})	 $4mm$ (C_{4v})	 422 (D_4)	 $4/mmm$ (D_{4h})
 6 (C_6)	 $\bar{6}$ (C_{3h})	 $\bar{6}2m$ (D_{3h})	 $6/m$ (C_{6h})	 $6mm$ (C_{6v})	 622 (D_6)	 $6/mmm$ (D_{6h})
 23 (T)			 $\bar{m}\bar{3}$ (T_h)	 $\bar{4}3m$ (T_d)	 432 (O)	 $\bar{m}3m$ (O_h)

Полярность

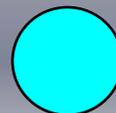
Центросимметричные



Нецентросимметричные
неполярные

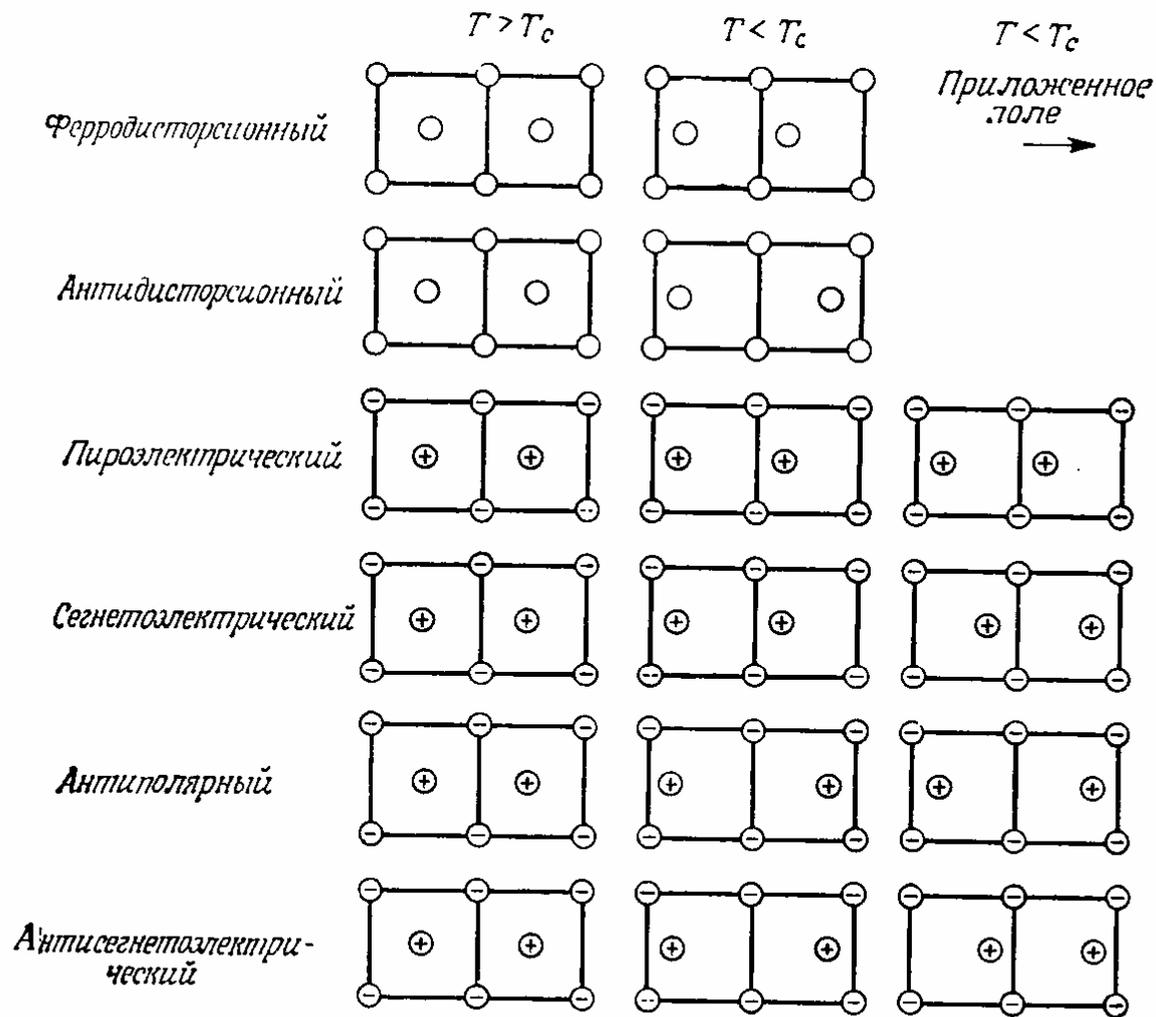


Нецентросимметричные
полярные



СЕГНЕТОЭЛЕКТРИКИ - кристаллические диэлектрики (полупроводники), обладающие в определённом диапазоне температур спонтанной поляризацией, которая существенно изменяется под влиянием внешних воздействий. Структуру сегнетоэлектриков можно представить как результат **фазового перехода кристалла** с искажением структуры (понижением симметрии) из неполярной структуры (параэлектрической фазы) в полярную (сегнетоэлектрическую фазу). В большинстве случаев это искажение структуры такое же, как и при воздействии электрического поля на кристалл в неполярной (параэлектрической) фазе.

Физическая энциклопедия.

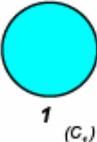
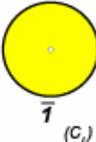
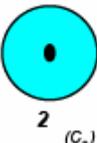
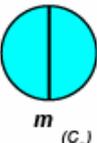
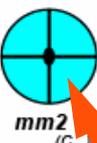
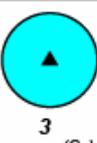
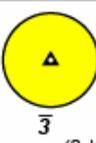
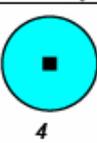
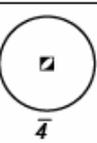
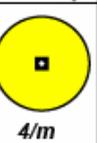
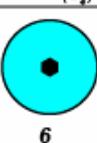
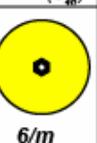


⊕ ⊖ Заряженные атомы или группы атомов

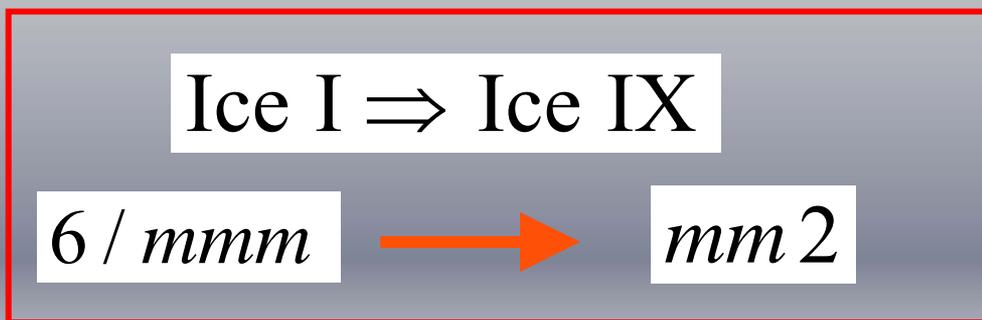
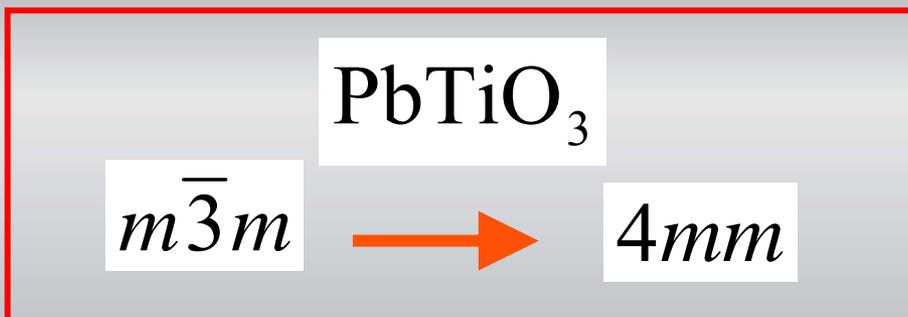
○ Незаряженные атомы или группы атомов

Рис. 1.1. Схематическое представление некоторых основных типов структурных фазовых переходов из centrosymmetric прототипа.

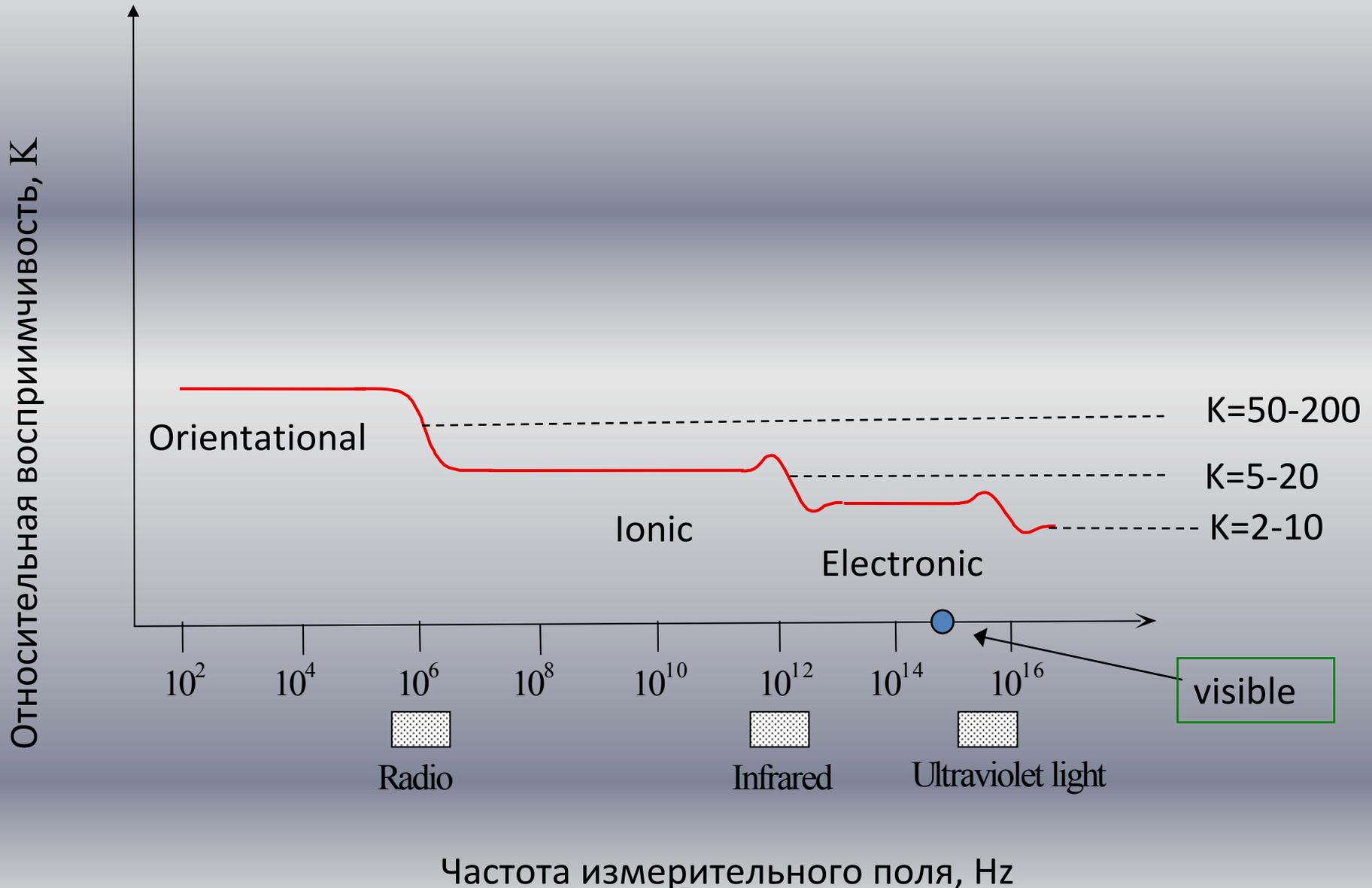
Сегнтоэлектрический фазовый переход

 1 (C_1)			 $\bar{1}$ (C_1)			
 2 (C_2)				 m (C_2)		 $2/m$ (C_{2h})
				 $mm2$ (C_{2v})	 222 (D_2)	 mmm (D_{2h})
 3 (C_3)			 $\bar{3}$ (S_6)	 $3m$ (C_{3h})	 32 (D_3)	 $\bar{3}m$ (D_{3d})
 4 (C_4)	 $\bar{4}$ (S_4)	 $\bar{4}2m$ (D_{2d})	 $4/m$ (C_{4h})	 $4mm$ (C_{4v})	 422 (D_4)	 mmm (D_{2h})
 6 (C_6)	 $\bar{6}$ (C_{3h})	 $\bar{6}2m$ (D_{3h})	 $6/m$ (C_{6h})	 $6mm$ (C_{6v})	 622 (D_6)	 $6/mmm$ (D_{6h})
 23 (T)			 $m\bar{3}$ (T_h)	 $\bar{4}3m$ (T_d)	 432 (O)	 $m\bar{3}m$ (O_h)

Фазовый переход из структуры с неполярной симметрией в структуру с полярной называется сегнетоэлектрическим

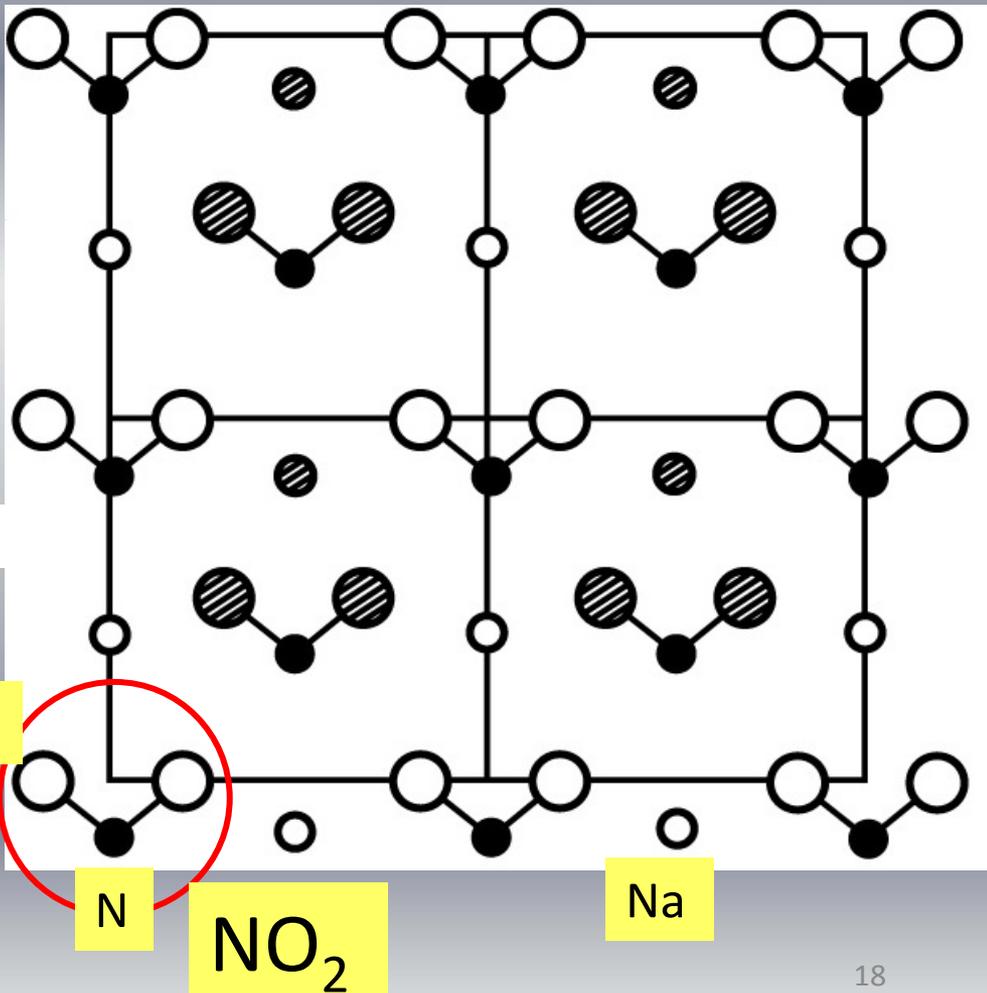


Поляризационный отклик в диэлектриках



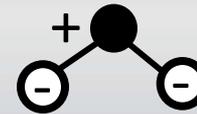
Ориентационный вклад

NaNO₂ at 250 °C



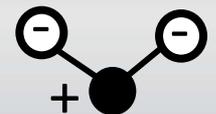
NO₂ groups
can independently
flip between positions

“up”



$$E = 0$$

“down”



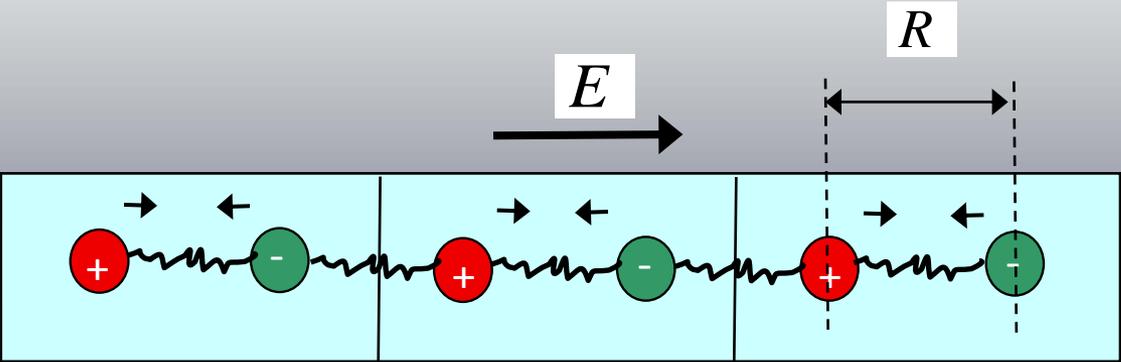
$$N_{\text{up}} = N_{\text{down}}$$

$$E \neq 0$$

$$N_{\text{up}} \neq N_{\text{down}}$$

$$P = \frac{\sum q_i \delta x_i}{V} \neq 0$$

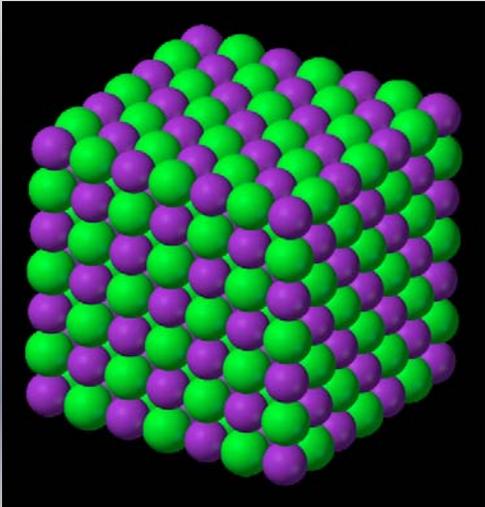
Ионный вклад



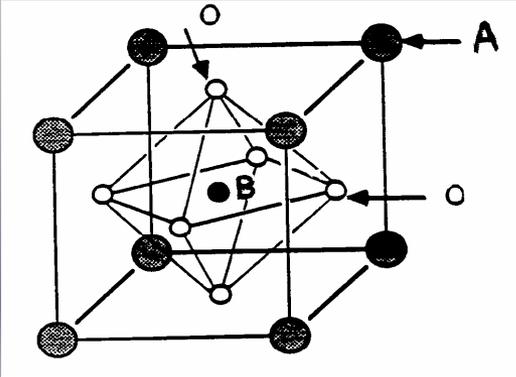
Produced polarization

$$P = \frac{eZ \delta R}{V_{cell}}$$

NaCl



PbTiO₃



A = Pb

B = Ti

Типы сегнетоэлектриков

- Сегнетоэлектрики типа порядок – беспорядок: Сегнетова соль, KH_2PO_4 , NaNO_2
- Сегнетоэлектрики типа смещения
 - Перовскиты
 - Соединения со структурой вольфрамовой бронзы

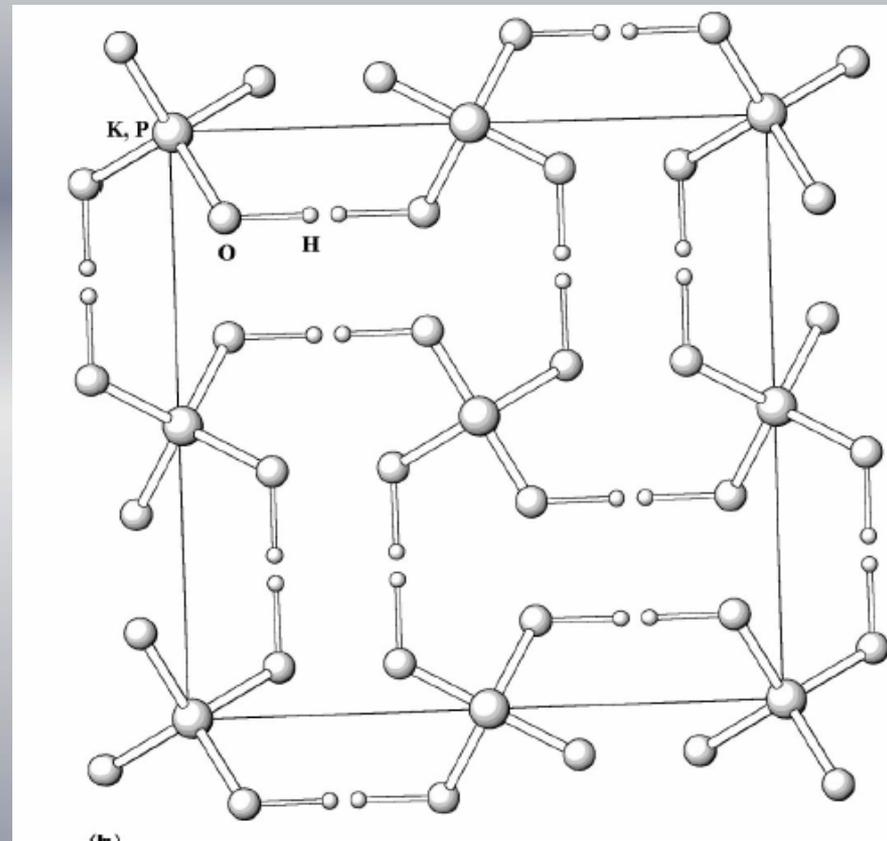
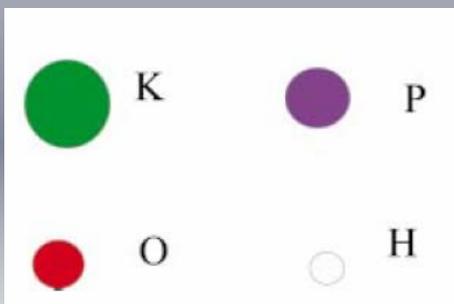
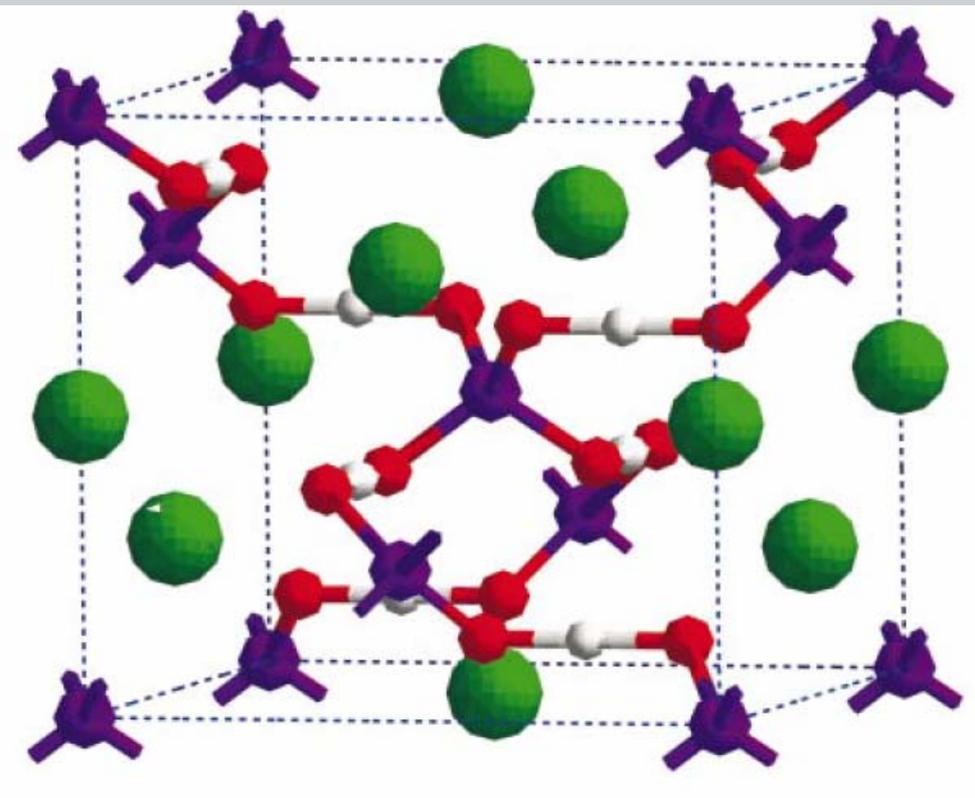
План основной части

- Порядок-беспорядок
 - KDP
 - NaNO_2 в условиях ограниченной геометрии
- Типа смещения (Перовскиты)
 - BaTiO_3 ; KNbO_3 – динамическая кристаллография
 - PbTiO_3 – типы критических колебаний
 - PbZrO_3 (антисегнетоэлектрик)

План основной части II

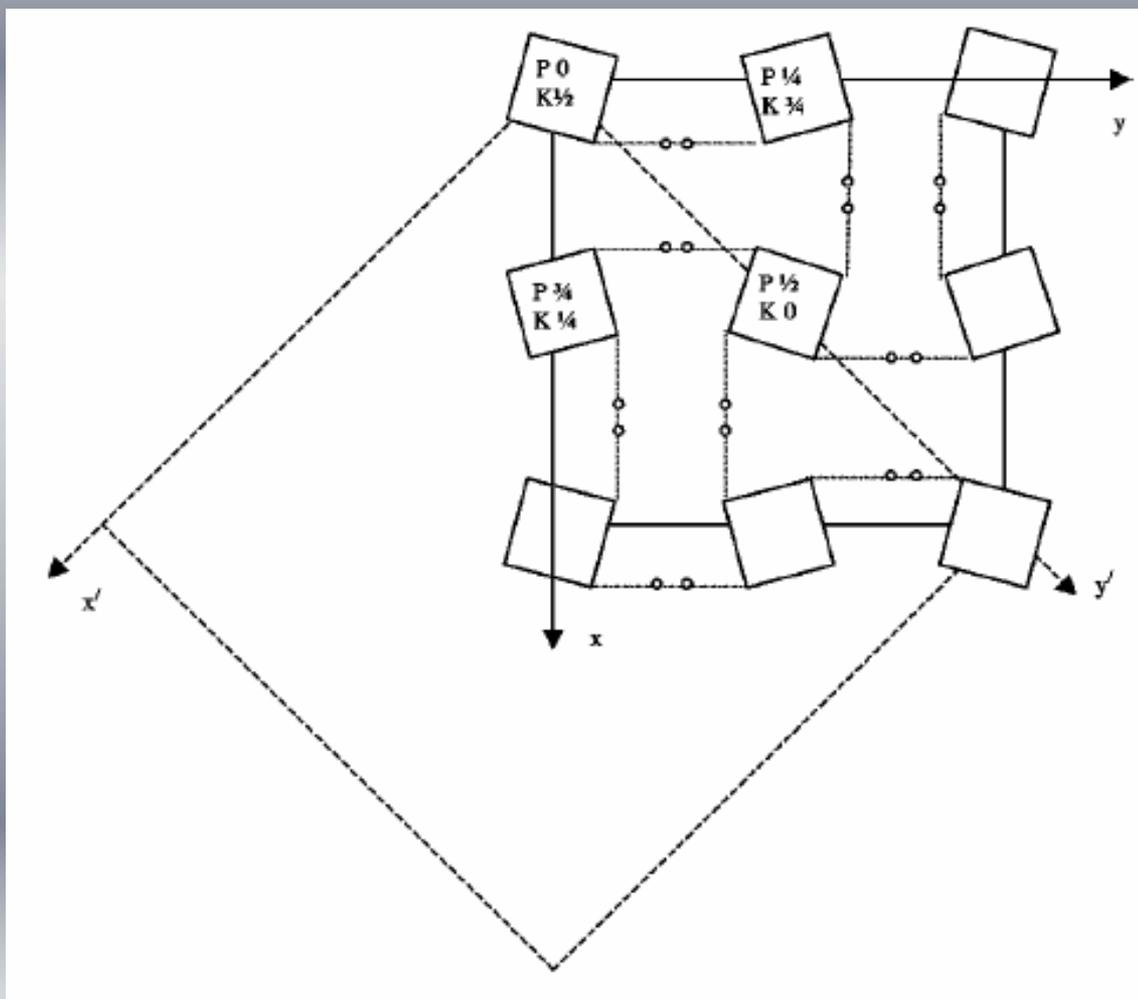
- PZT – морфотропная фазовая граница
- Релаксоры
 - Структура парафазы, функция плотности вероятности
 - Парная корреляционная ф-я (ф-я Паттерсона)
 - Статическая и динамическая структура
 - Полярные нанобласти???

Структура KDP

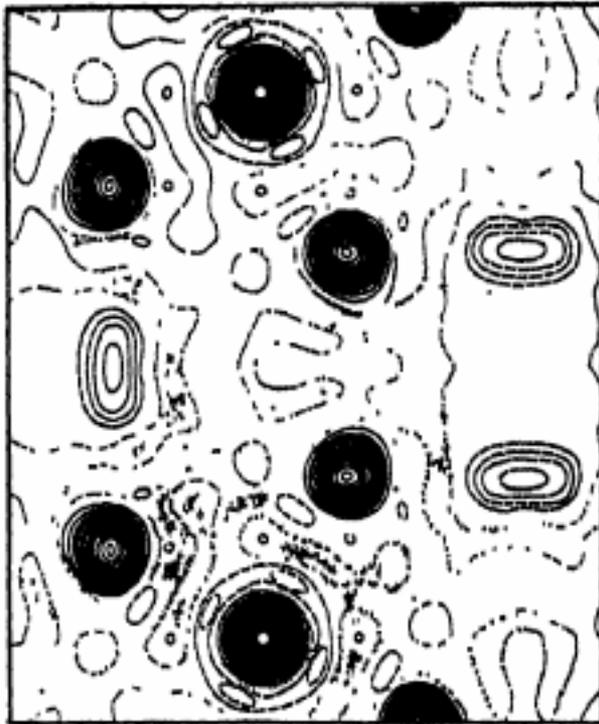


Проекция на ось Z

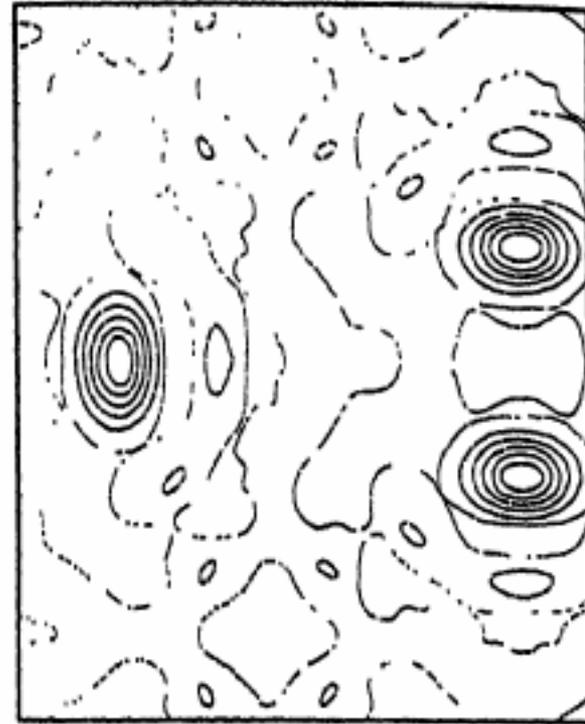
KDP Тетрагональная фаза



KDP карты ядерной плотности - парафаза

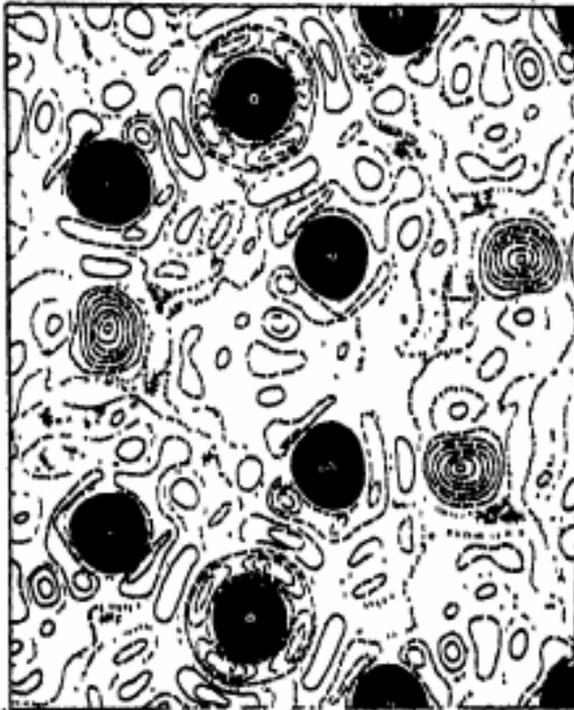


(i) Synthesis of F_0
(Structure at 20°C, tetragonal)

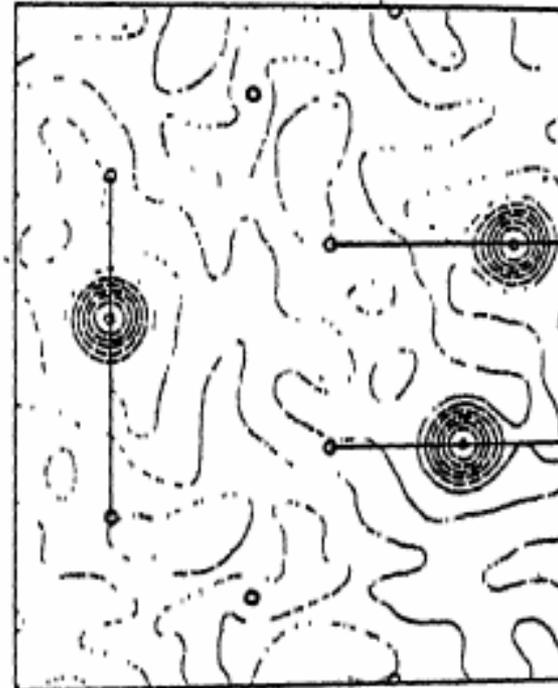


(ii) Synthesis of $F_0 - F_{KPO}$

KDP карты ядерной плотности - сегнетофаза



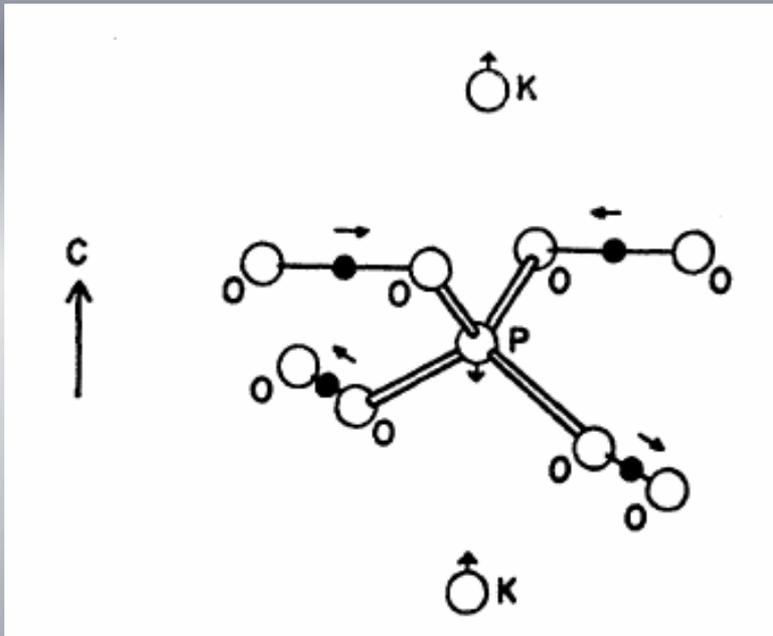
(iii) Synthesis of F_0



(iv) Synthesis of $F_0 - F_{KPO}$

Structure at -180°C (orthorhombic, ferroelectric)

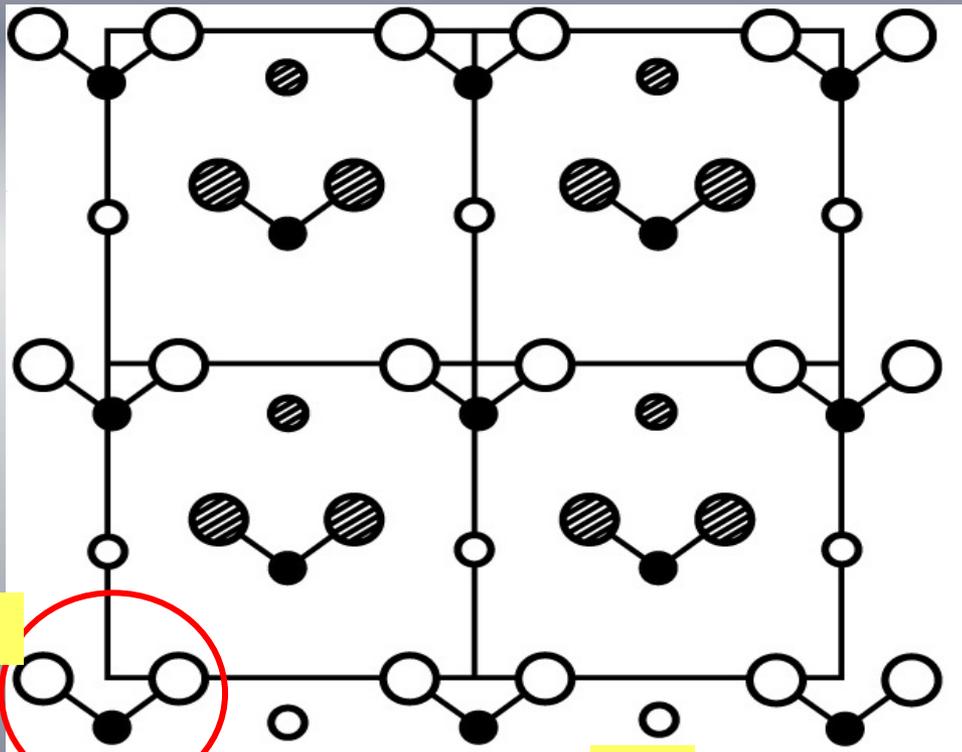
KDP – «сегнетомода»



Т.о. природа поляризации в
межмодовом взаимодействии

Нитрит натрия NaNO_2 – условия ограниченной геометрии

NaNO_2 at 250 °C



O

N

NO_2

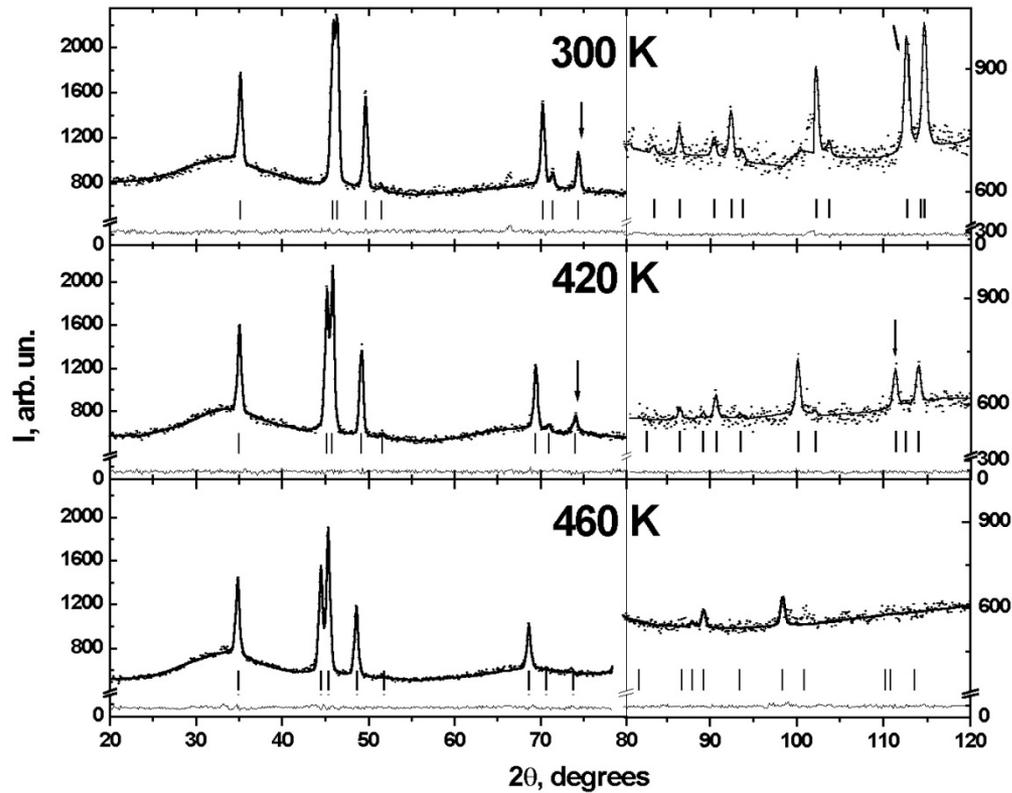
Na

Structure factors

$$F^2 = F_{\text{Re}}^2 + \eta^2 * F_{\text{Im}}^2$$

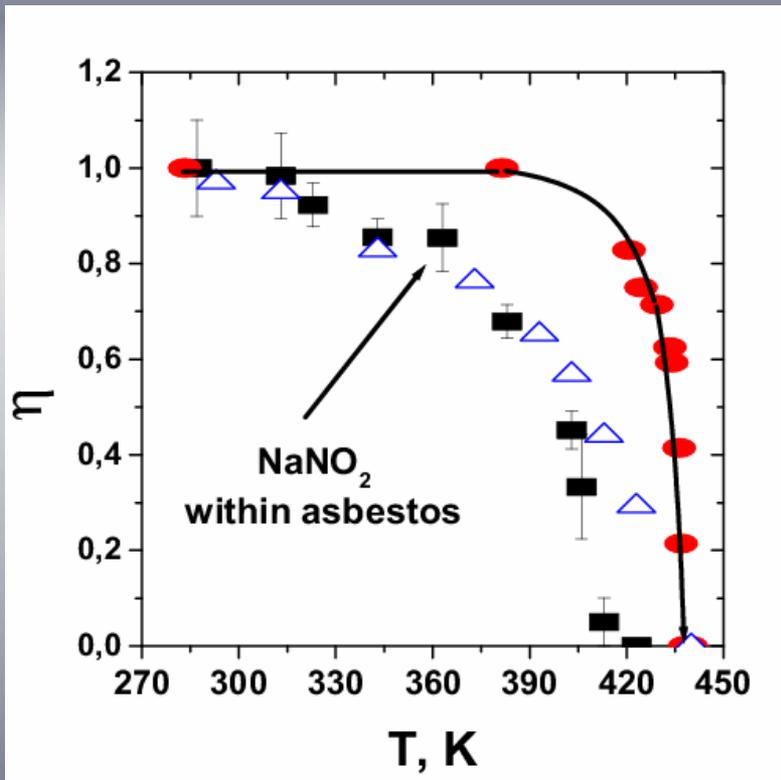
(101) $F_{\text{Re}} = 2.62$ $F_{\text{Im}} = 0$
 (022) $F_{\text{Re}} = 0.46$ $F_{\text{Im}} = 2.04$

Дифрактограмма NaNO_2 в пористом стекле



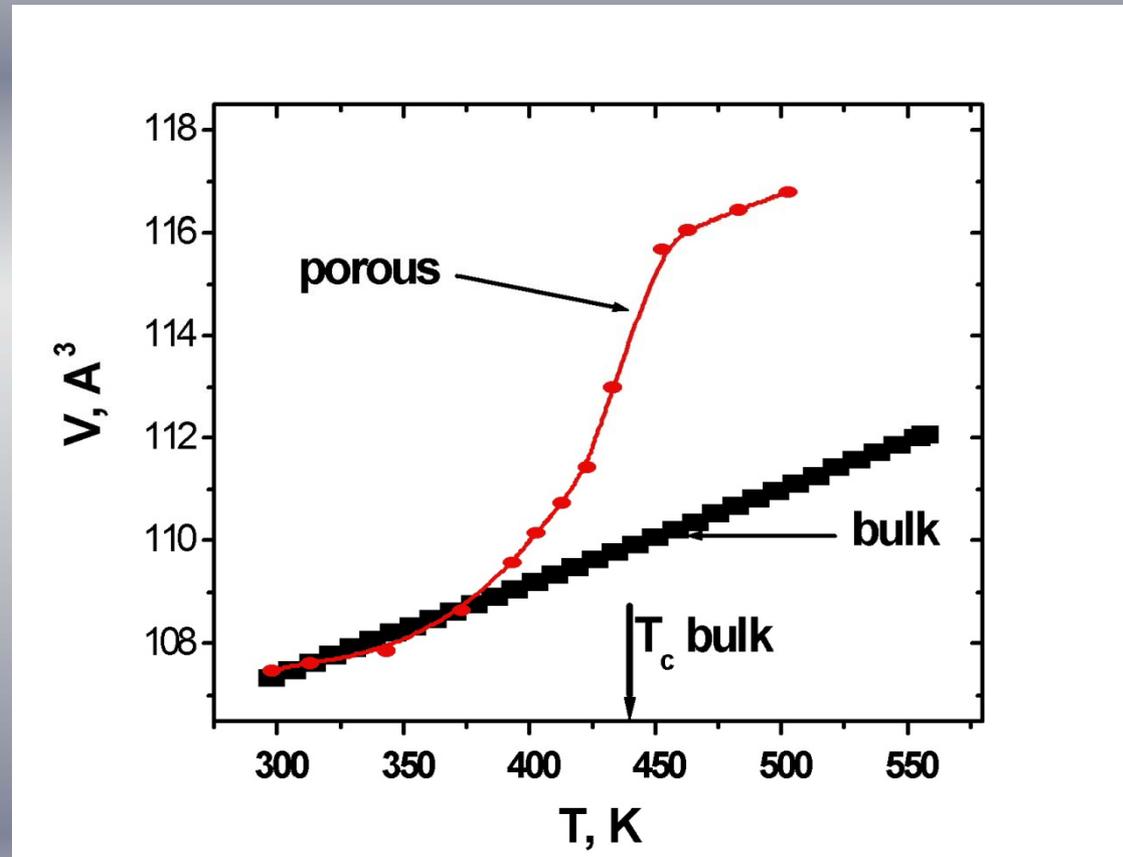
Средний диаметр пор 7 nm
Средний размер кластера 45 nm

NaNO₂ Temperature dependence of the order parameter

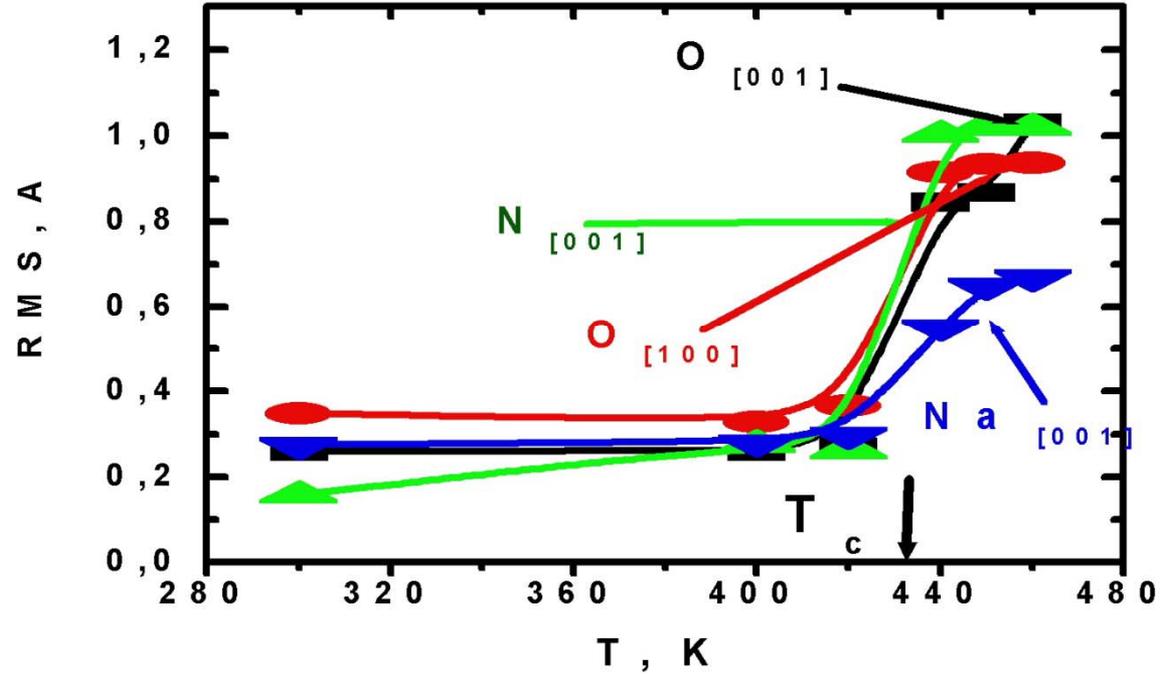


- **Bulk: 1-st order**
 $T_c \approx 437$ K
- **Glass: continuous**
 $\eta = (1-T/T_c)^\beta$
 $T_c = 425.6$ K
 $\beta = 0.31$
- **Asbestos continuous**
 $\eta = (1-T/T_c)^\beta$
 $T_c = 413$ K
 $\beta = 0.34$

Temperature dependence of the unit cell volume

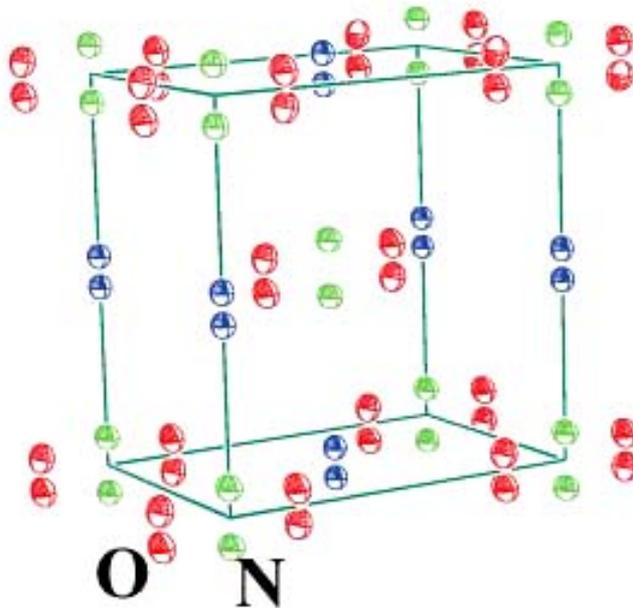


Temperature dependence of the RMS displacements

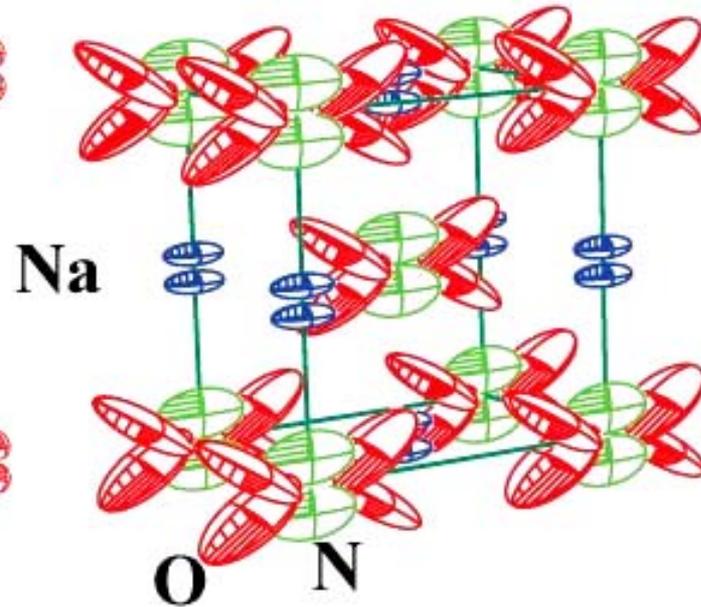


Ellipsoids of ion thermal motions above T_c

458 K bulk

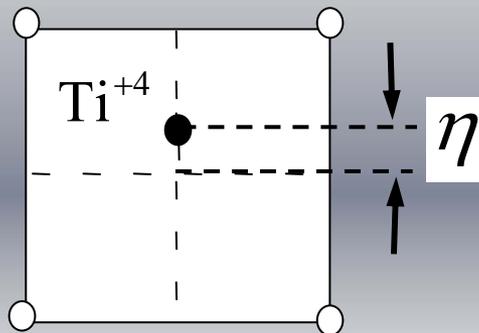
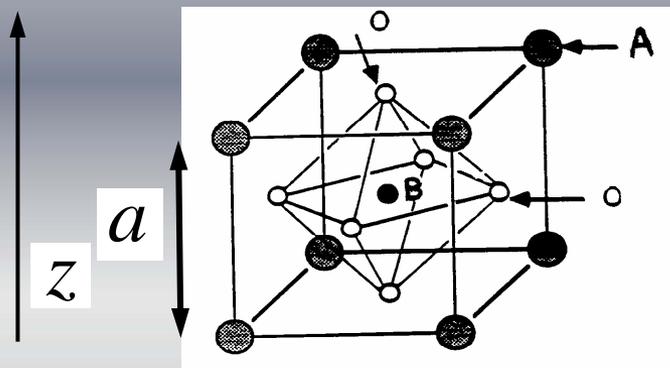


460 K glass



ПЕРОВСКИТЫ

Сегнетоэлектрики типа смещения



$$P_z \equiv P = \frac{Ze\eta}{a^3}$$

$$Z \cong 4$$

$$T > T_c$$

$$T < T_c$$

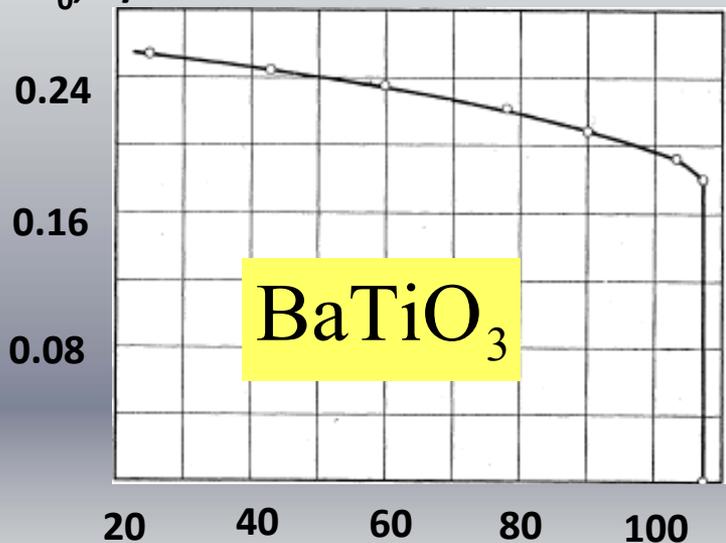
$$\eta = 0$$

$$\eta = \eta_0 \neq 0$$

$$P_{\text{at } E=0} = 0$$

$$P_{\text{at } E=0} = P_0 \neq 0$$

$P_0, \text{C/m}^2$



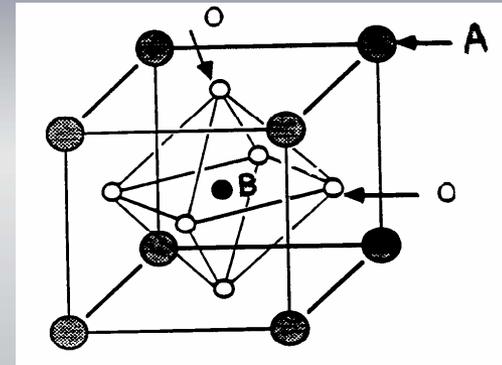
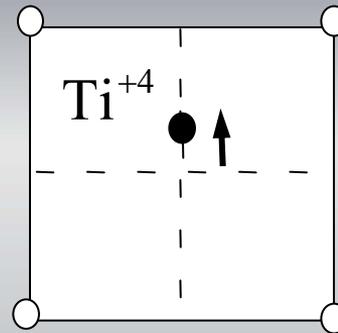
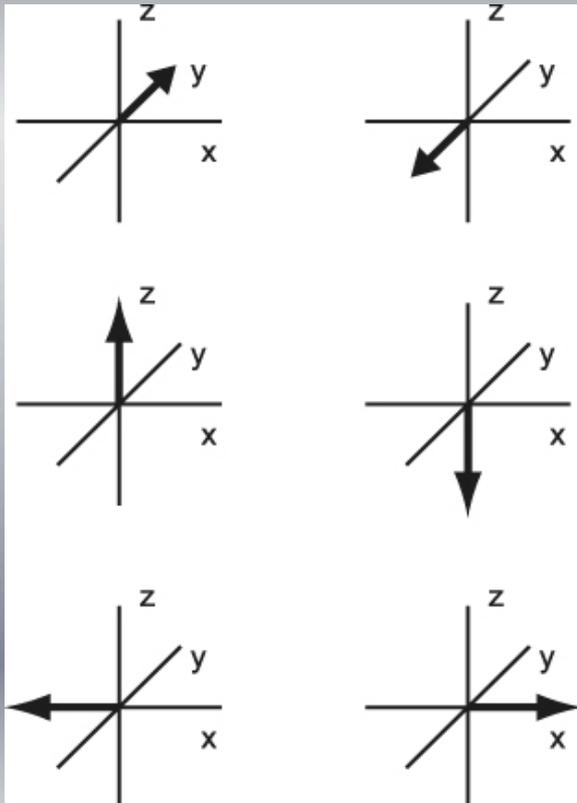
spontaneous polarization

$$P_0 = \frac{Ze\eta_s}{a^3}$$

Domain states

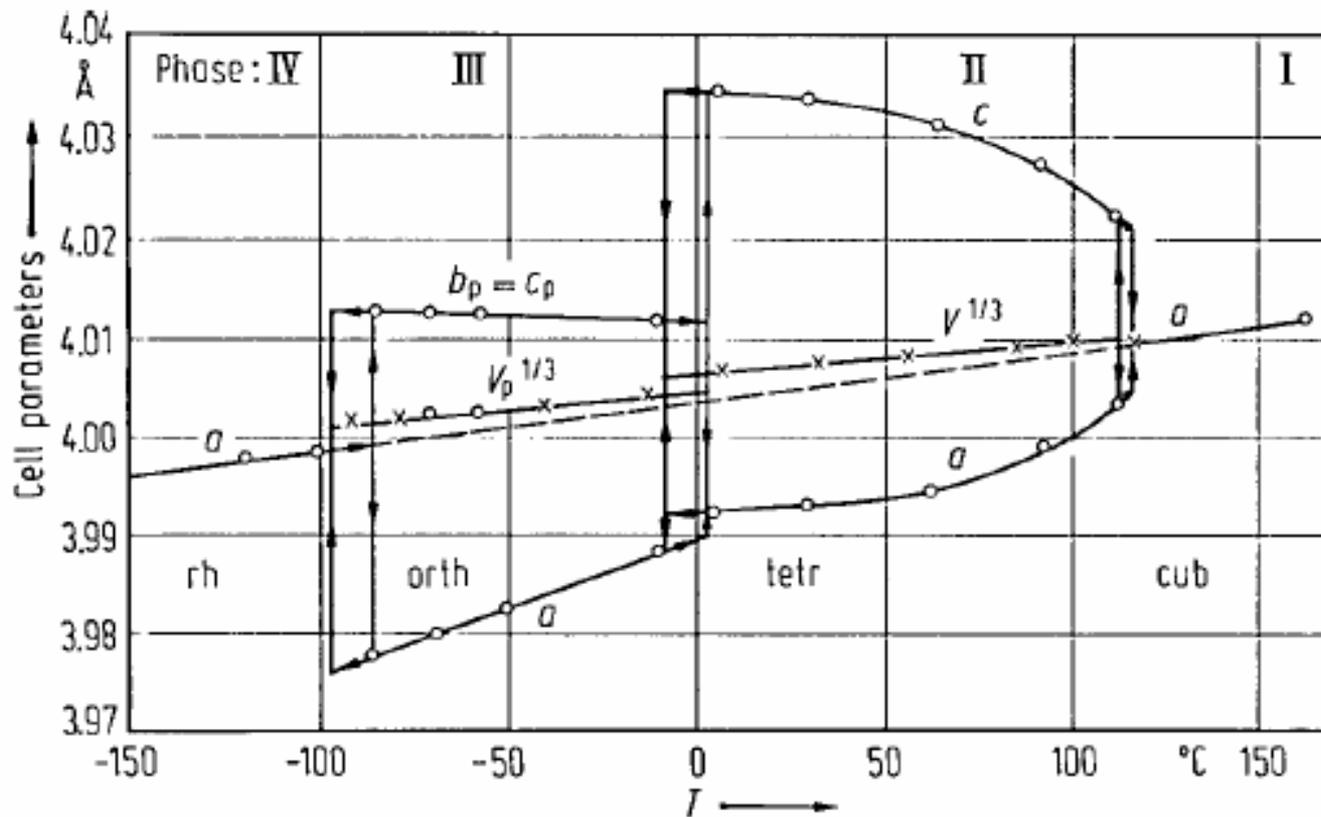
$m\bar{3}m$ \longrightarrow $4mm$

6 possible orientations of spontaneous polarization

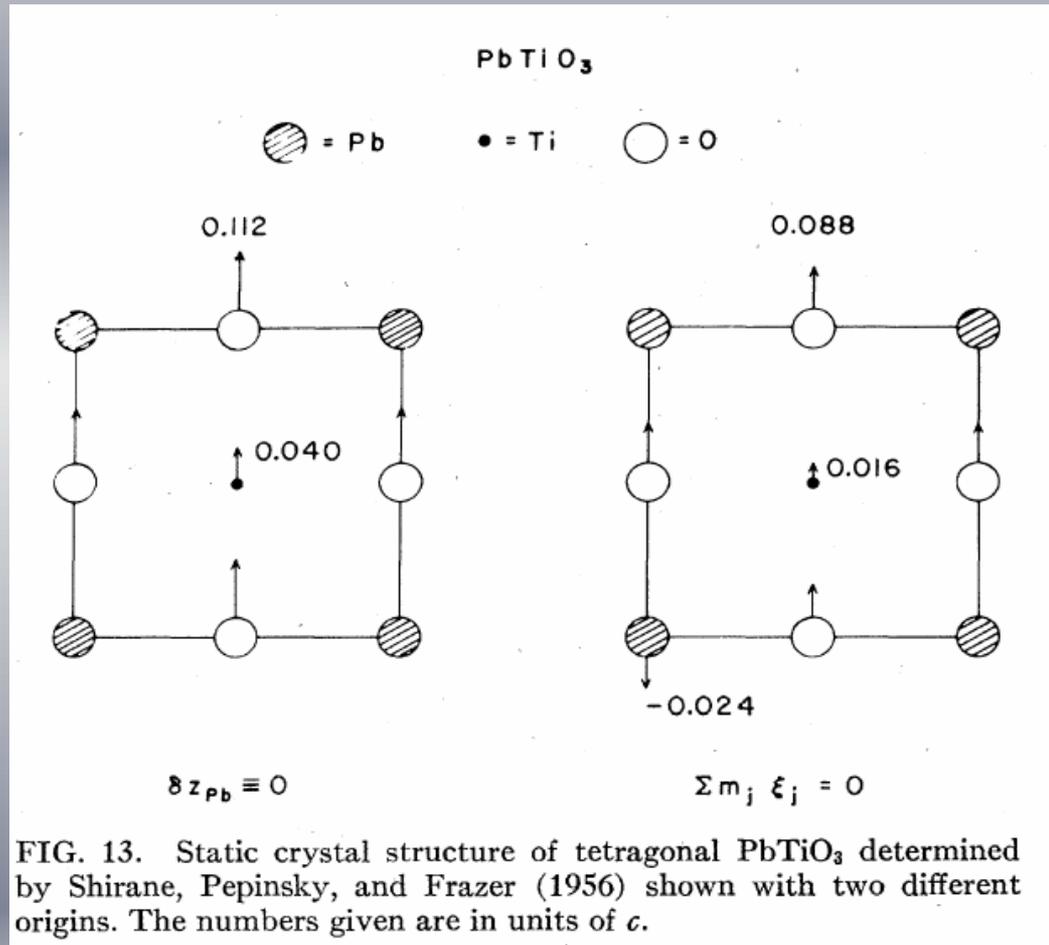


6 domain states

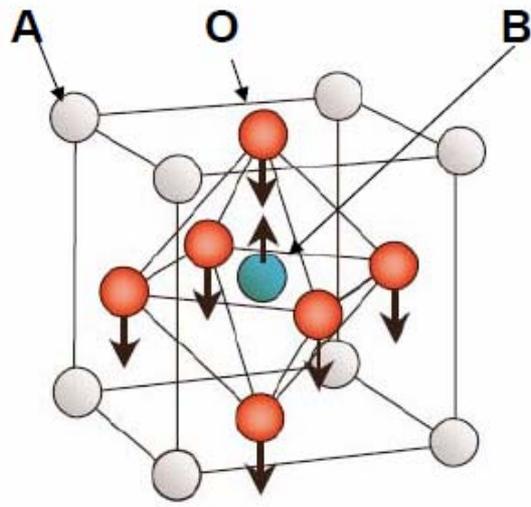
Phase transitions in BaTiO₃



Неоднозначность уточнения структуры



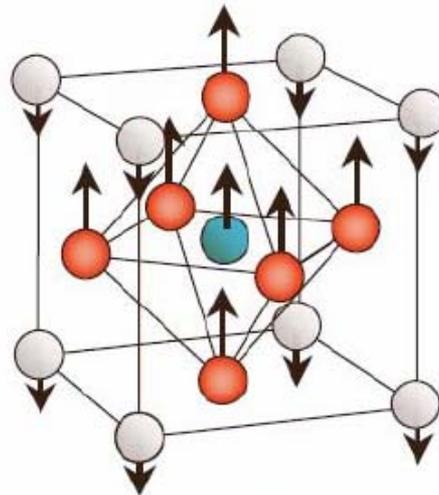
Колебательные моды в перовскитах



(a)

(a) Slater mode

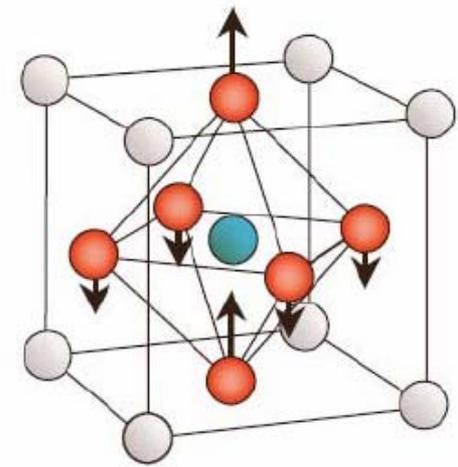
Ferroelectric soft mode
in non-Pb perovskites



(b)

(b) Last mode

Ferroelectric soft mode
in Pb-containing perovskites

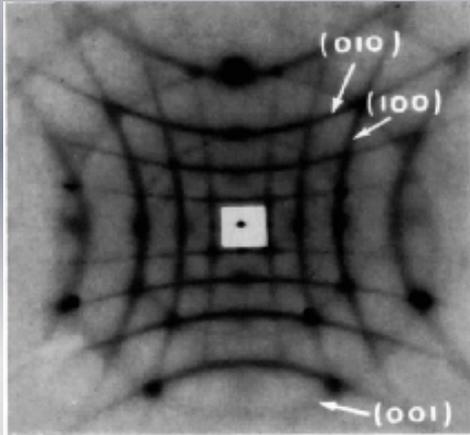


(c)

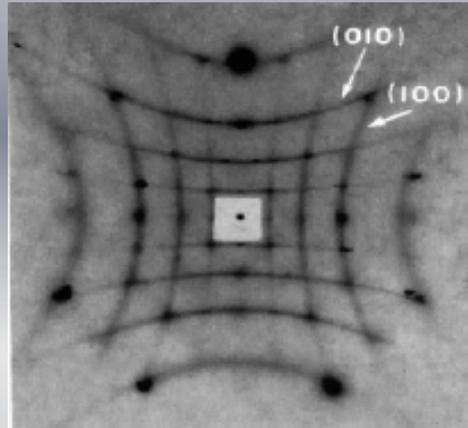
(c) Axe mode

Highest frequency

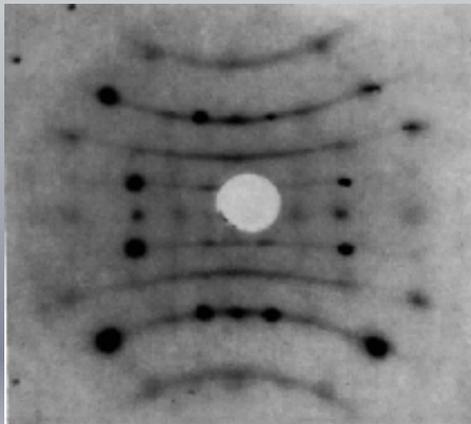
Диффузное (критическое) рассеяние BaTiO_3 KNbO_3



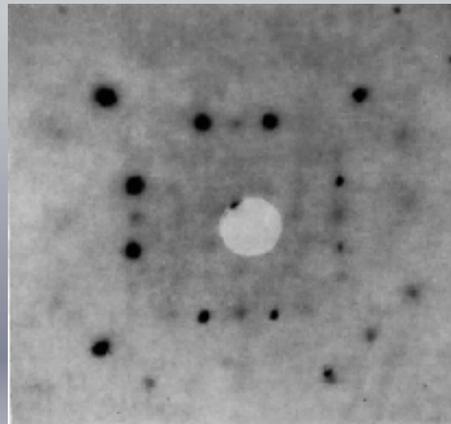
Cubic



Tetra.



Ortho.



Rhomb.

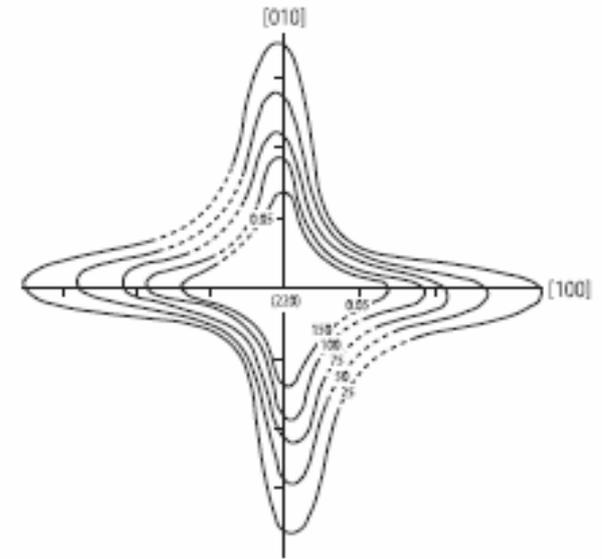


Fig. 1A-10-215. BaTiO_3 . Intensity distribution of the quasi-elastic scattering in q -space around (220) [69Yam]. $T = 137$ °C.

Критическое рассеяние

$$\left(\frac{d^2\sigma}{d\Sigma d\Omega}\right)_c^\pm =$$
$$= \frac{k' (2\pi)^2}{k 2v_0} \sum_{\tau} \sum_{\mathbf{q}^j} |F_j(\mathbf{q}, \mathbf{Q})|^2 \times$$
$$\times \frac{1}{1 - \exp(-\beta\omega)} \chi''(\mathbf{Q}, i\omega) \delta(\mathbf{Q} \mp \mathbf{q} - \tau)$$

$$F_j(\mathbf{q}, \mathbf{Q}) = \sum_k \frac{b_k}{M_k^{1/2}} \exp(i\mathbf{Q} \cdot \mathbf{r}_k) \exp(-W_k(\mathbf{Q})) [Q \cdot \mathbf{e}_k^j(q)]$$

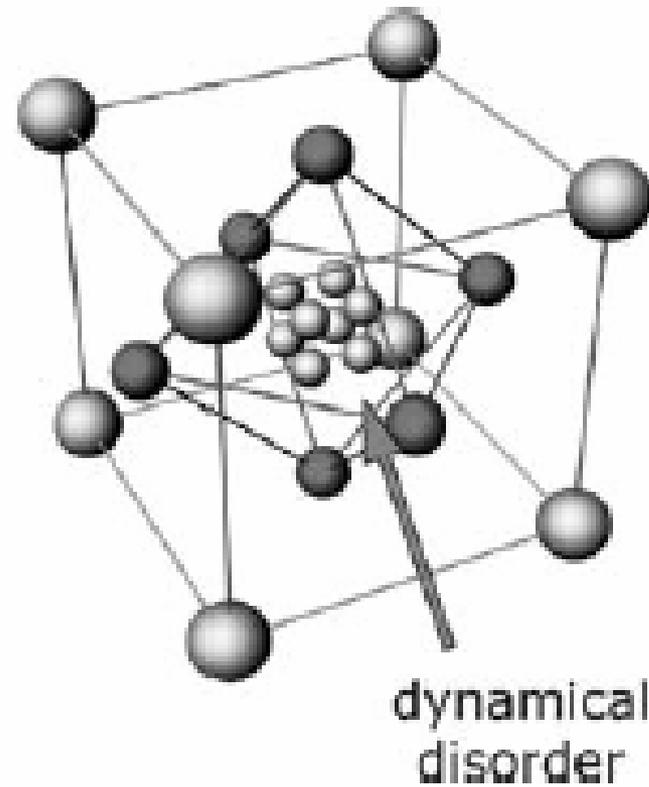
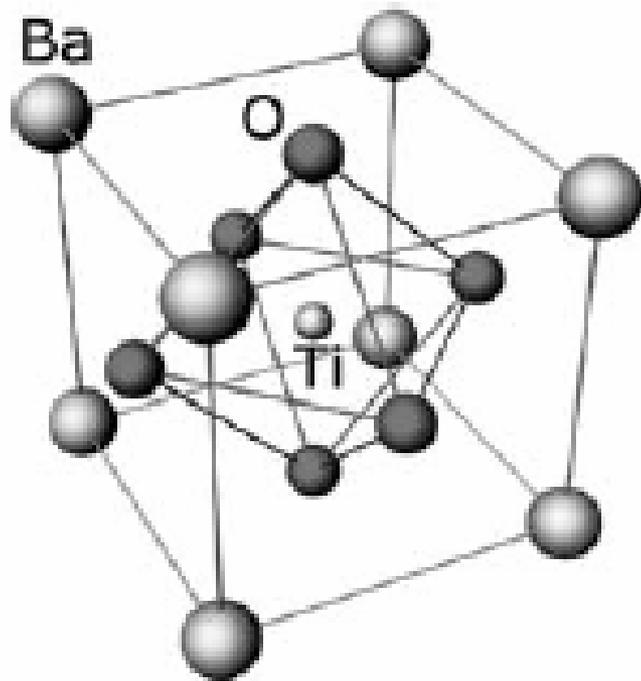
Критическое рассеяние

$$G(q) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\omega}{\omega} \text{Im} \chi_j(q, \omega) = \chi_j^0(q)$$

$$\omega^2 = \omega_0^2 + Dq^2 = \omega_0^2 \left(1 + \frac{q^2}{\kappa^2} \right)$$

$$I(Q) = |F(\vec{Q}, \vec{q}_j)|^2 \frac{k_B T}{q^2 + \kappa^2}$$

Смещение или порядок-беспорядок



Смещение или порядок-беспорядок

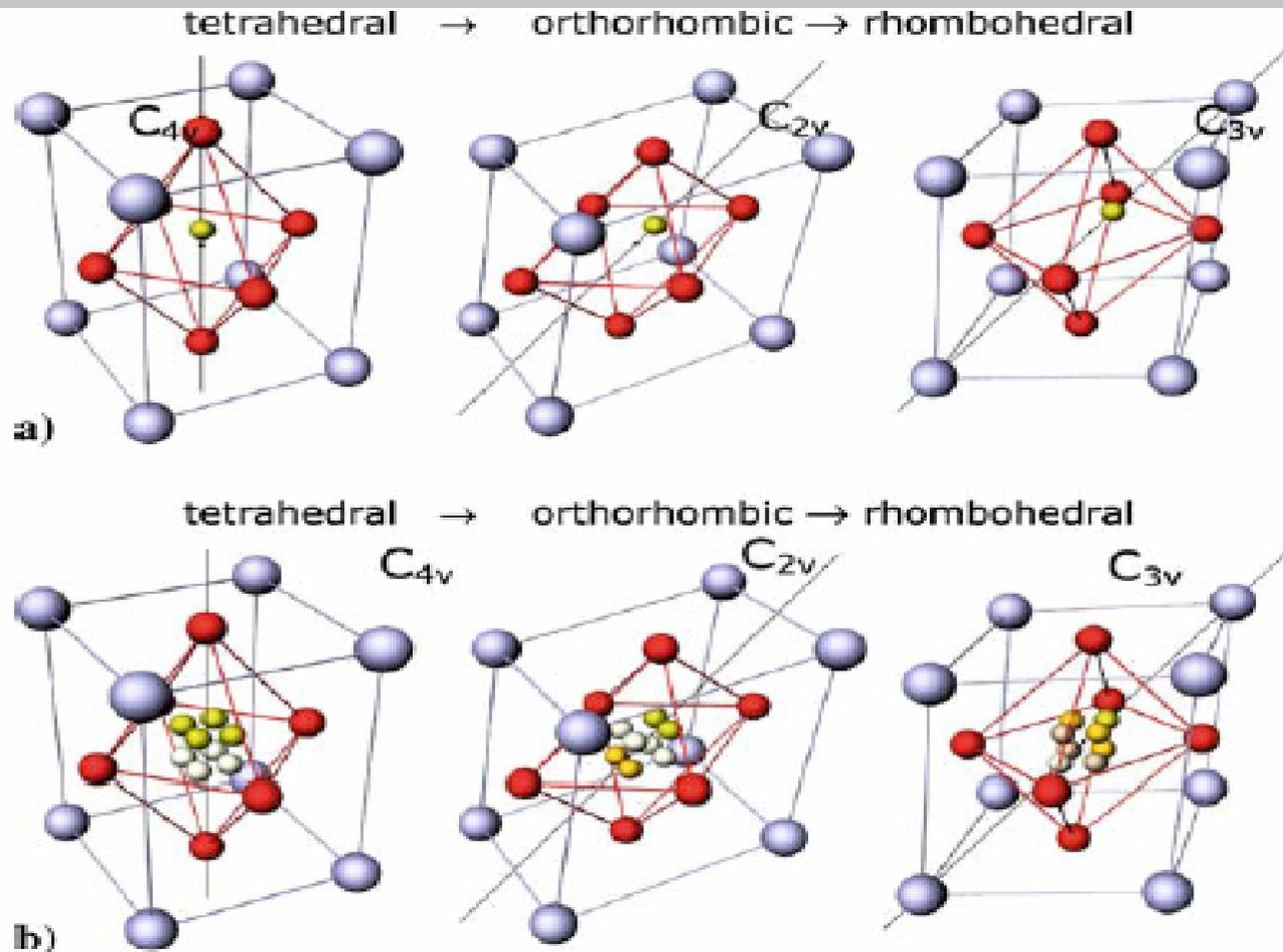
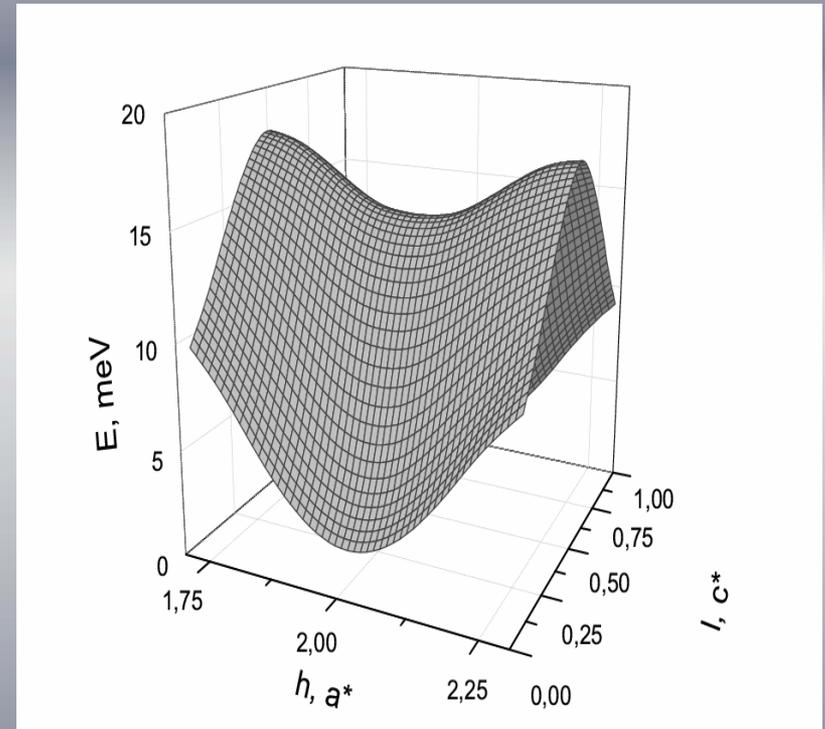
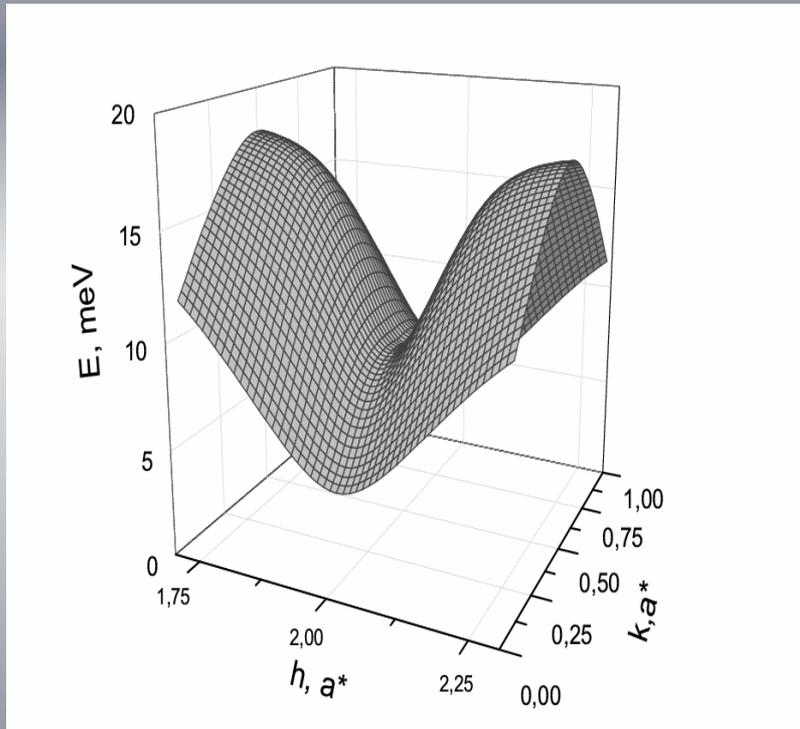


Fig.3 **a** Structural transitions in BaTiO_3 according to the displacive scenario involving the freezing of the soft TO lattice mode (Cochran 1960) [3]. **b** Structural transitions in BaTiO_3 according to the order-disorder scenario. Different Ti ion colors denote different occupancies (Chaves et al. 1976) [18]

TA phonons dispersion surfaces



In cubic phase deep valley for the phonons polarized along 3 major cubic axes
For Tetragonal along X & Y
For Orthorhombic along Y (**O(I)**) or Z (**O(II)**)

Динамический структурный анализ KTaO₃

$$F_j(\vec{q}\vec{Q}) = \sum_k \frac{b_k}{m_k} e^{-W_k} e^{i\vec{Q}\vec{R}_k} (\vec{Q}\vec{u}_k^j(\vec{q}))$$

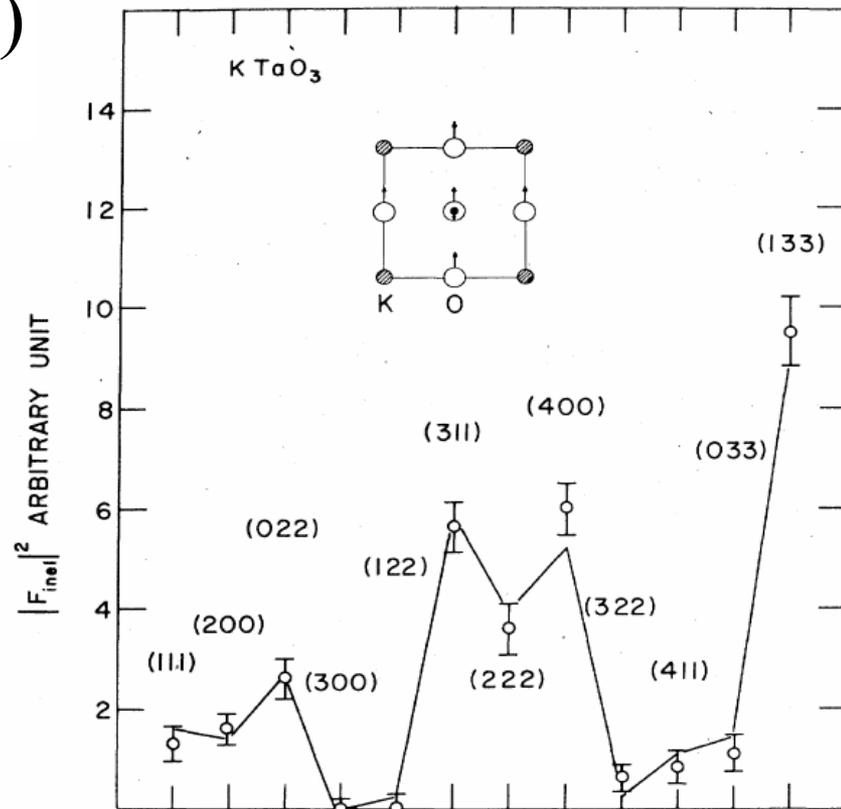


FIG. 12. Mode determination of ferroelectric TO phonon in KTaO₃, after Harada, Axe, and Shirane(1970). The solid line represents calculated values for the Slater mode as shown in the insert.

Смешивание мод, KNbO_3

$$F_j(\vec{q}\vec{Q}) = \sum_k \frac{b_k}{m_k} e^{-w_k} e^{i\vec{Q}\vec{R}_k} (\vec{Q}\vec{u}_k^j(\vec{q}))$$

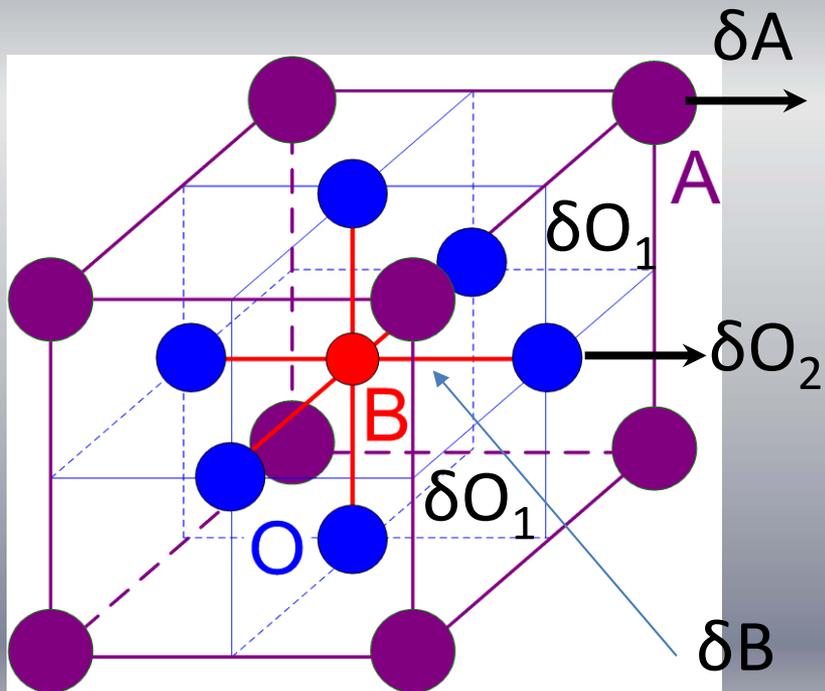
$Q=0.13$, TO

$$w_{\text{Nb}} = 0.007$$

$$w_{\text{K}} = 0.136$$

$$w_{\text{O}_1} = 0.080$$

$$w_{\text{O}_2} = 0.070$$



From R. Currat et al. J.Phys.C 7, 2521 (1974)

At $q=0$ we expect TO to be Slater mode, i.e. $\delta K \approx 0$

Смешивание мод, PbTiO_3

TABLE I. Atomic shifts in tetragonal PbTiO_3 in units of c . Model (II) assumes that the center of mass is not displaced. The notations, S_1 and S_2 , are used here in a somewhat different way from those in Ref. 11.

	(I)	(II) = $S_1 + S_2$	S_1	S_2
Pb	0	-0.024	0	-0.024
Ti	0.040	0.016	-0.036	0.052
O	0.112	0.088	0.036	0.052

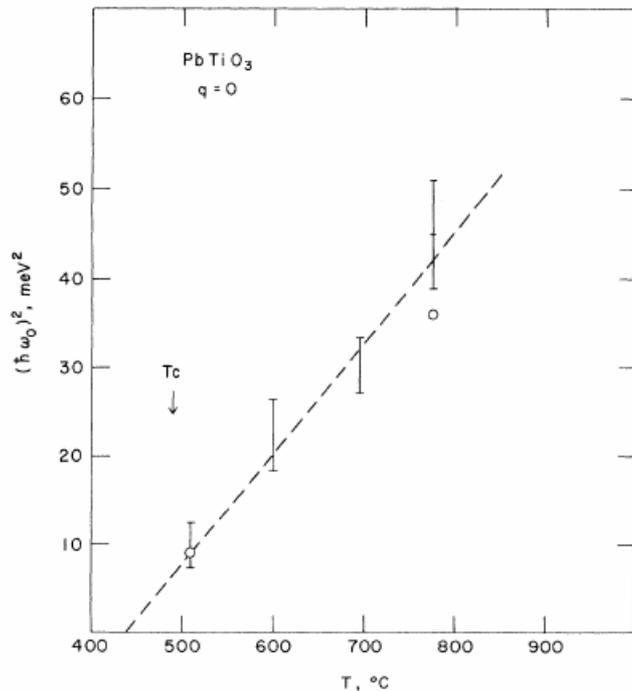
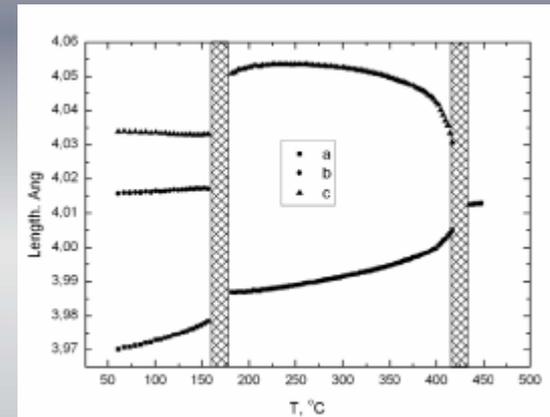
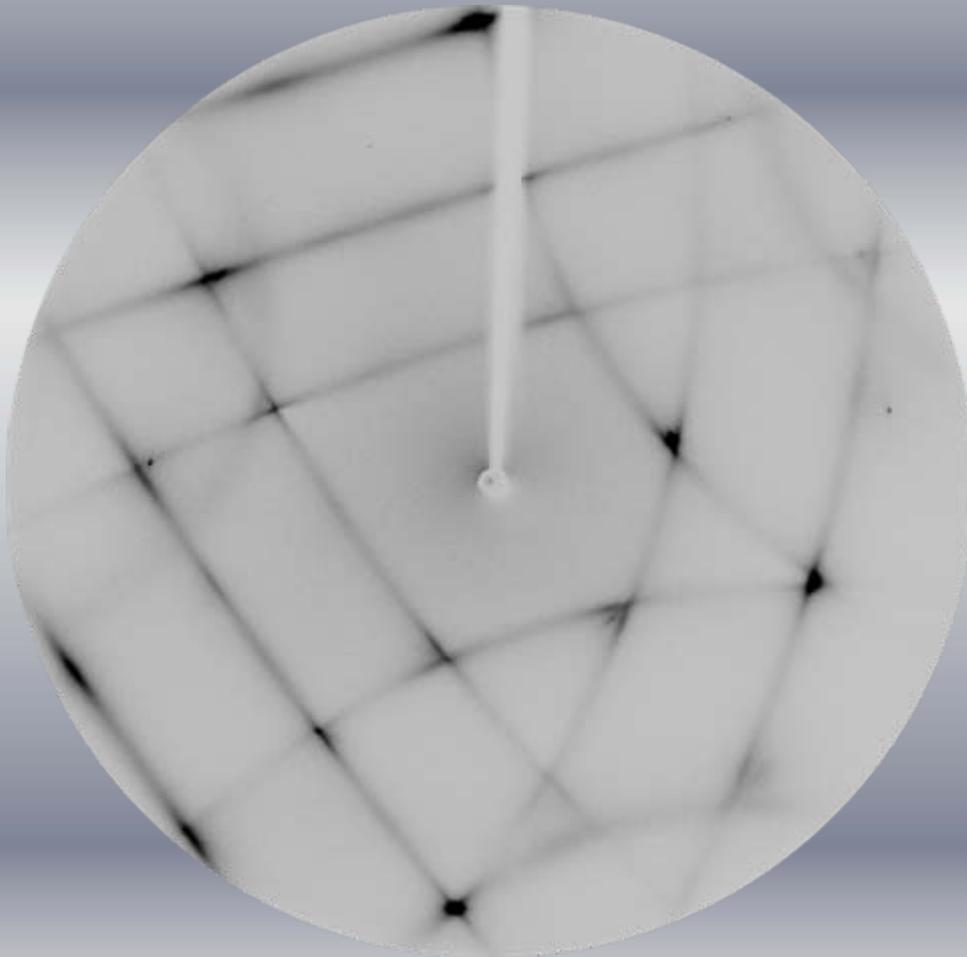


FIG. 3. Soft-mode energy $\hbar\omega_0$ as a function of temperature. Vertical lines represent extrapolation from finite q values as described in the text. Open circles are direct measurements of partially damped mode at $q=0$.

In PbTiO_3 eigenvectors – combination of Slater (S_1) and Last (S_2) modes

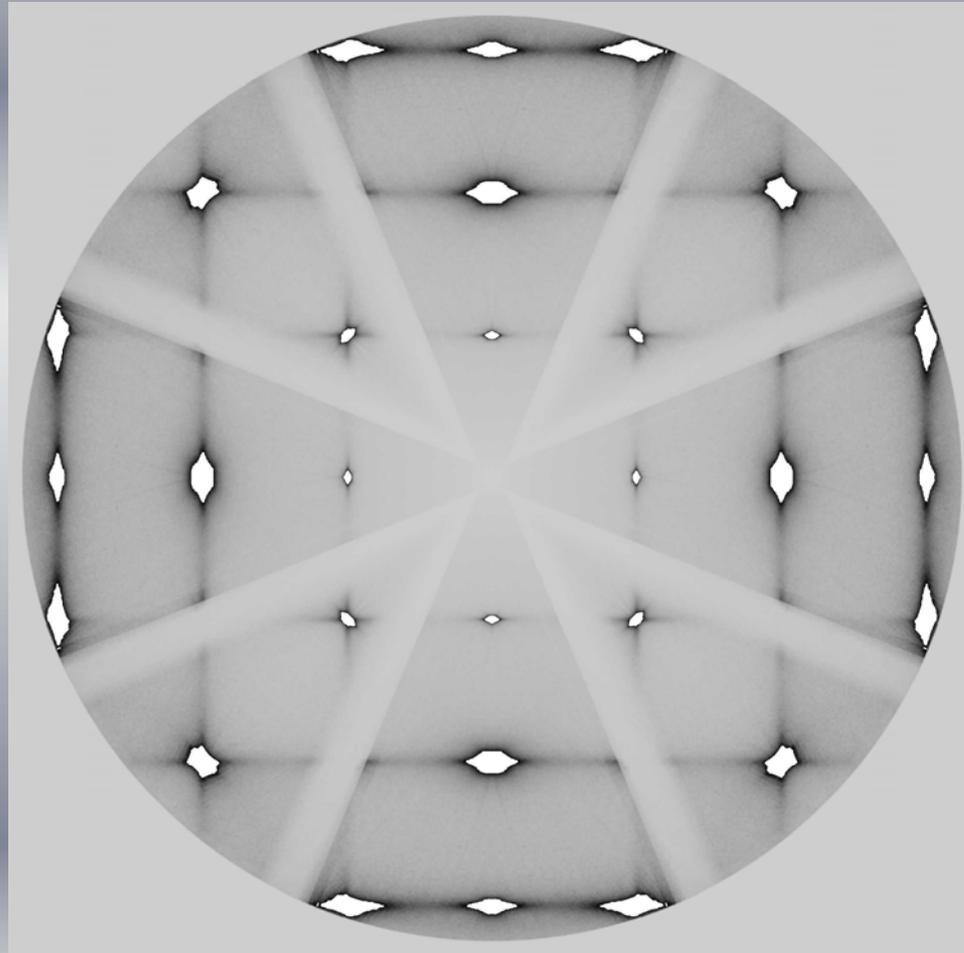
Diffuse scattering in perovskite



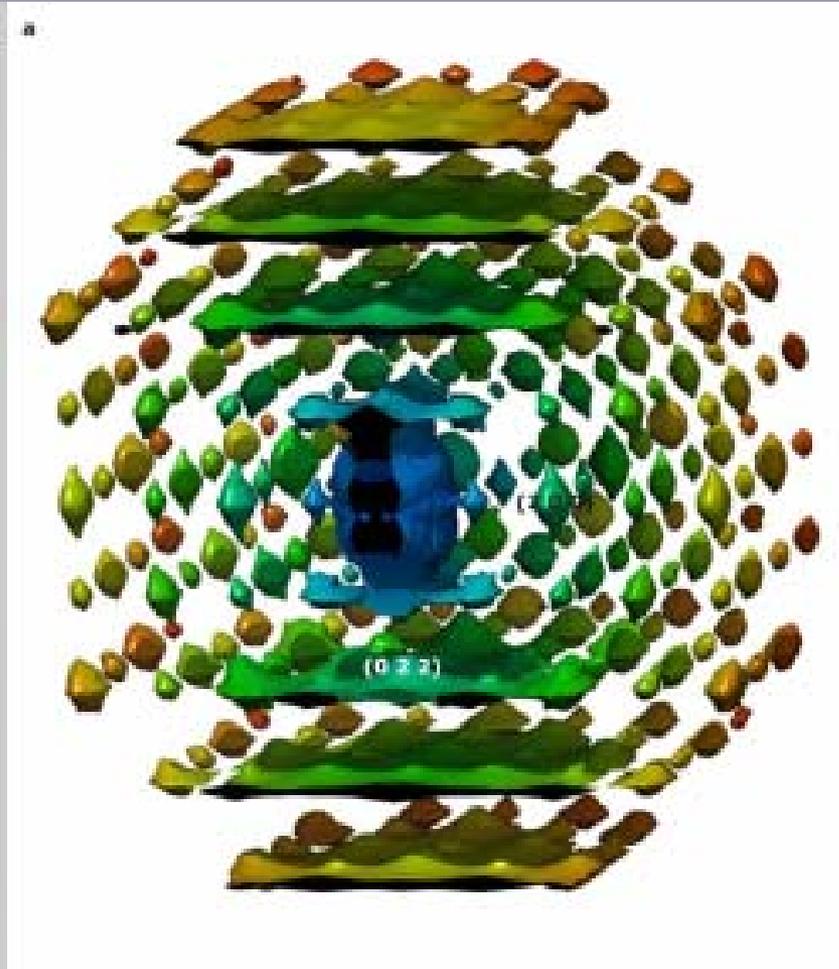
High temperature:

cubic phase, three families of diffuse planes normal to $\langle 100 \rangle$, $\langle 010 \rangle$, $\langle 001 \rangle$

KNN (hk0) crosssection



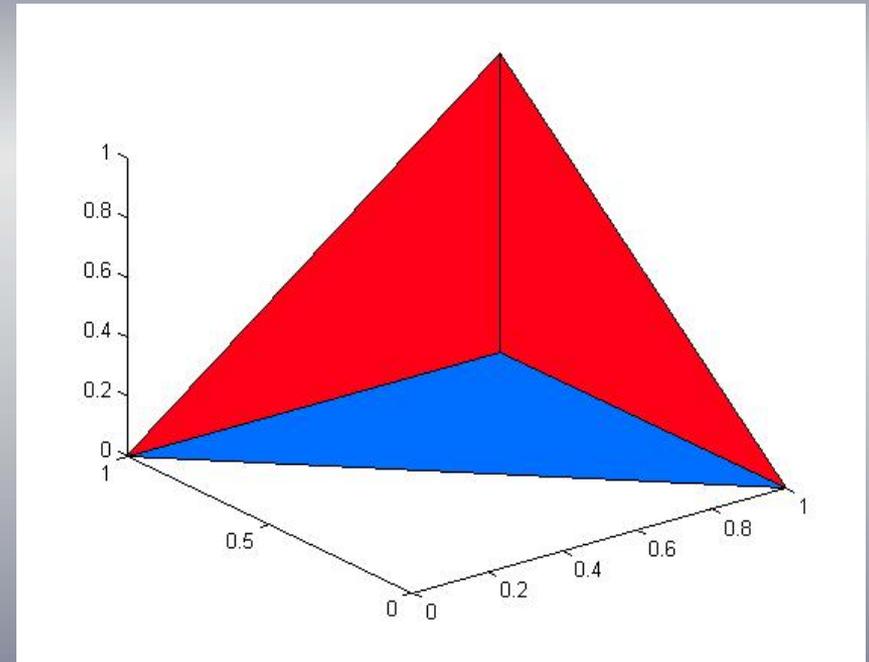
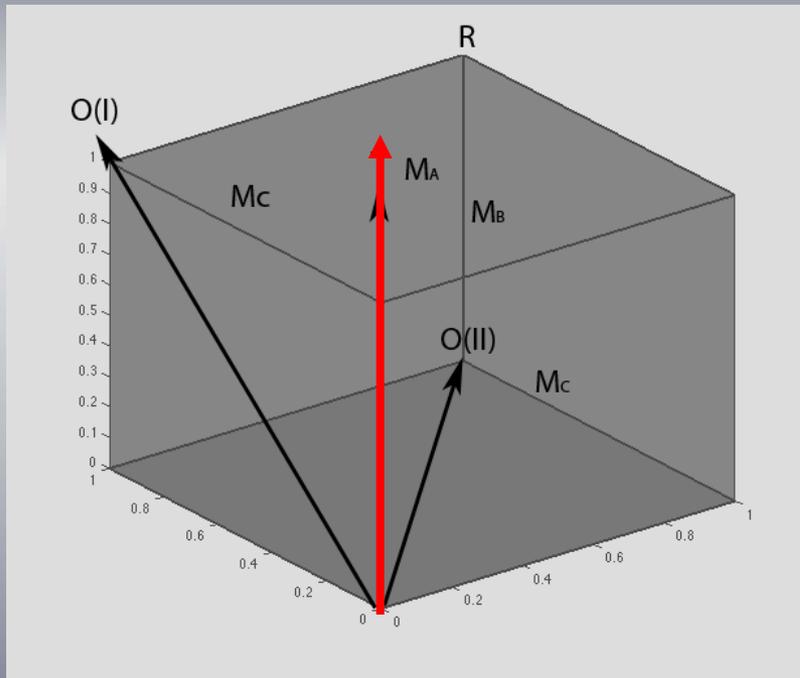
Diffuse scattering in perovskite Piezoelectrics



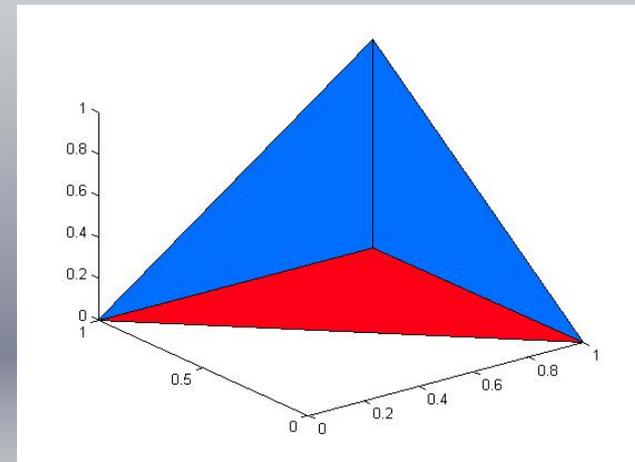
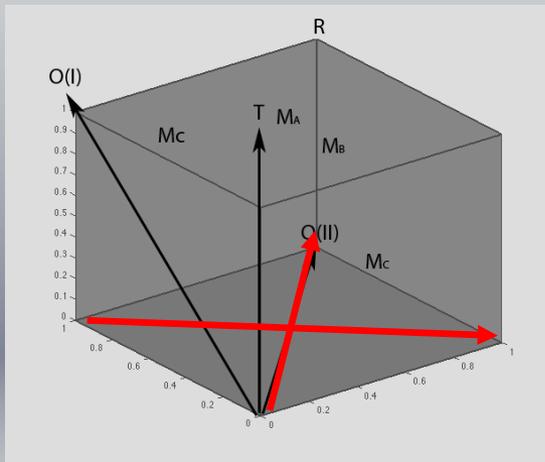
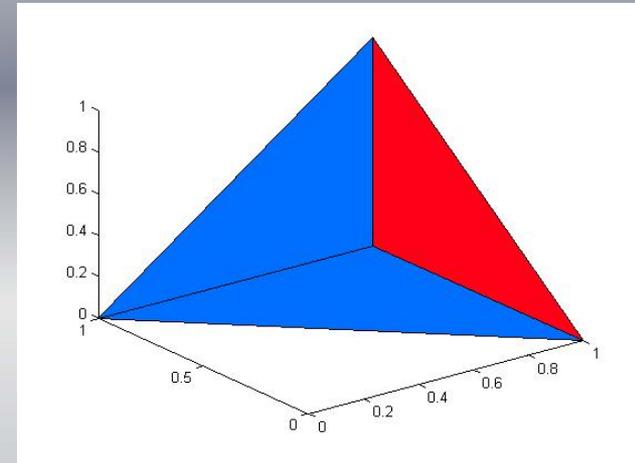
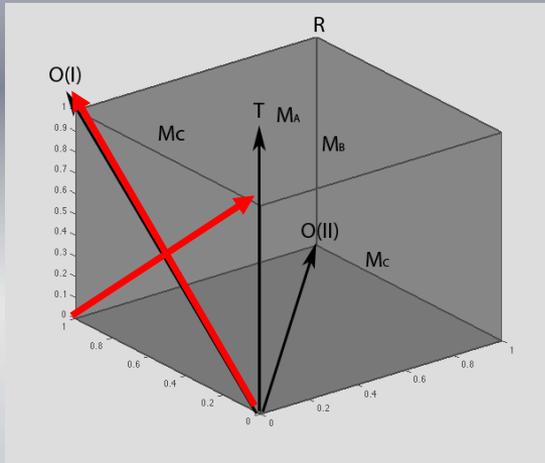
Room temperature:

orthorhombic phase one family
of diffuse planes normal to
 $\langle 100 \rangle$, $\langle 010 \rangle$, $\langle 001 \rangle$

Schematic picture of DS in tetragonal phase

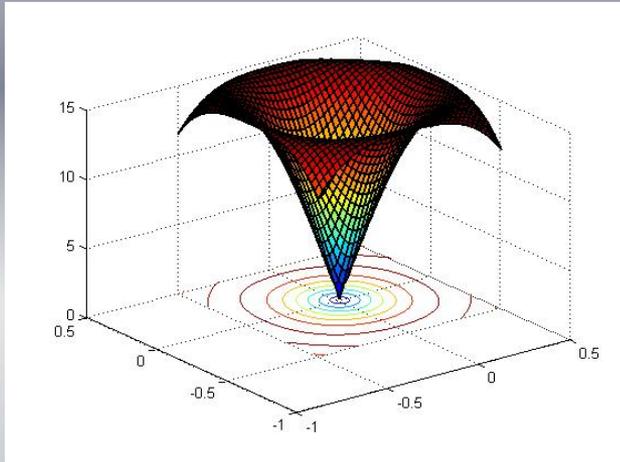


Schematic picture of DS in orthorhombic phase

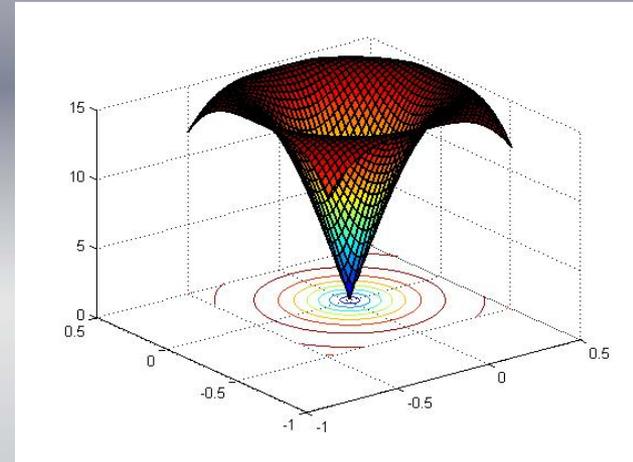


KNN uncoupled modes

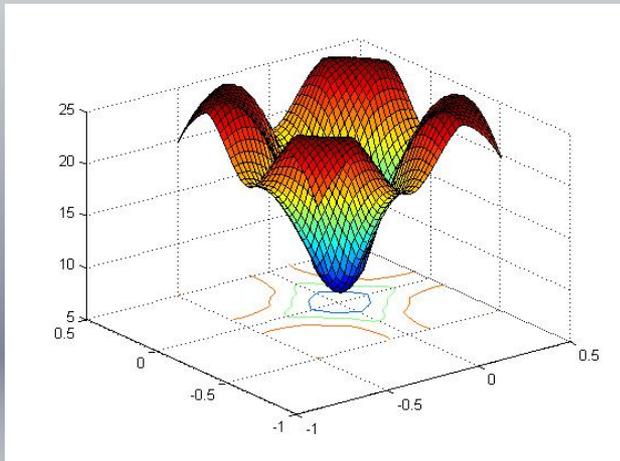
TA1



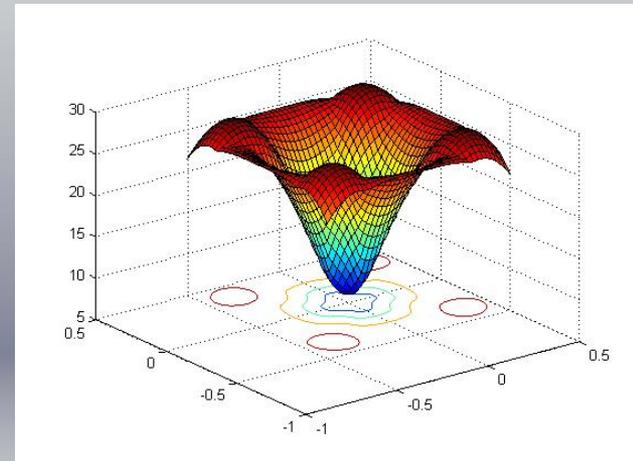
TA2



TO1

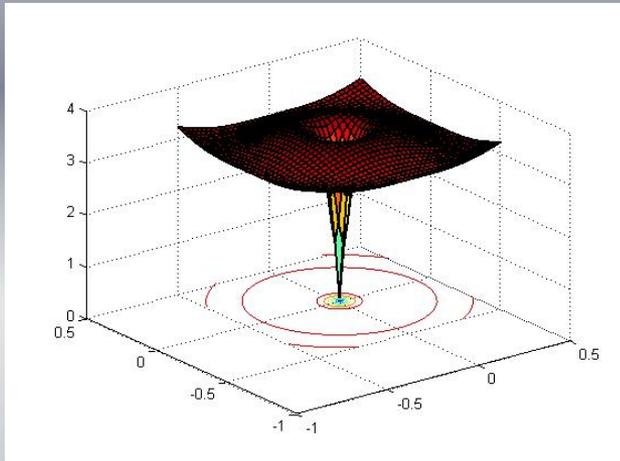


TO2

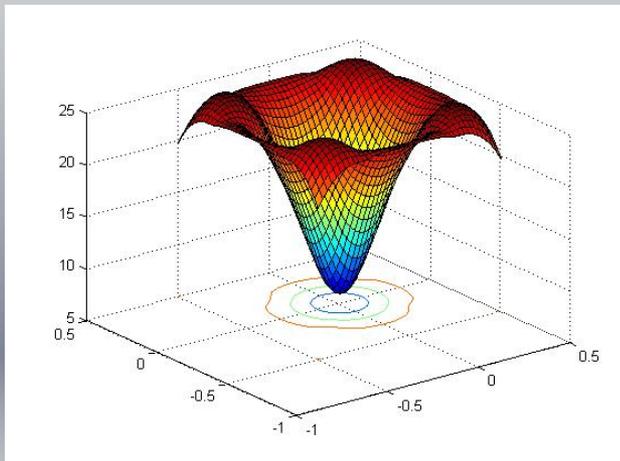
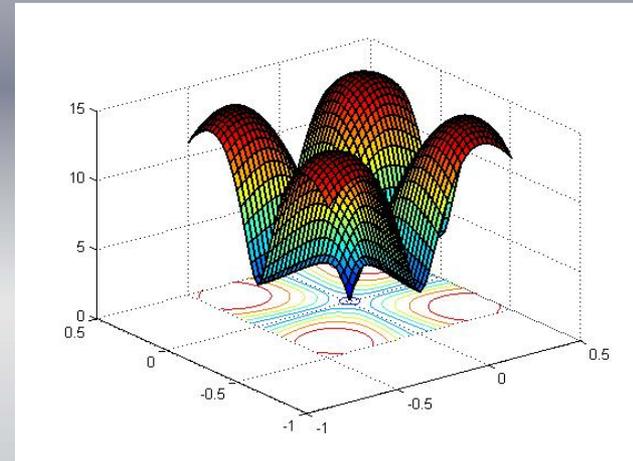


KNN coupled modes

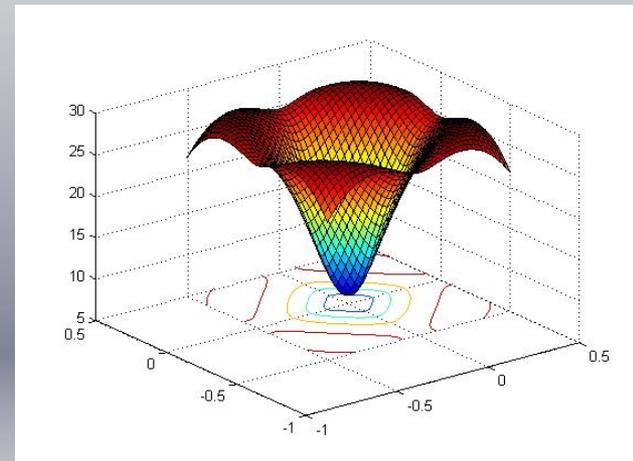
TA1



TA2

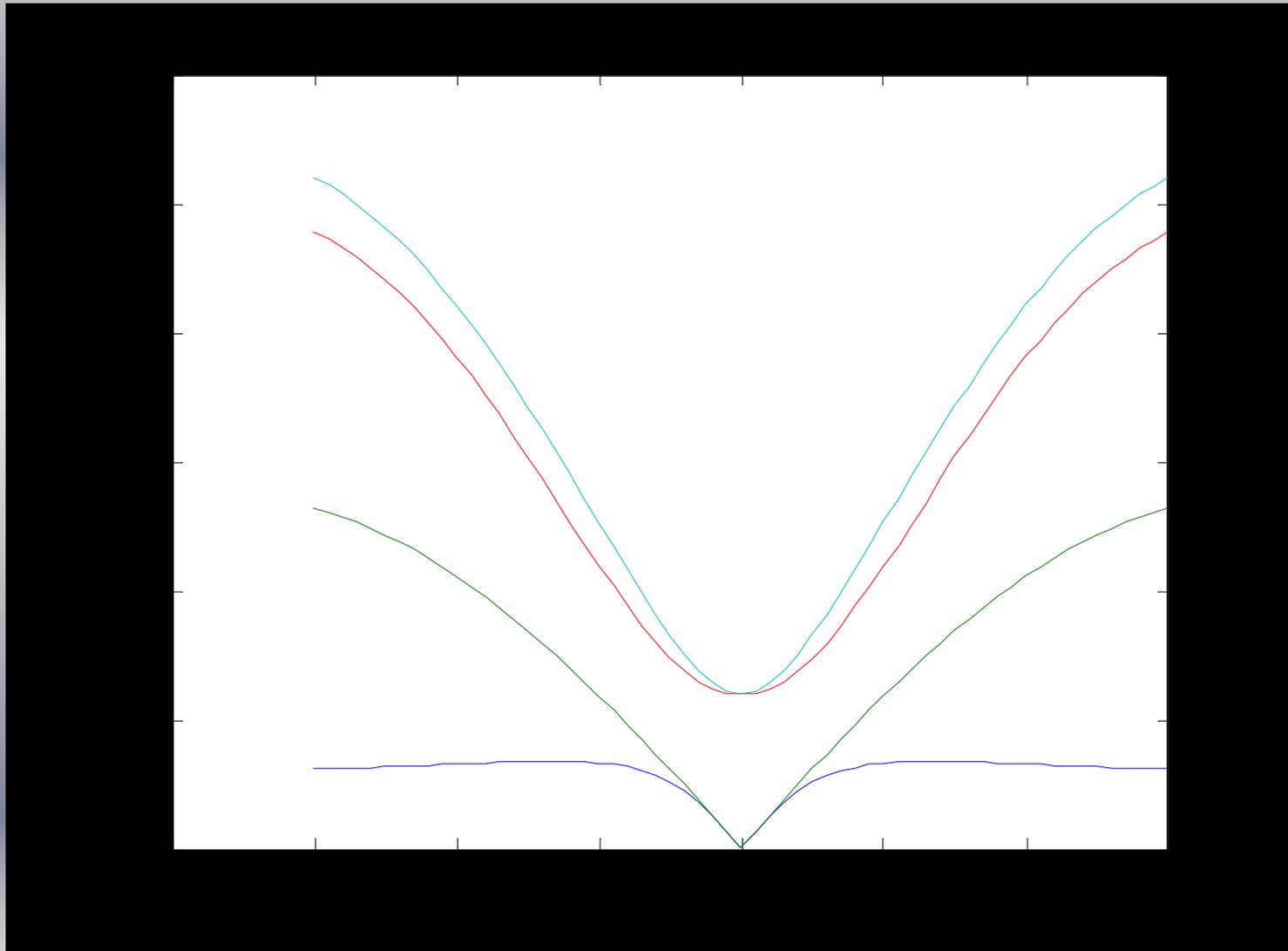


TO1



TO2

1-d along (110) (transverse modes only)



Антисегнетоэлектрик PbZrO_3

- For the first time reported by S. Roberts (J. Am. Cer. Soc. 33, 63 (1950)) as an analog of BaTiO_3
- First recognized as **not** being ferroelectric by G. Shirane (G. Shirane, E. Sawaguchi, A Takeda Phys. Rev. 80, 485 (1950))
- PZ first interpreted as ANTIFERROELECTRIC by G. Shirane (G. Shirane, E. Sawaguchi, Y. Takagi, Phys. Rev. 84, 476 (1954))
- First X-ray diffraction demonstration of the antiferroelectric order (E. Sawaguchi, H. Maniwa and S. Hoshino, Phys. Rev. 83, 1078 (1951))
- First theory of antiferroelectricity (C. Kittel, Phys. Rev. 82, 729 (1952)) based on private communications about WO_3

Dielectric studies

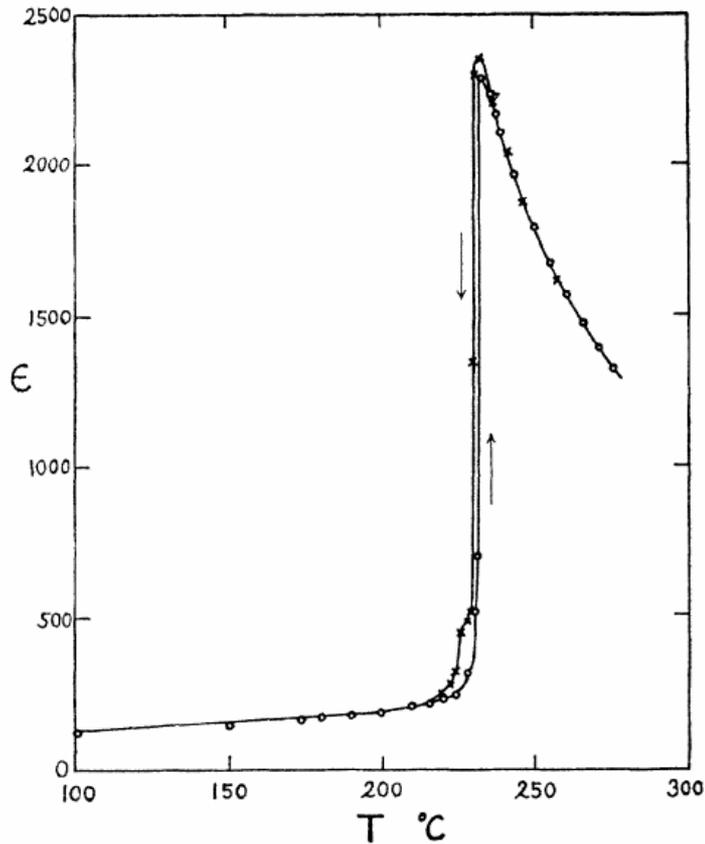


FIG. 2. Dielectric constant of lead zirconate at varying temperatures.

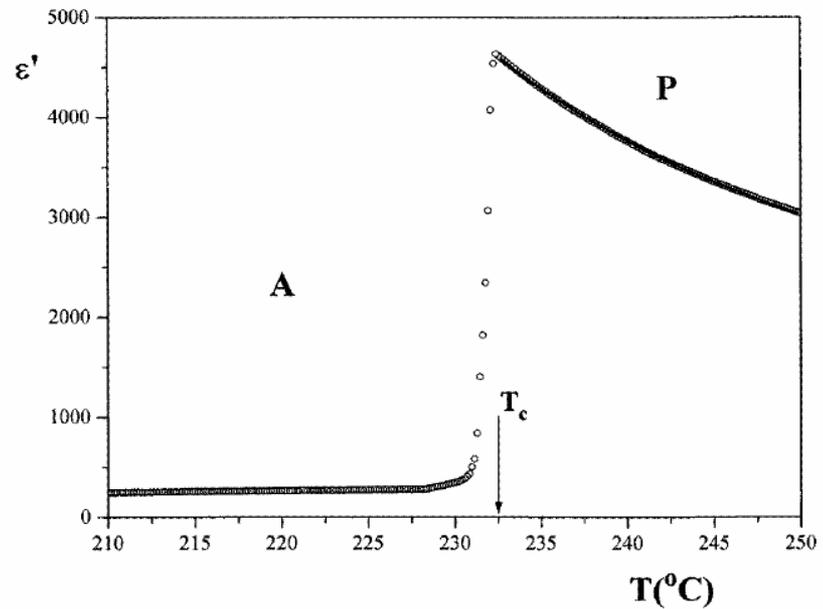
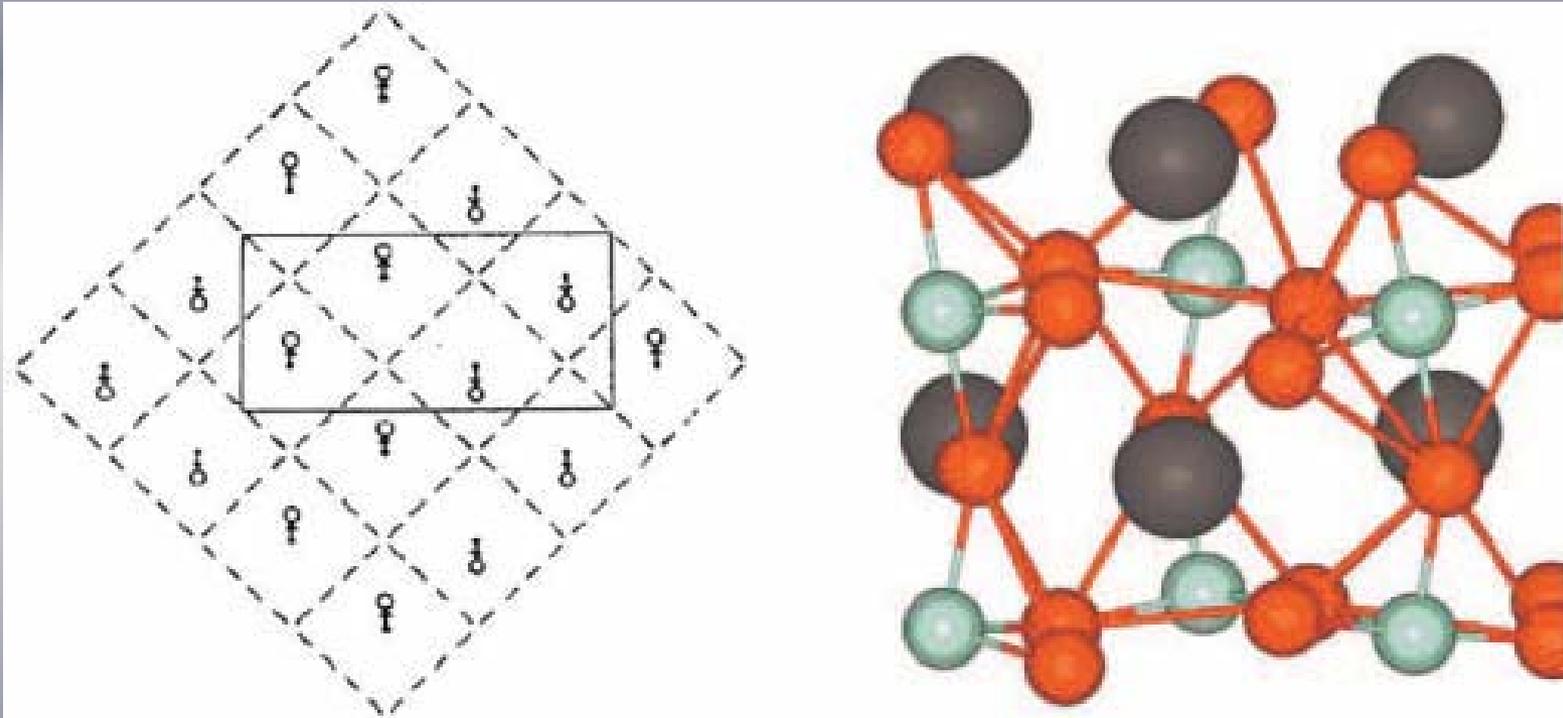


Figure 1. Temperature dependence of the real part ϵ' of the dielectric permittivity (10^3 Hz) in the vicinity of the phase transition from the paraelectric (P) to the antiferroelectric (A) phase in a PbZrO_3 single crystal. In the paraelectric phase the dielectric permittivity was fitted to equation (2) with $C = 1.54 \times 10^5 \pm 200$ and $T_0^* = 199.1 \pm 0.05$ (solid curve).

K. Roleder et al., C. Phys.: Cond. Mat. 8, 10669 (1996)

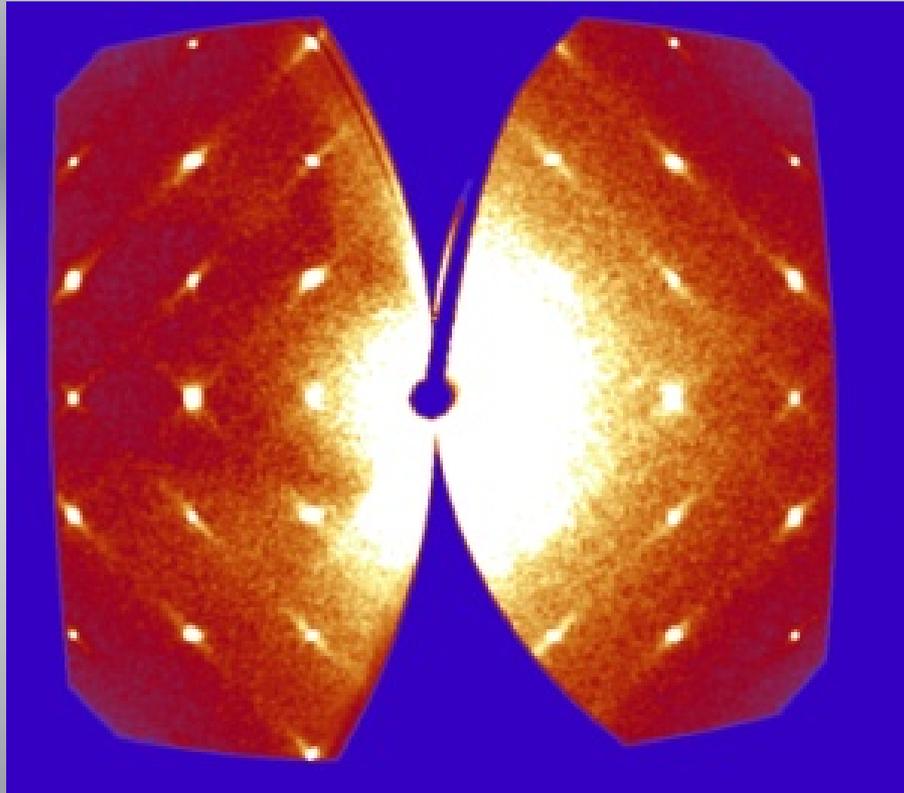
G. Shirane et al., 1951

Room temperature structure of PZ

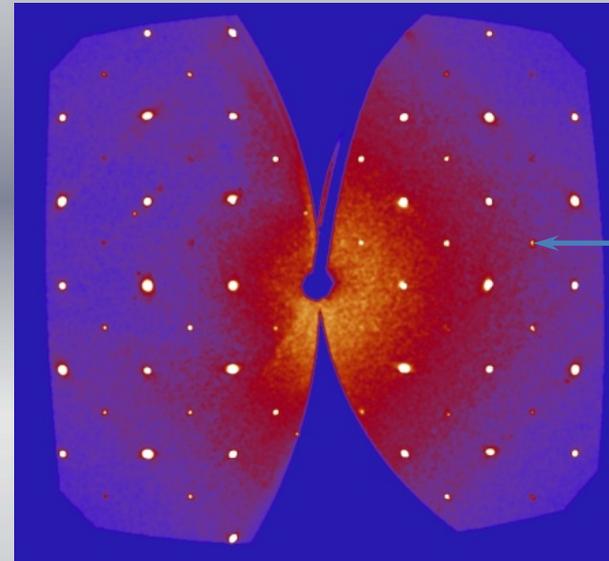


Combination of antiferroelectric displacements of Pb, described by $q_{\Sigma}=(\frac{1}{4} \frac{1}{4} 0)$
and oxygen octahedra tilts, described by $q_{R}=(\frac{1}{2} \frac{1}{2} \frac{1}{2})$

Bragg and diffuse scattering (hk0)

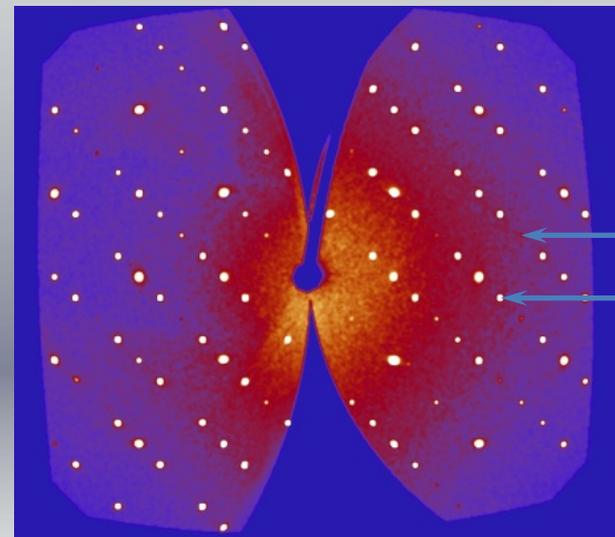


473K



462K

M

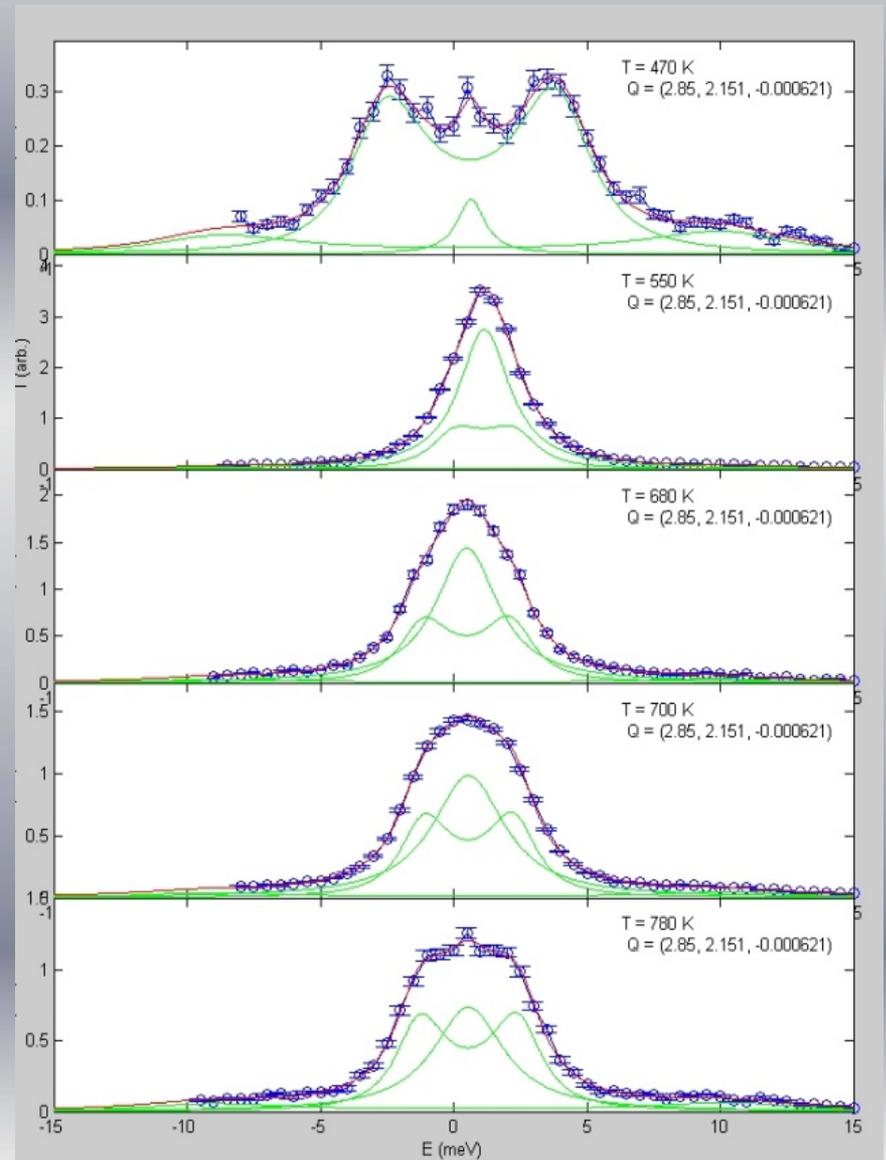
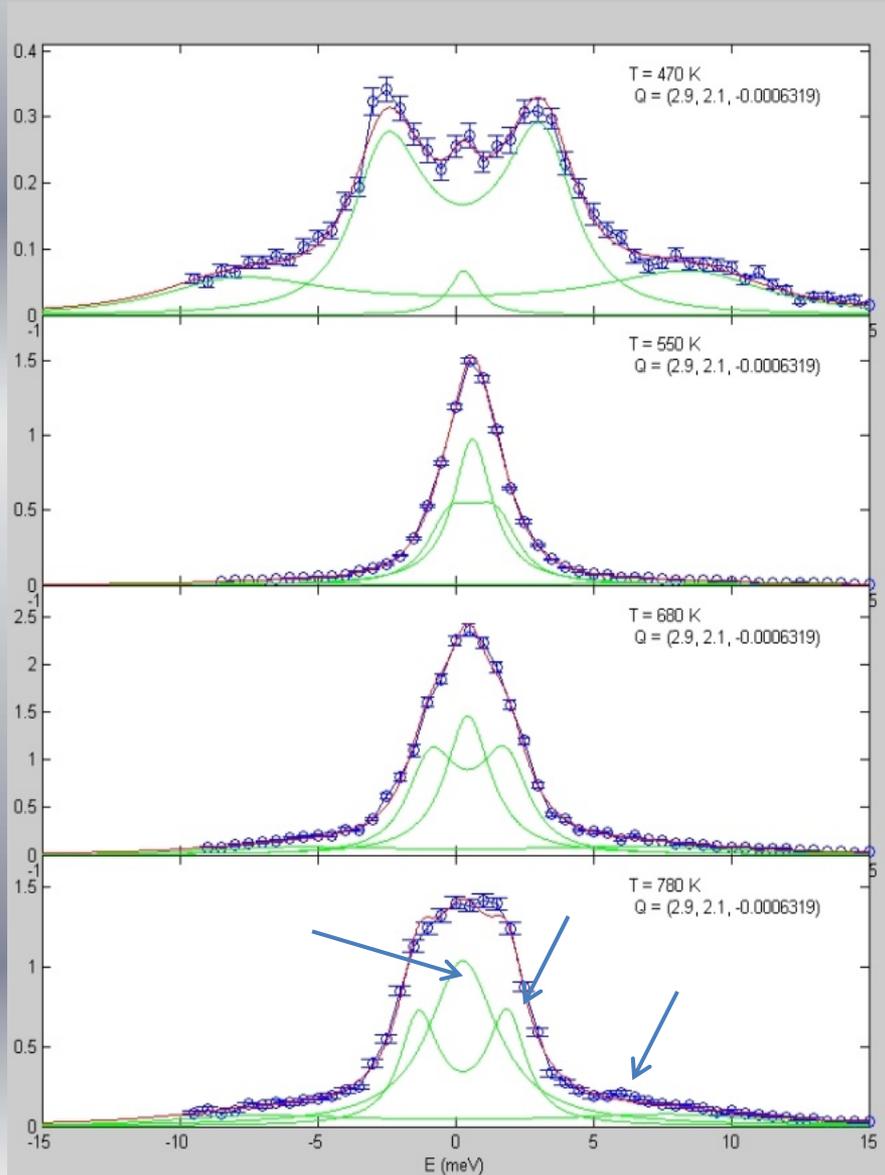


461K

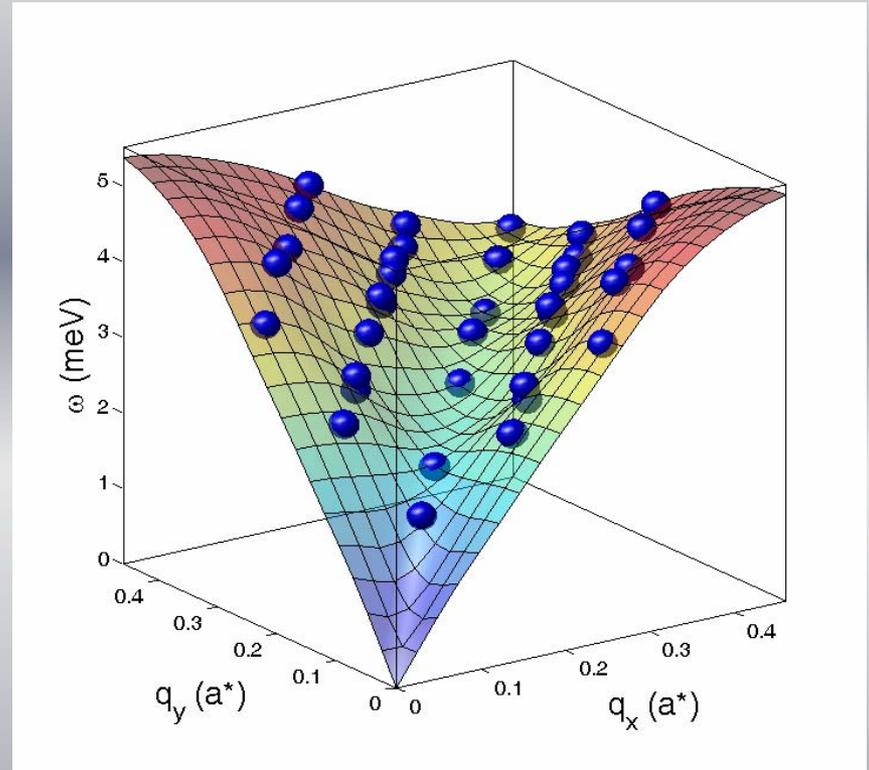
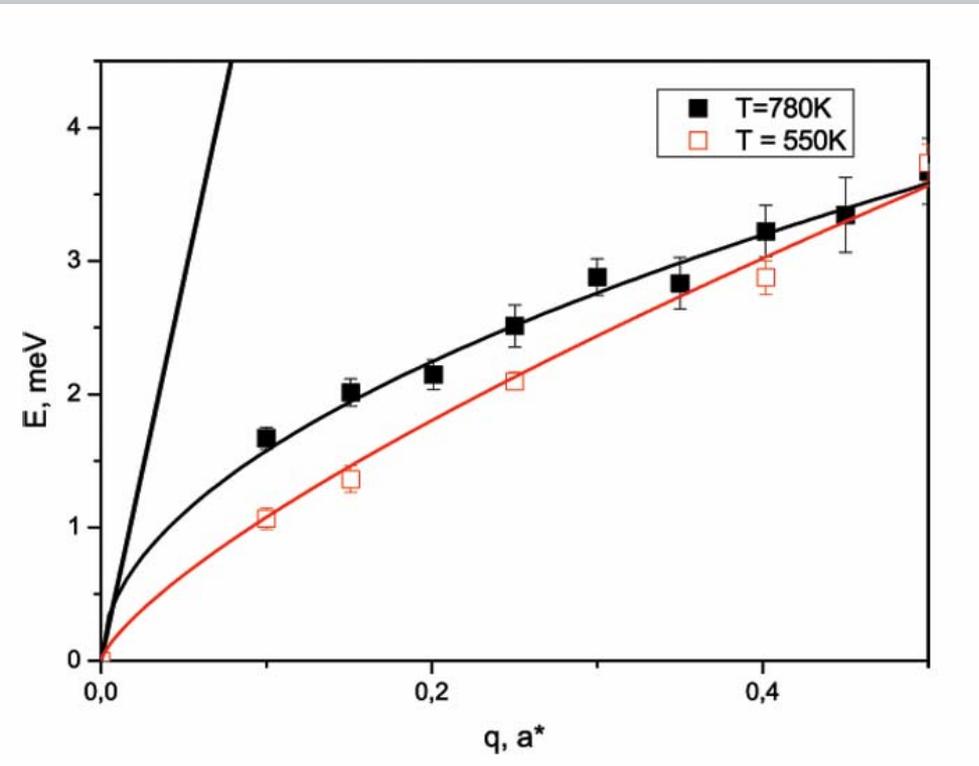
M

Σ

Phonon resonances q along (110), in-plane polarized PbZrO_3



Phonon dispersion in PZ

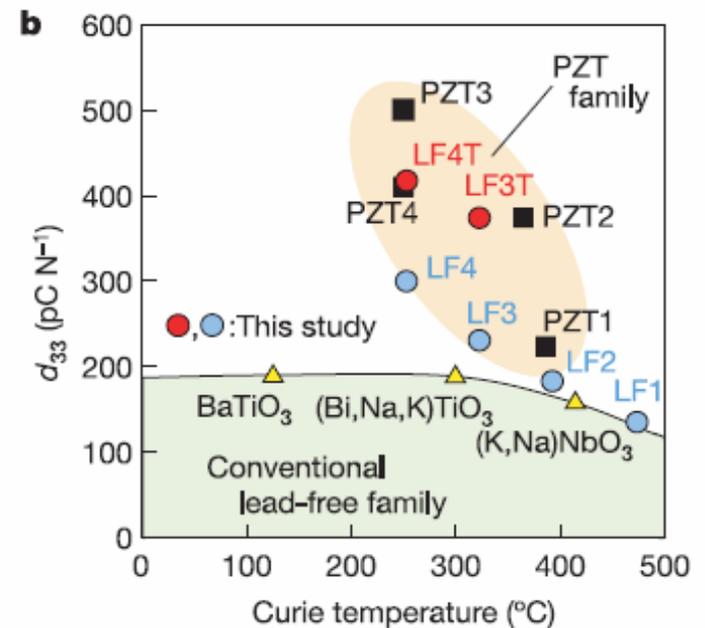
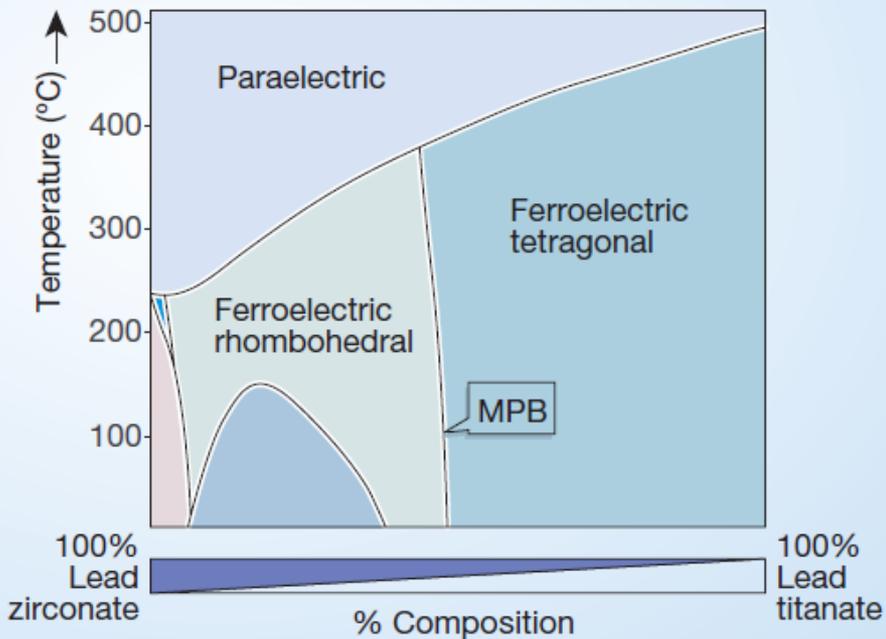


Природа антисегнетоэлектричества в PZT – межмодовое взаимодействие

Deep valley for $q \parallel (110)$ and in-plane polarized.

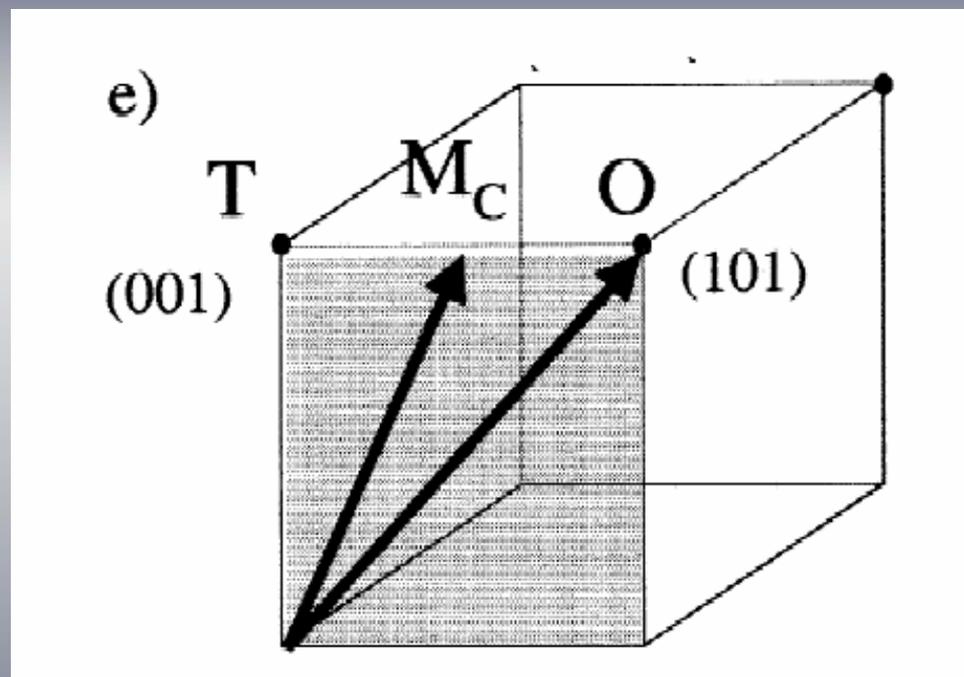
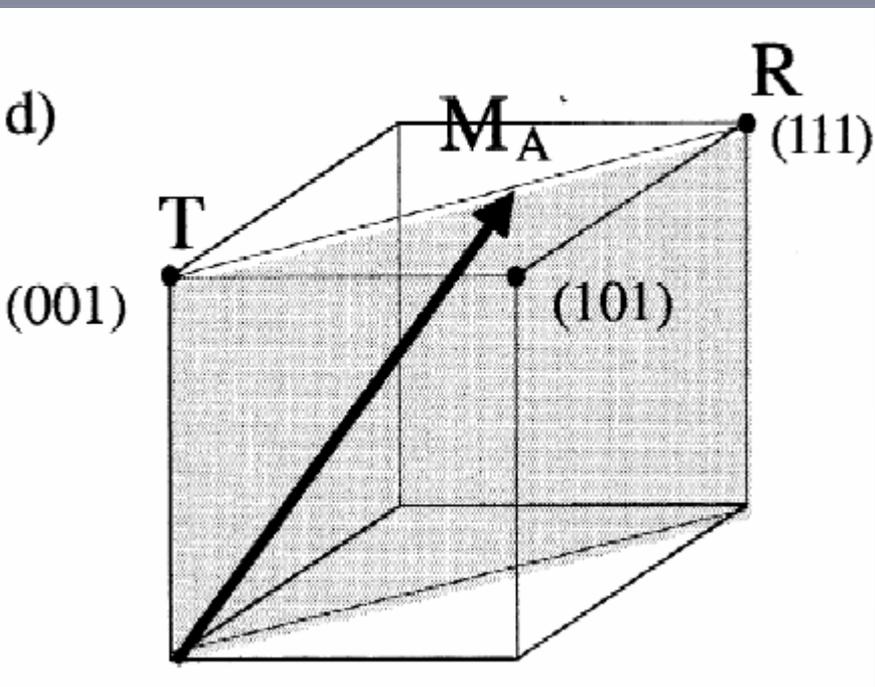
Смешанные перовскиты

- 1954 – Jaffe – открытие $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT, ЦТС)



Почему интересна промежуточная фаза

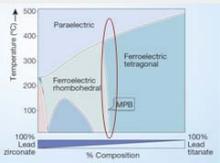
«Свободное вращение поляризации»



Структура PZT48

TABLE I. Structure refinement results for tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ at 325 K, space group $P4mm$, lattice parameters $a_t=4.0460(1)$ Å, $c_t=4.1394(1)$ Å. Fractional occupancies N for all atoms taken as unity except for Pb in model II, where $N=0.25$. Agreement factors, R_{wp} , R_{F^2} , and χ^2 are defined in Ref. 33.

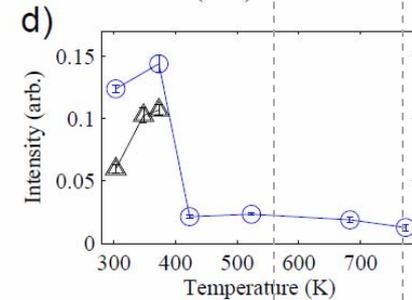
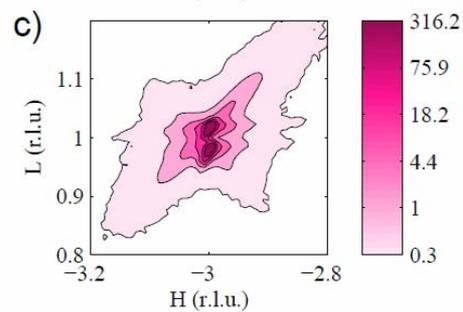
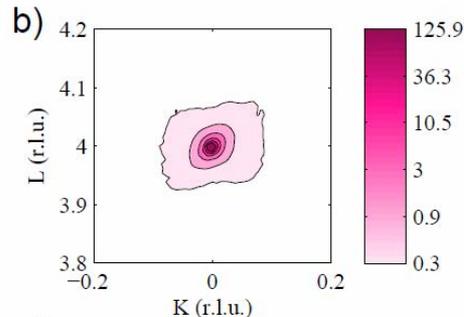
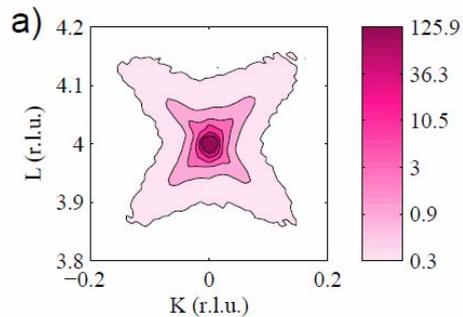
	Model I anisotropic lead temperature factors				Model II local $\langle 110 \rangle$ lead shifts			
	x	y	z	$U(\text{Å}^2)$	x	y	z	$U_{\text{iso}}(\text{Å}^2)$
Pb	0	0	0	$U_{11}=0.0319(4)$ $U_{33}=0.0127(4)$	0.0328(5)	0.0328(5)	0	0.0127(4)
Zr/Ti	0.5	0.5	0.4517(7)	$U_{\text{iso}}=0.0052(6)$	0.5	0.5	0.4509(7)	0.0041(6)
O(1)	0.5	0.5	-0.1027(28)	$U_{\text{iso}}=0.0061(34)$	0.5	0.5	-0.1027(28)	0.0072(35)
O(2)	0.5	0	0.3785(24)	$U_{\text{iso}}=0.0198(30)$	0.5	0	0.3786(24)	0.0197(30)
R_{wp}	4.00%				3.99%			
R_{F^2}	6.11%				6.04%			
χ^2	11.4				11.3			



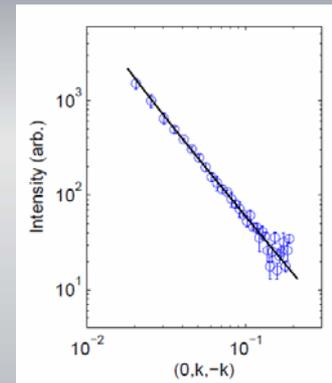
Diffuse scattering in PZT

Room temperature

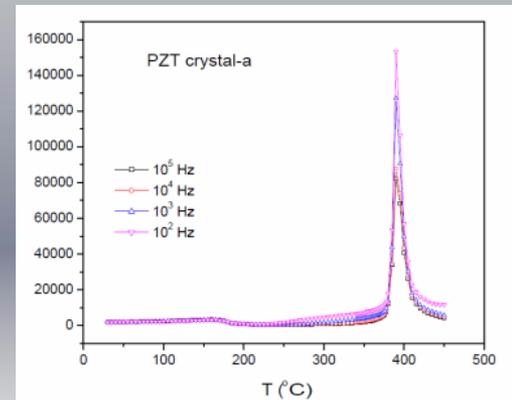
High temperatures



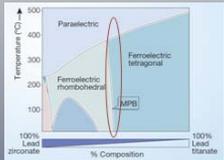
Scattering law $I = q^{-2}$



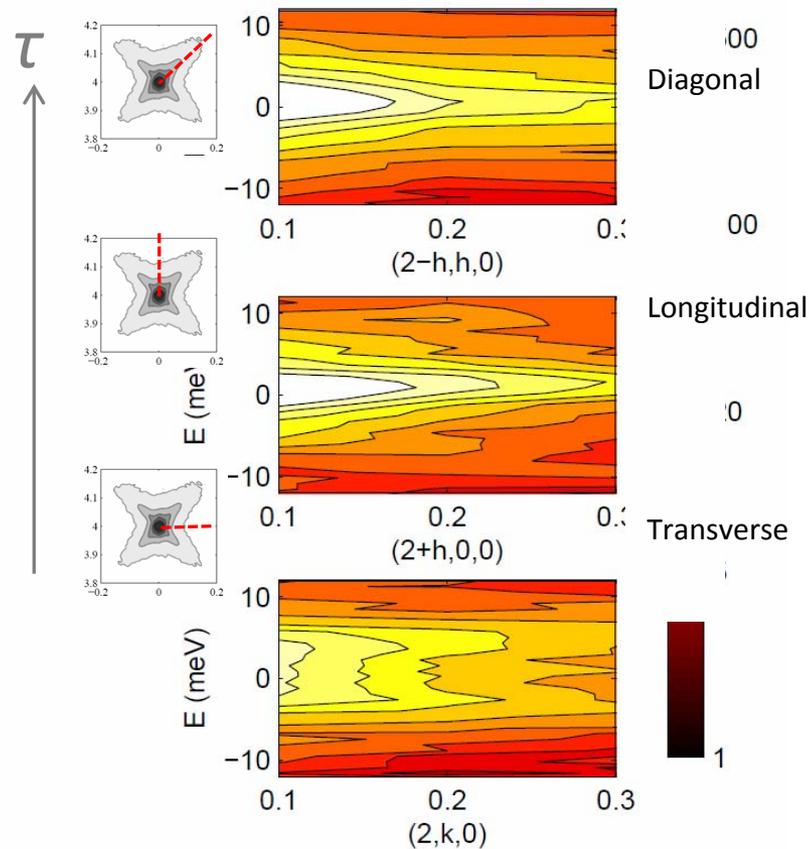
Dielectric constant



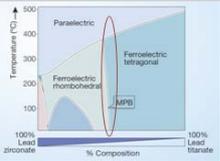
Inelastic scattering in PZT



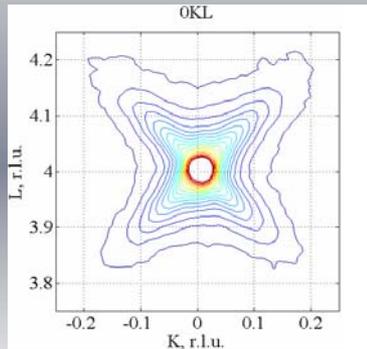
PZT @ ID28 @ ESRF



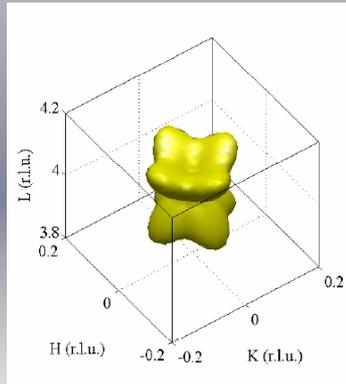
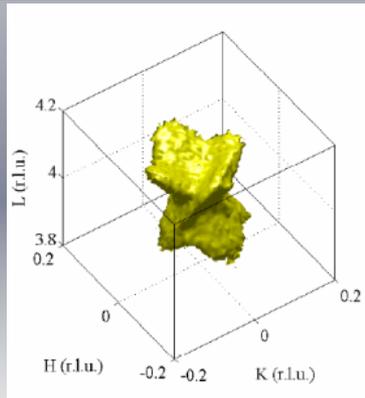
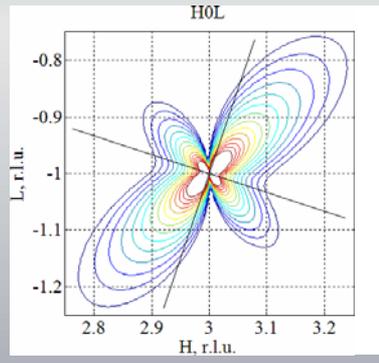
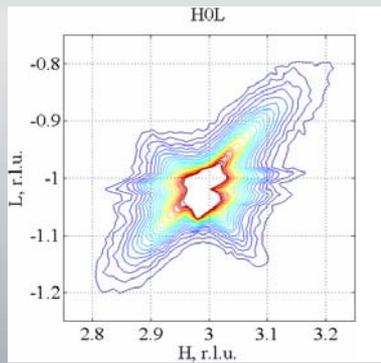
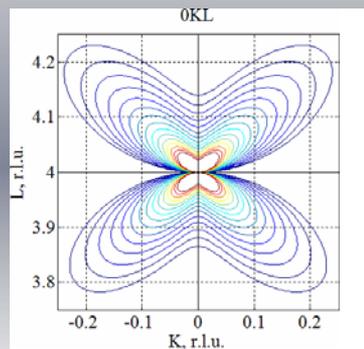
Huang scattering in PZT



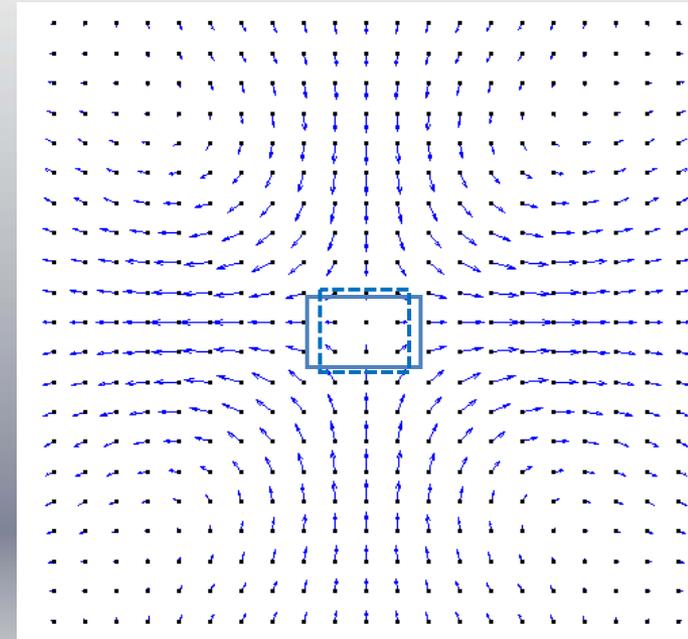
Experiment



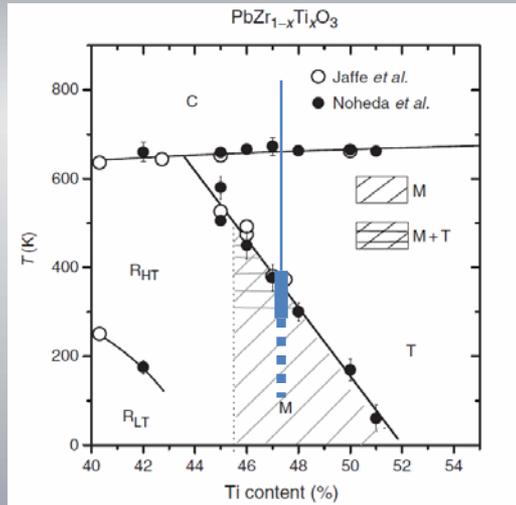
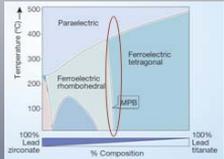
Calculations



Atomic displacements due to volume-conserving tetragonal defects



Неоднородность PZT вблизи МРВ



1. Morphotropic PZT single crystals have strong anisotropic diffuse scattering below MPB.
2. DS evidences for essential structural heterogeneity in PZT single crystals.
3. Structural heterogeneity is realized by particles of tetragonal phase remaining in the host, probably monoclinic, phase below morphotropic phase boundary.

РЕЛАКСОРЫ

РЕЛАКСОРЫ

(В 2012 ГОДУ ~ 1700 ПУБЛИКАЦИЙ)

Cubic:

1. $\text{PbB}'_{1/3}\text{B}''_{2/3}\text{O}_3$
 $\text{B}'=\text{Mg, Zn}; \text{B}''=\text{Nb, Ta}$ $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN)
2. $\text{PbB}'_{1/2}\text{B}''_{1/2}\text{O}_3$
 $\text{B}'=\text{In, Sc}; \text{B}''=\text{Nb, Ta}$
3. $\text{A}'_{1/2}\text{A}''_{1/2}\text{BO}_3$
 $\text{Na}'_{1/2}\text{Bi}''_{1/2}\text{TiO}_3$
4. Lead-Free Relaxors

Uniaxial

1. $\text{Sr}'_{1-x}\text{Ba}'_x\text{Nb}_2\text{O}_6$

Polymeric Relaxors

Диэлектрическая проницаемость

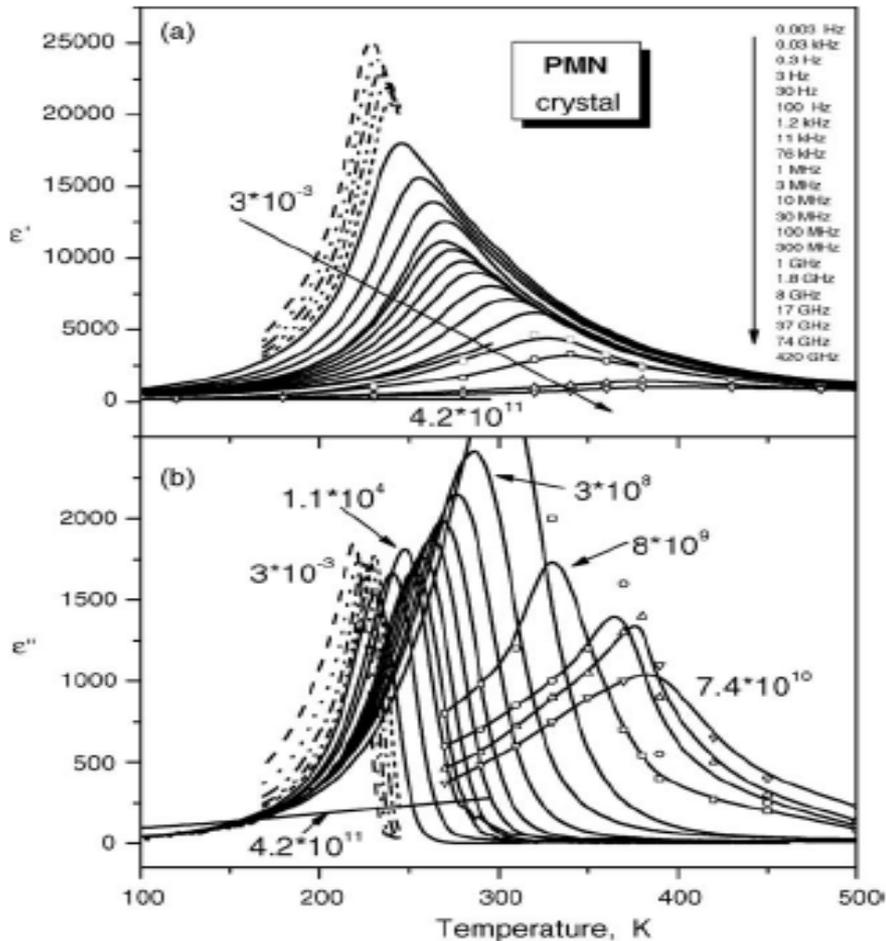


Fig. 1. Temperature dependences of dielectric permittivity ϵ' and loss ϵ'' of PMN single crystal at various frequencies. The numbers near curves denote the frequency in Hz.

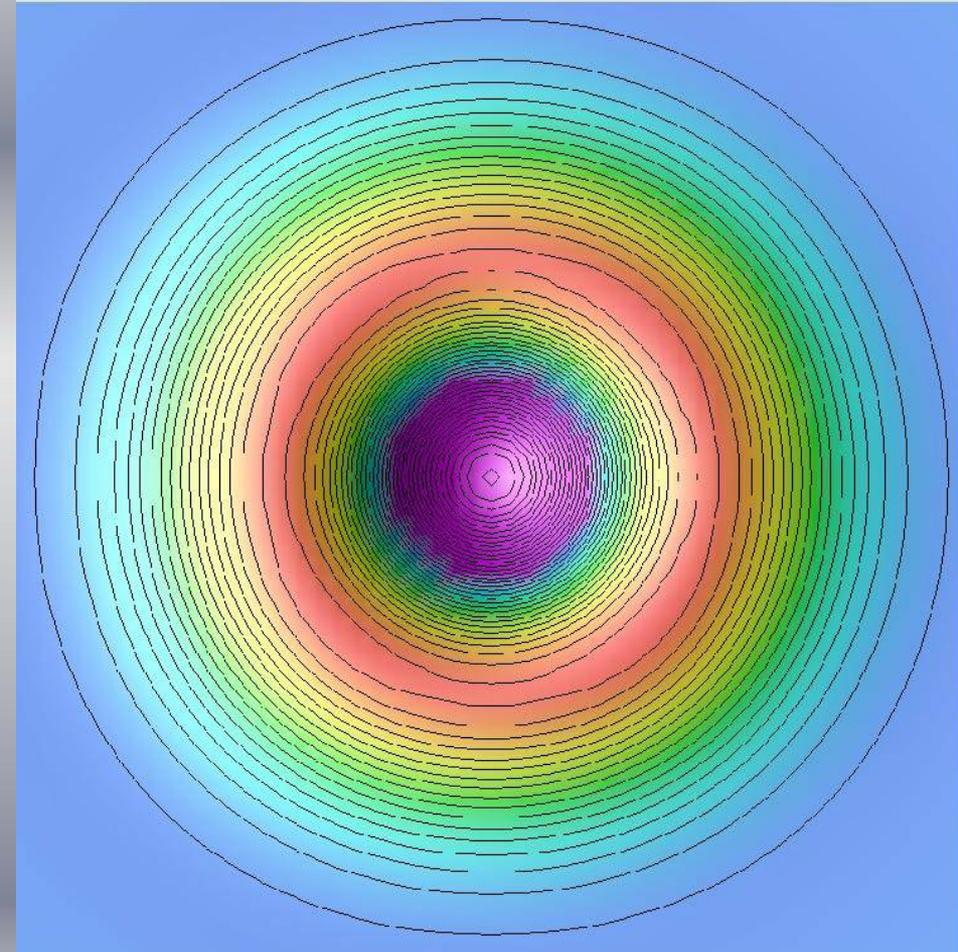
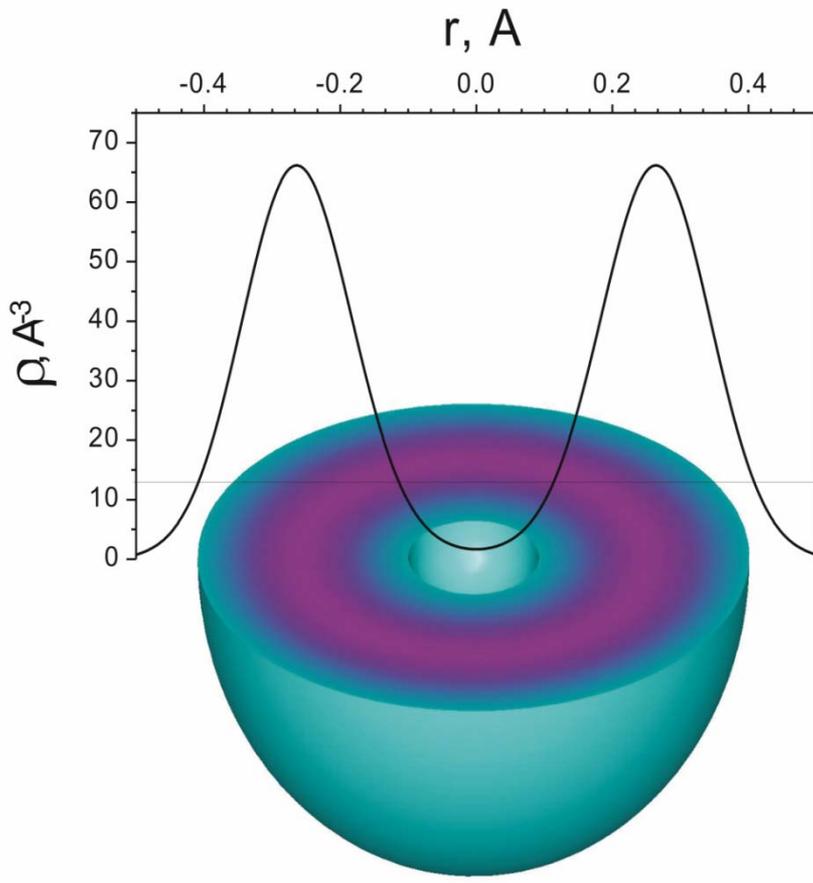
V. Bovtun et al., "Broad-band dielectric response of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ relaxor ferroelectrics: Single crystals, ceramics and thin films" *J. Eur. Cer. Soc.* v.26, p.2867, (2006)

- Значения $\epsilon > 25000$
- Диэлектрическая дисперсия до mHz
- При низких температурах отсутствие искажений решетки

Probability density function for Pb^{2+} in PMN 300K

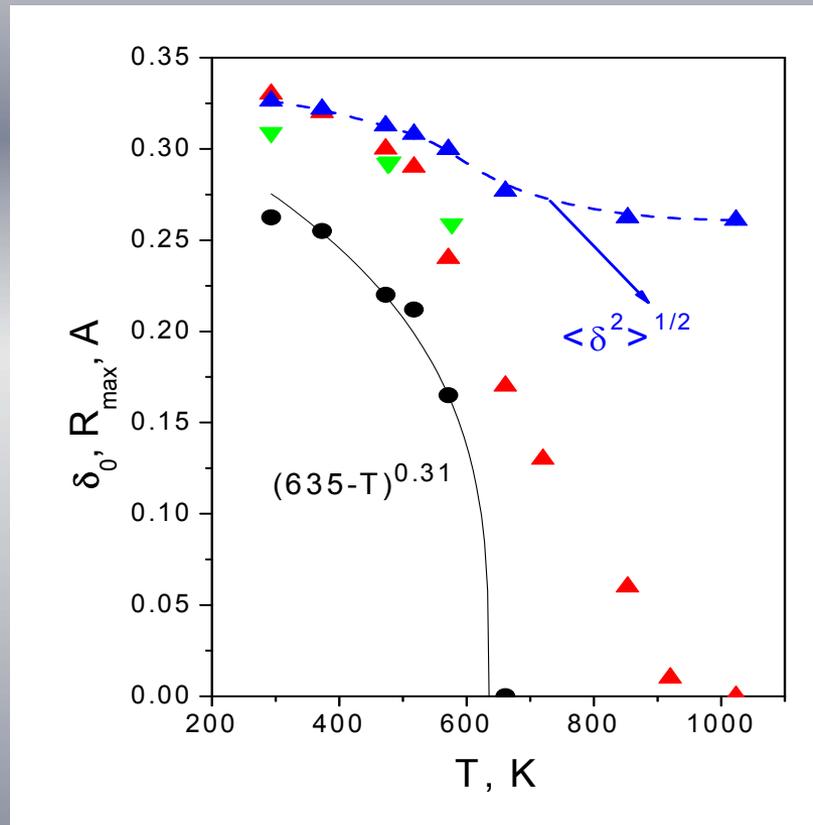
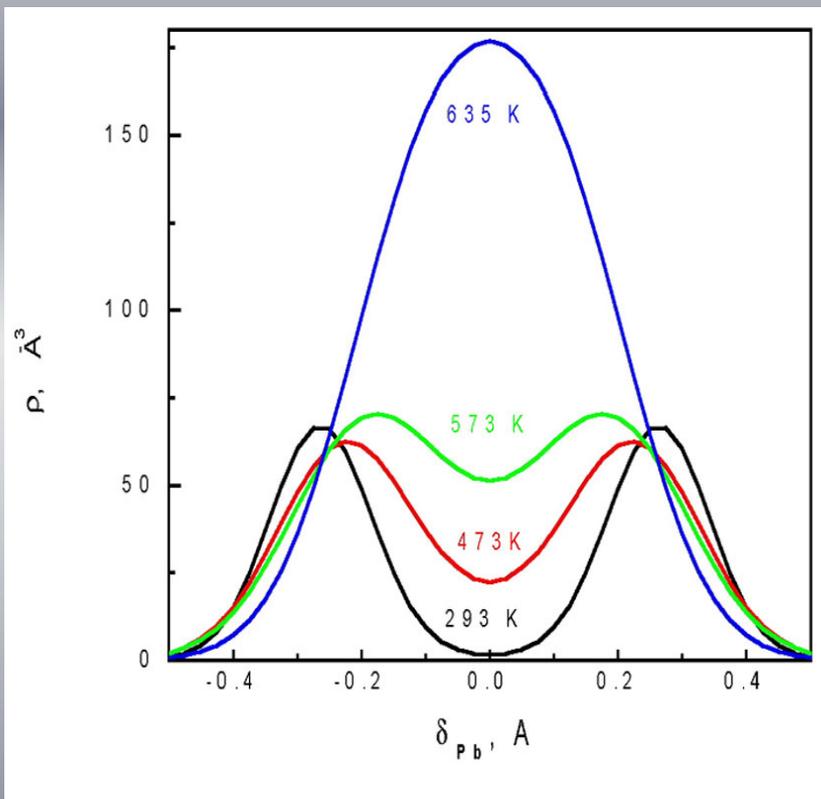
“Rotator model”

Gram-Charli expansion”



Spherical layer is formed

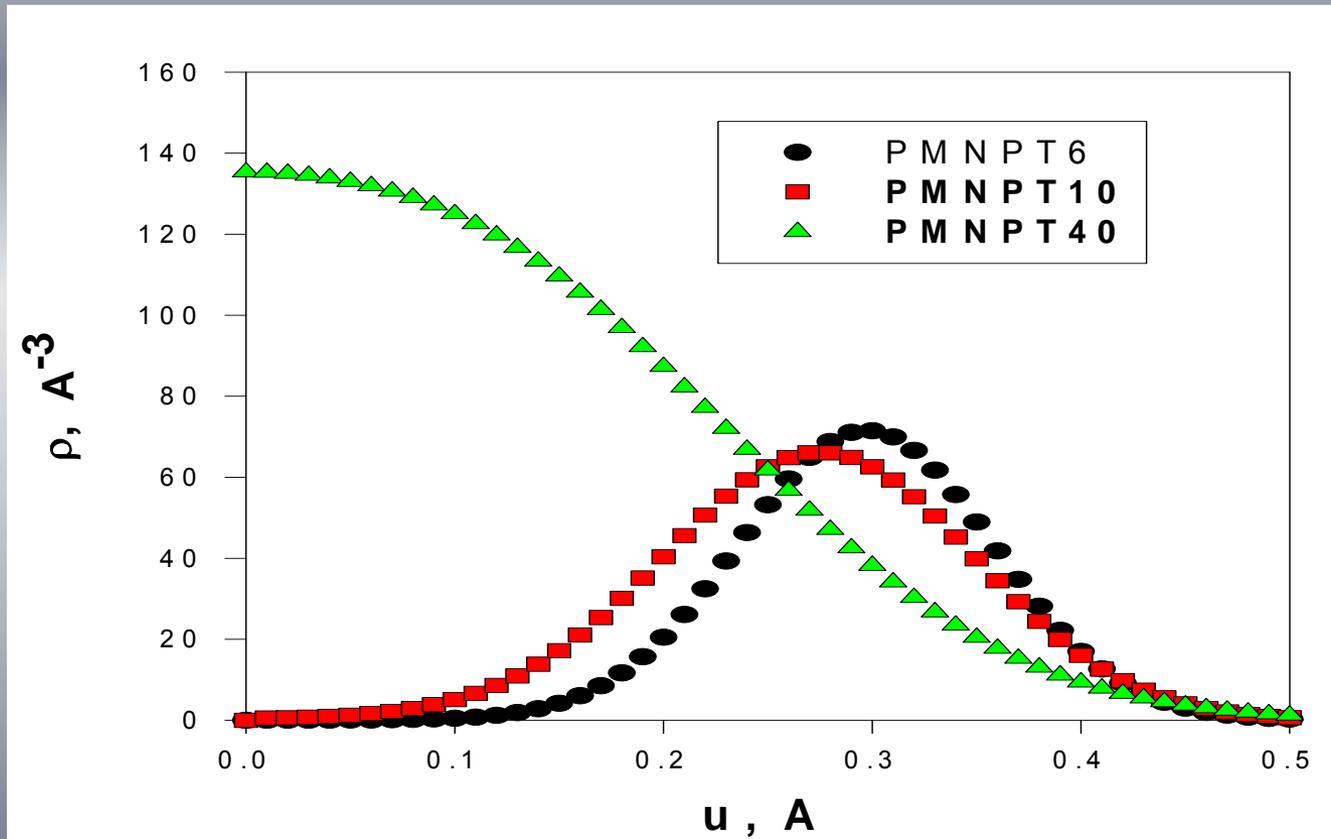
Temperature evolution of PMN structure



At and below room temperature

NO PARAELECTRIC MATRIX

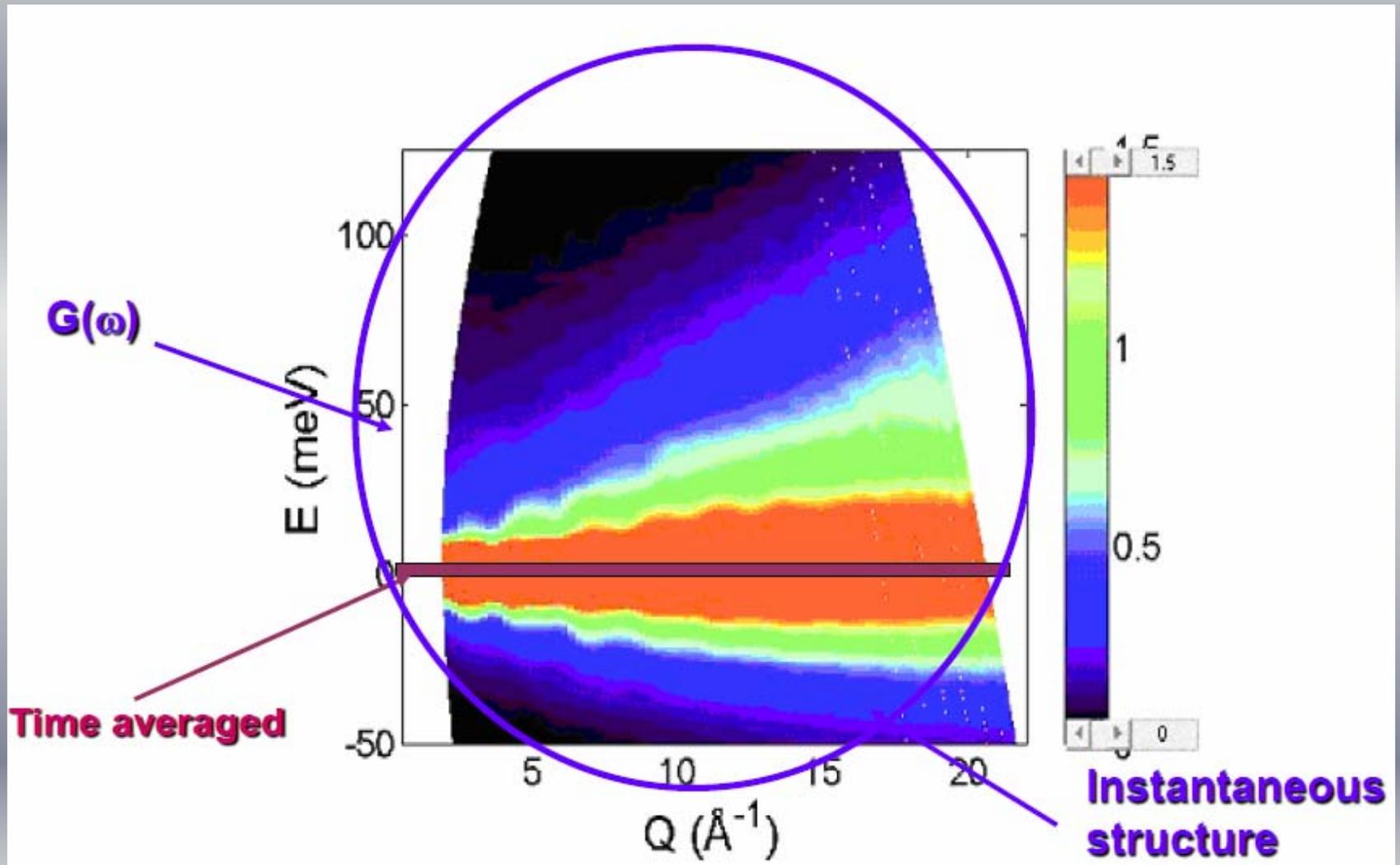
PDF for Pb²⁺ in PMNPT6 PMNPT10 and PMNPT40



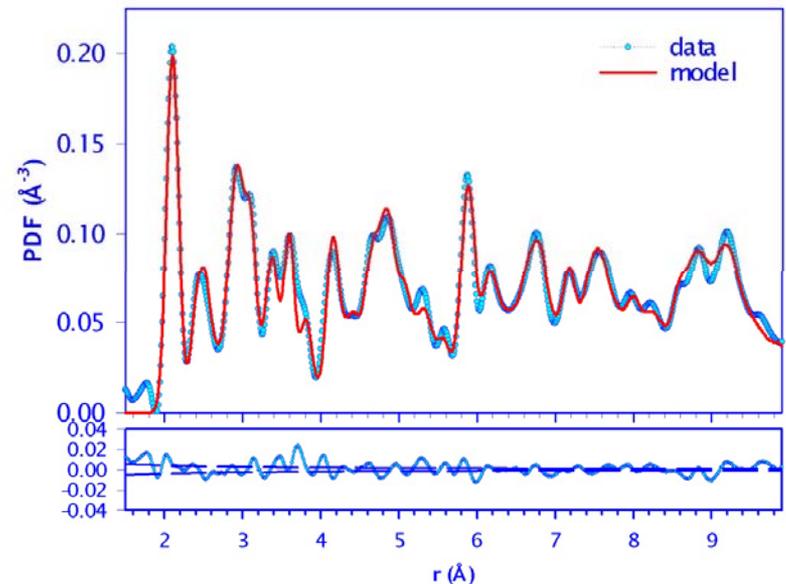
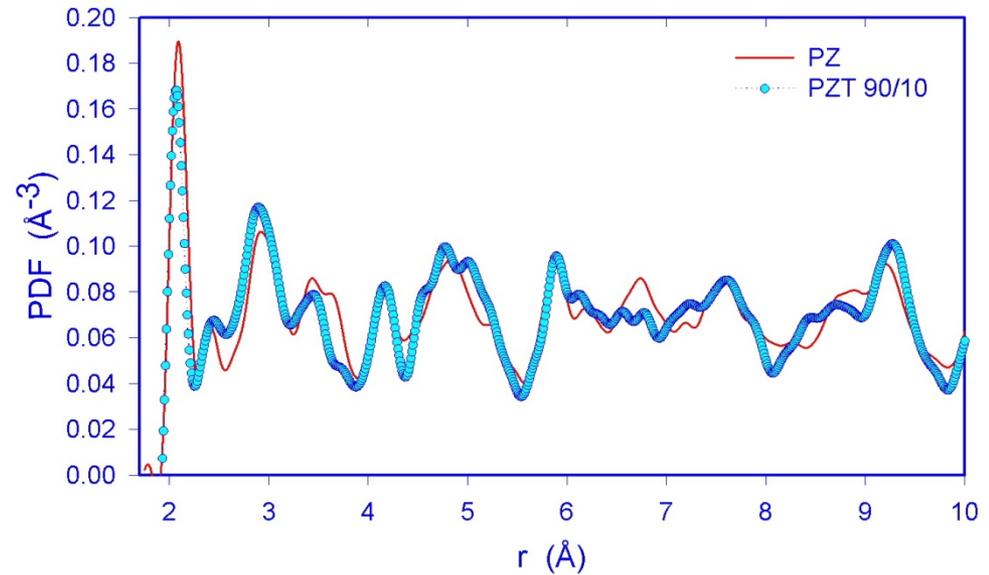
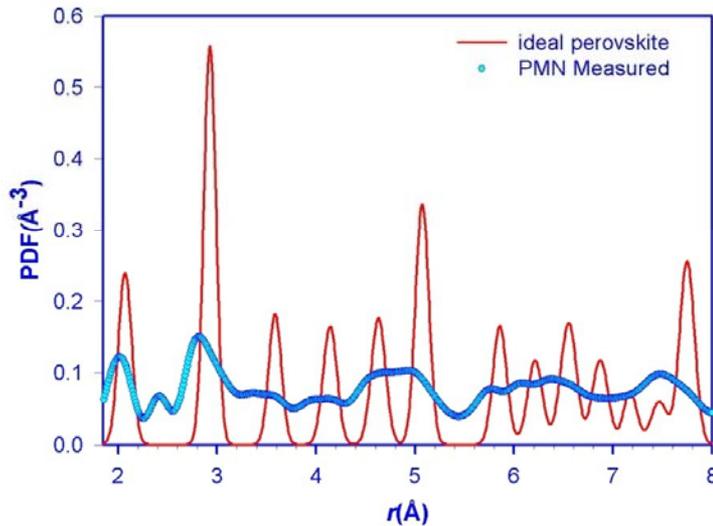
ЛОКАЛЬНОЕ ОКРУЖЕНИЕ

ЛОКАЛЬНАЯ ДИНАМИКА

Что мы измеряем в эксперименте



Pb polarization

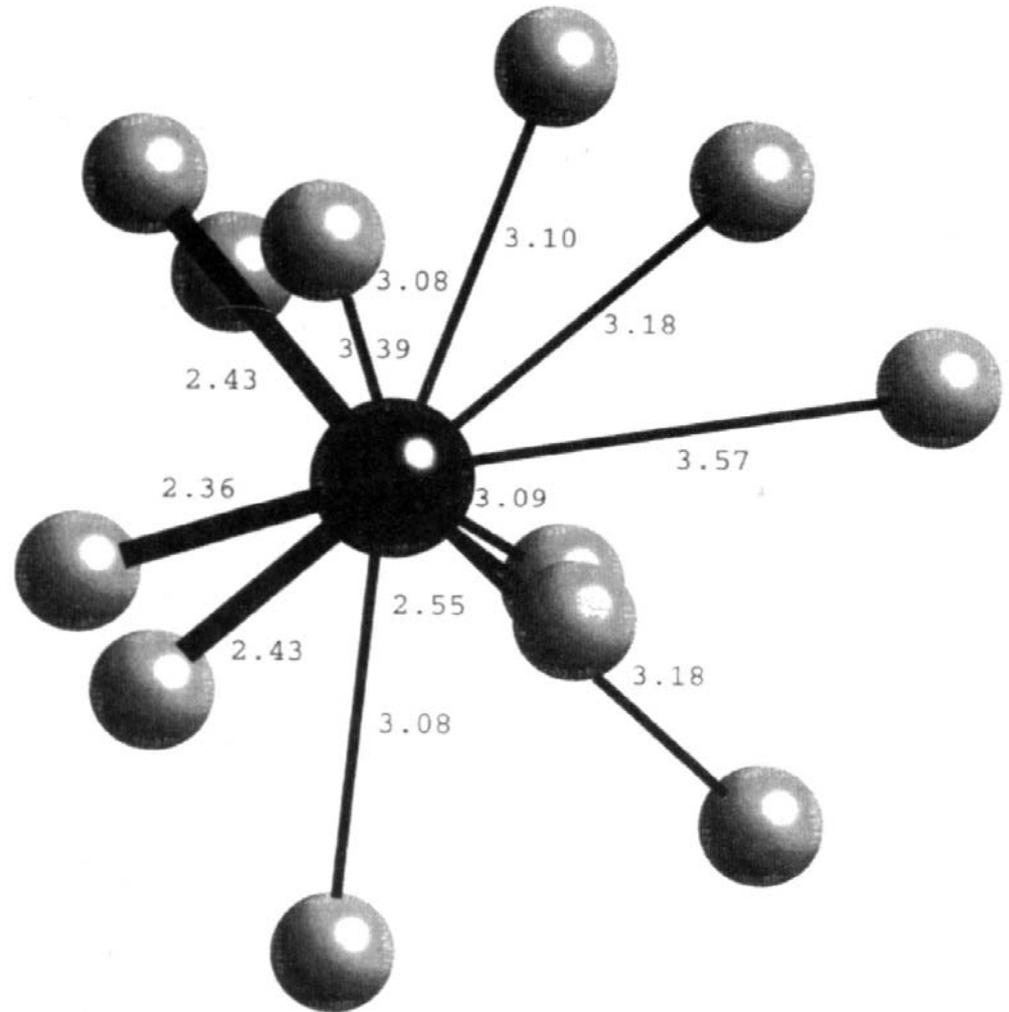


- PDF of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and PbZrO_3 (PZ).

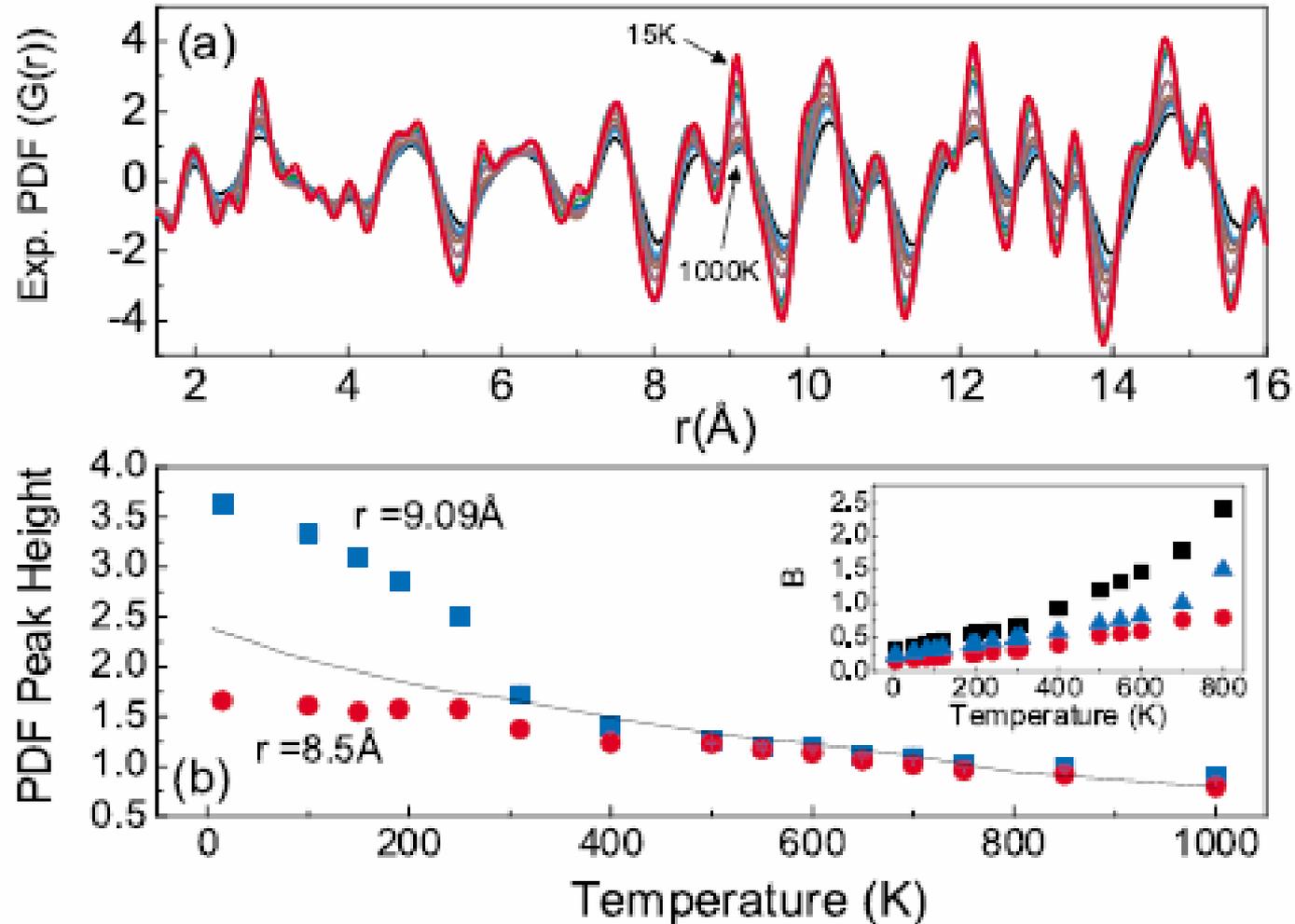
Pb^{2+} in PbZrO_3

Pb is off-centered by 0.5 \AA in the O_{12} cage

Lone-pair s - p electrons of Pb

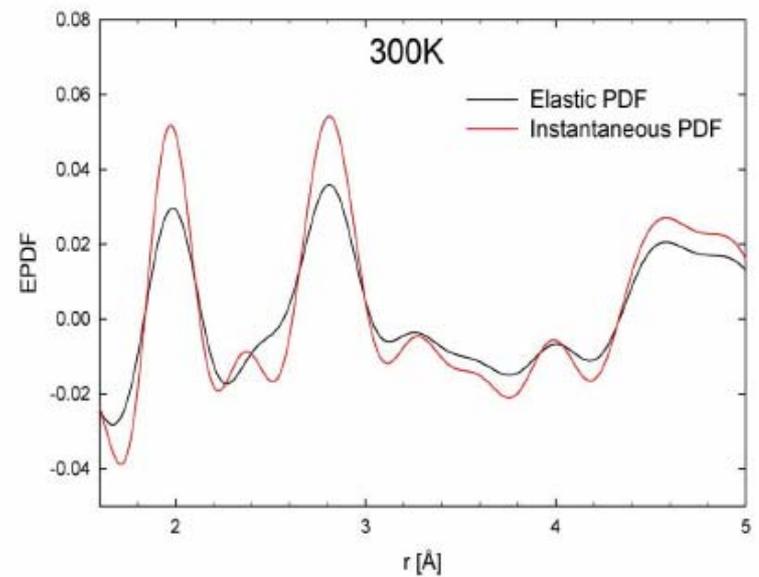
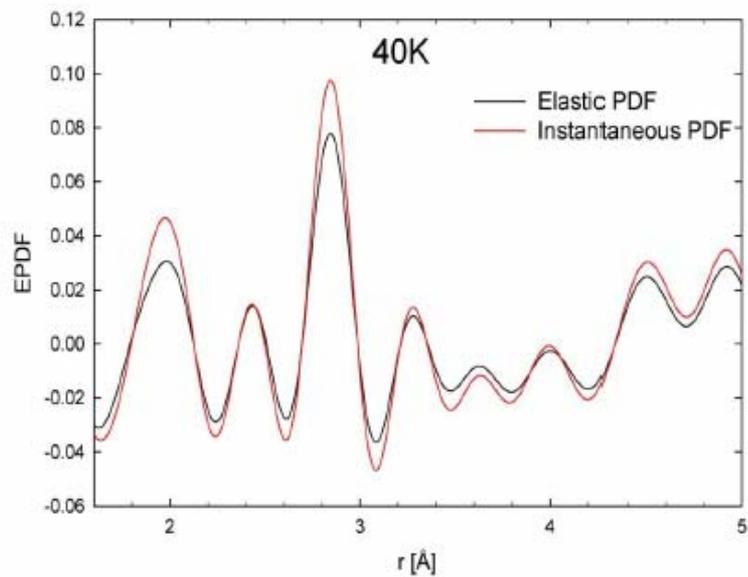


Эффекты на «больших» расстояниях



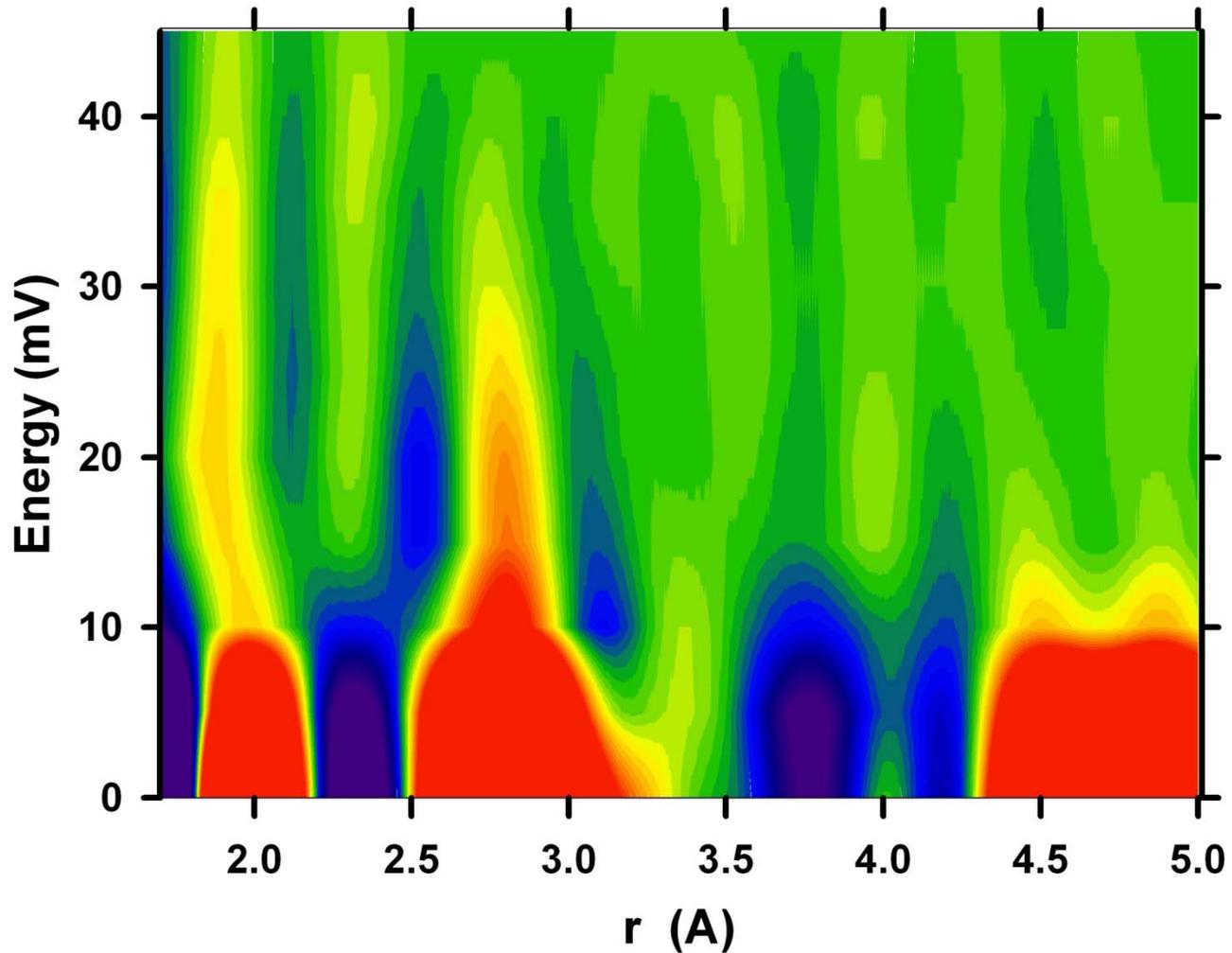
I.-K. Jeong, T. W. Darling, J. K. Lee, Th. Proffen, R. H. Heffner, J. S. Park, K. S. Hong, W. Dmowski and T. Egami, *Phys. Rev. Lett.*, **94**, 147602 (2005)

Средняя по времени и «мгновенная» структура



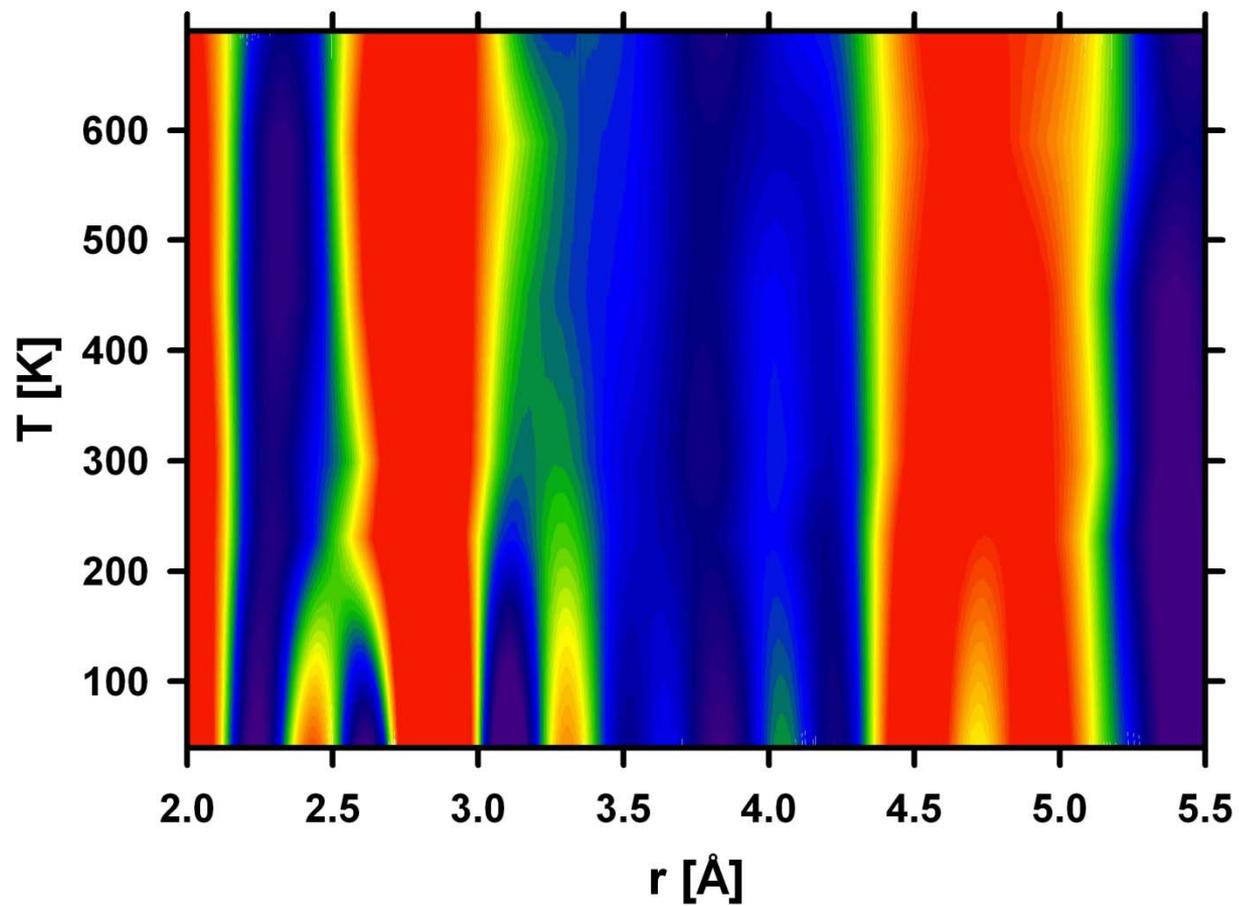
Dynamic PDF

T = 450K



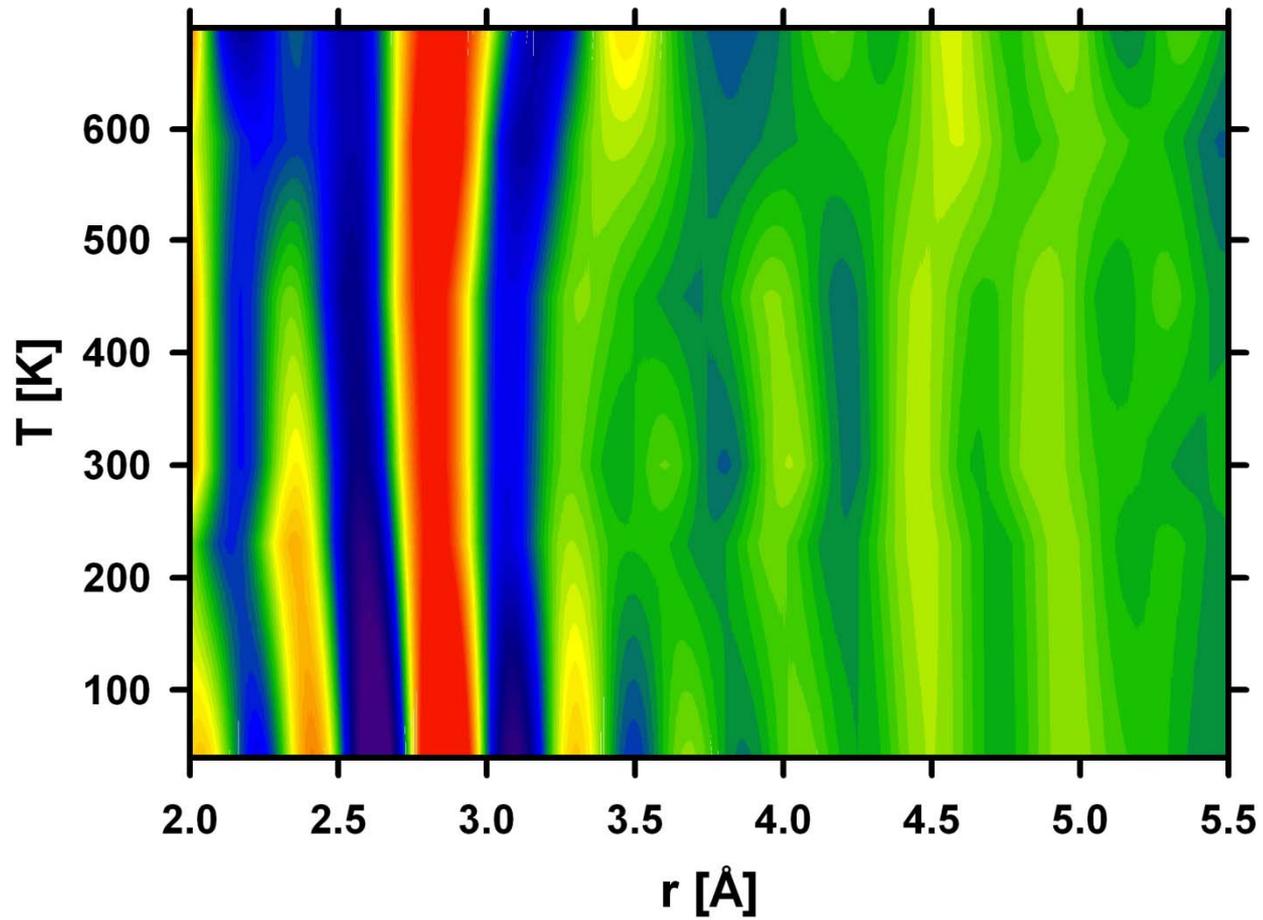
W. Dmowski, et al., *Phys. Rev. Lett.*, **100**, 137602 (2008)

-5 to 5 meV



Average (Static) Structure

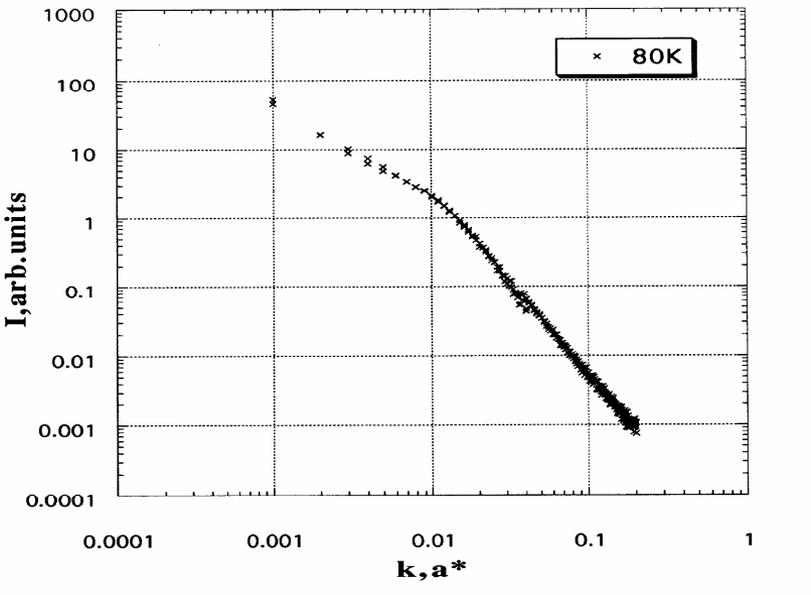
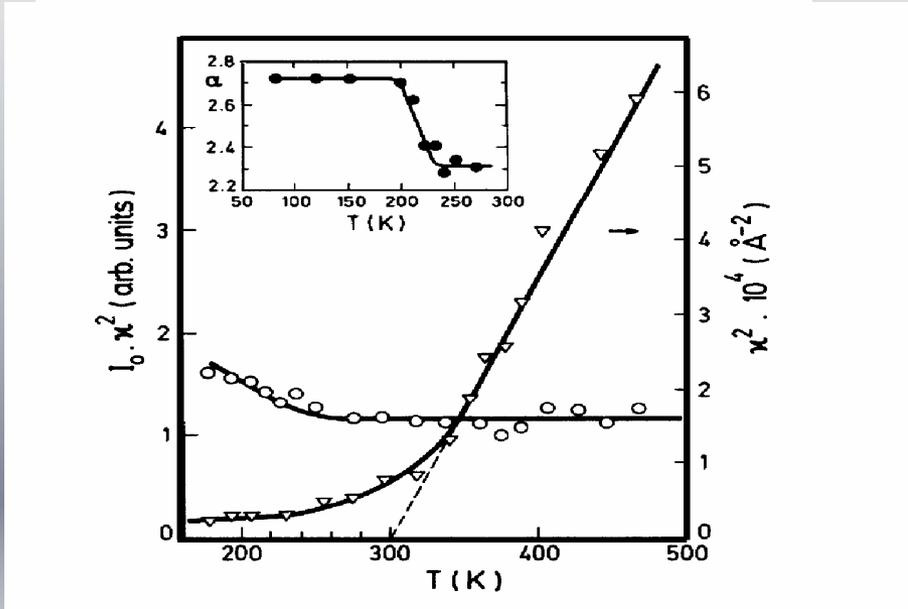
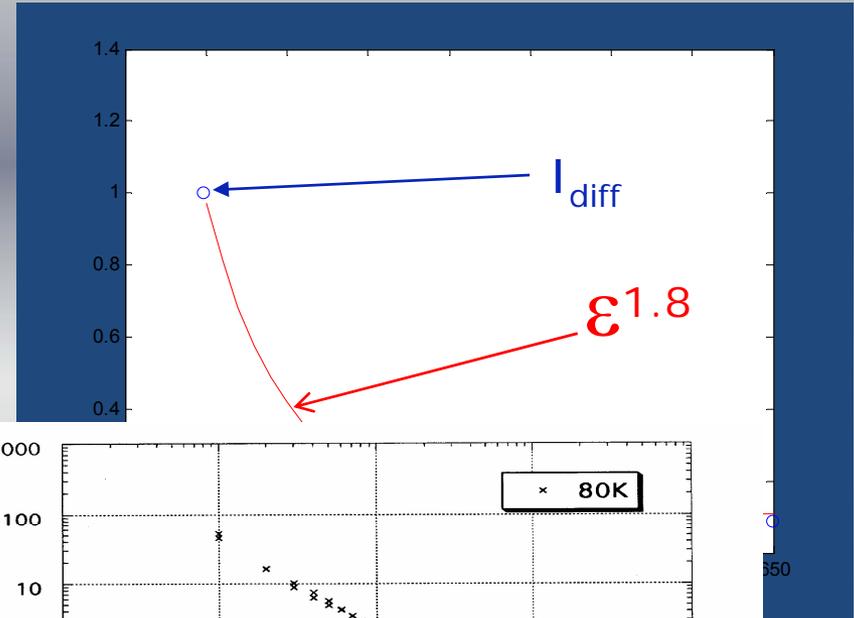
10 to 20 meV



Dynamic PDF

Diffuse scattering in relaxors

- It is anisotropic
- Increases on cooling;
follows $\epsilon^{1.8}$
- Follows $q^{-\alpha}$ law with α
changing from 2.25 to 2.7



Что и как смещается

Table II. Summary of atomic displacements from refs. 129 and 82.

κ	δ	δ_{CM}	δ_{shift}
Pb	1.00	0.42	0.58
Mg/Nb	0.18	-0.40	0.58
O	-0.64	-1.22	0.58

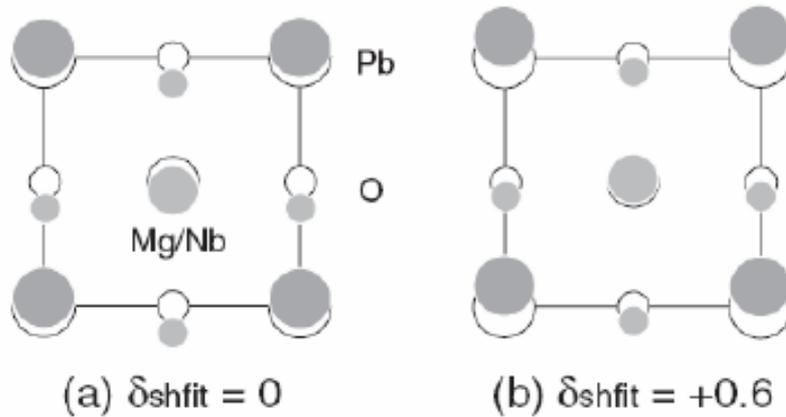
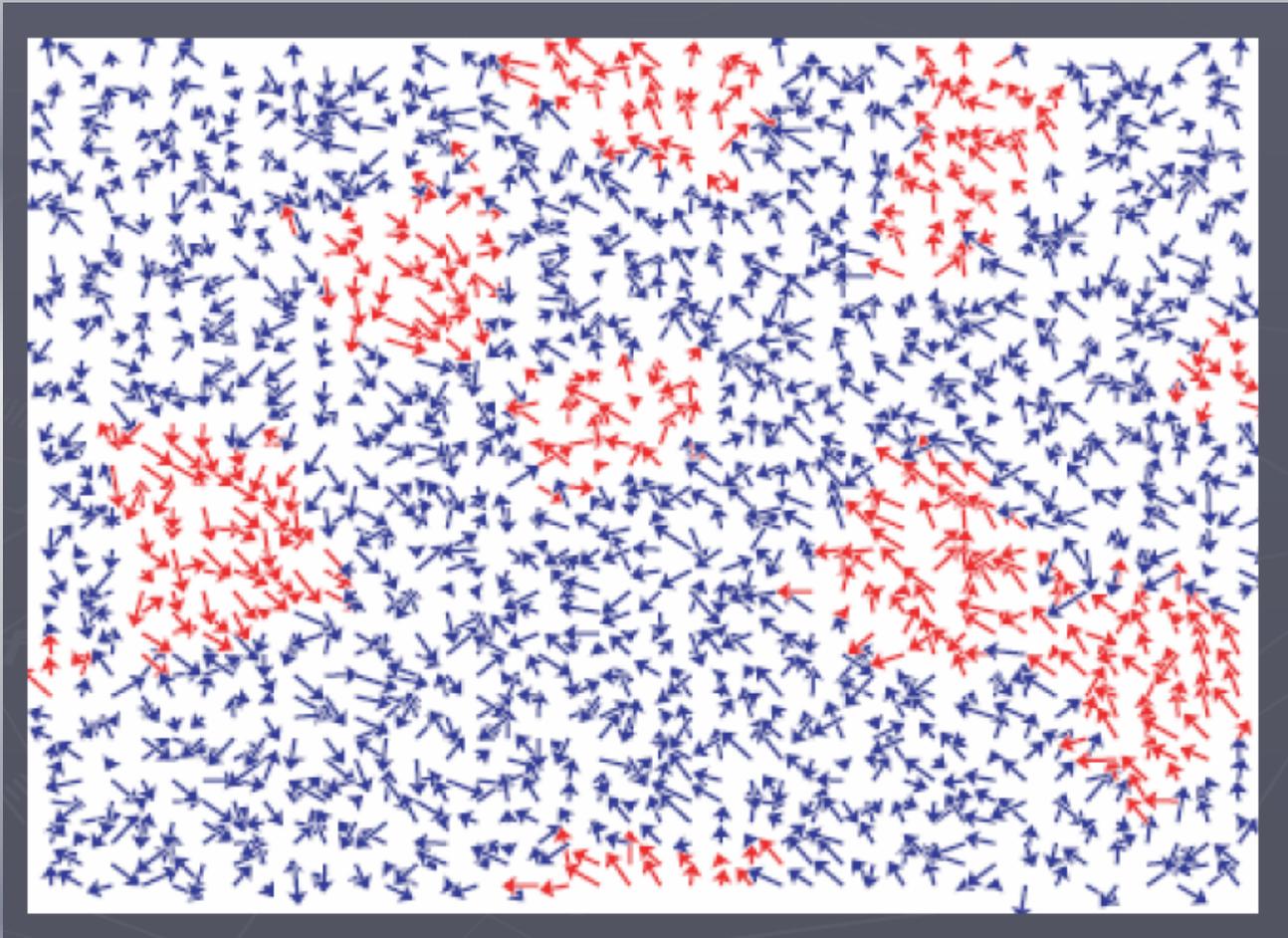


Fig. 13. Atomic displacements in PMN (see ref. 82).

Собственные вектора
НЕ ОПТИЧЕСКИЕ и
НЕ АКУСТИЧЕСКИЕ

Мезоскопическая структура релаксоров

Теоретическое моделирование распределения поляризации

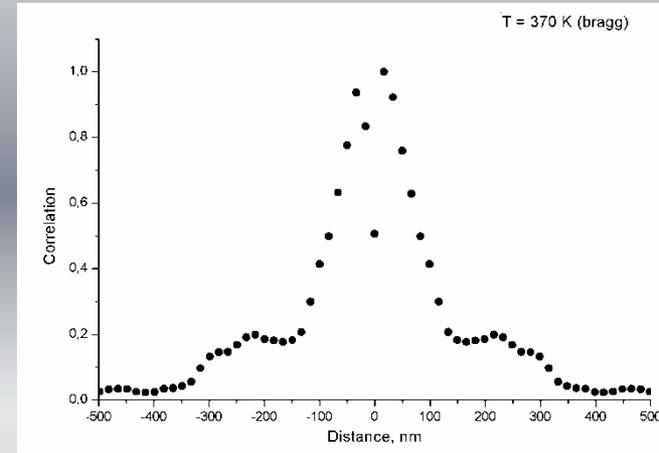
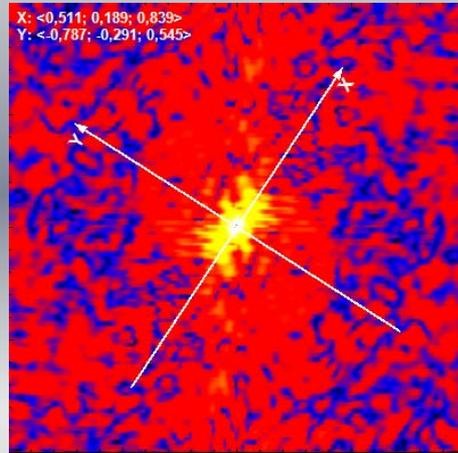


following B.Burton et al., Phase Transitions 79,91 (2006)

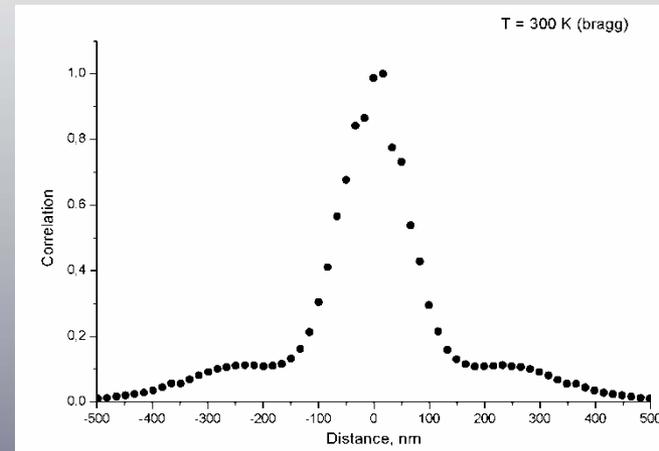
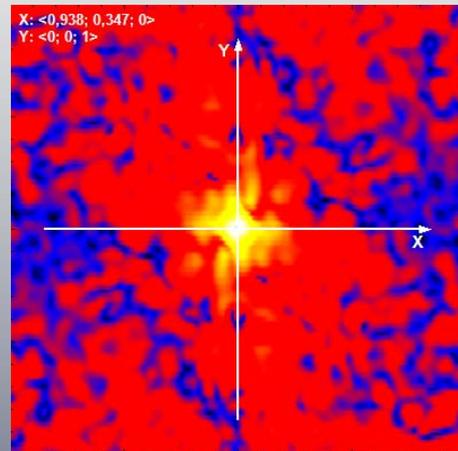
Coherent X-rays Speckles

Брэгговское рассеяние.

T=370 K

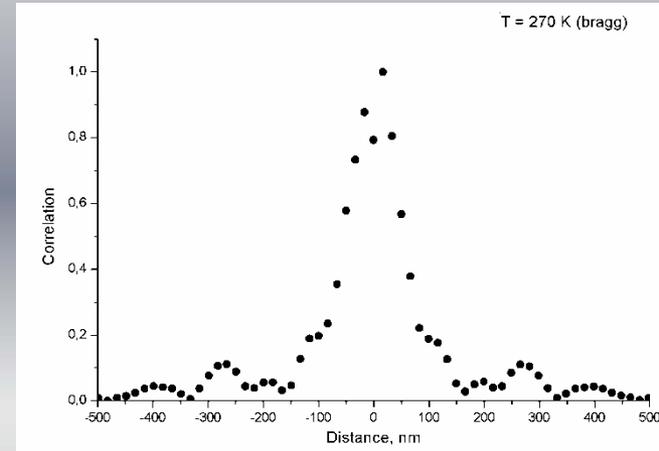
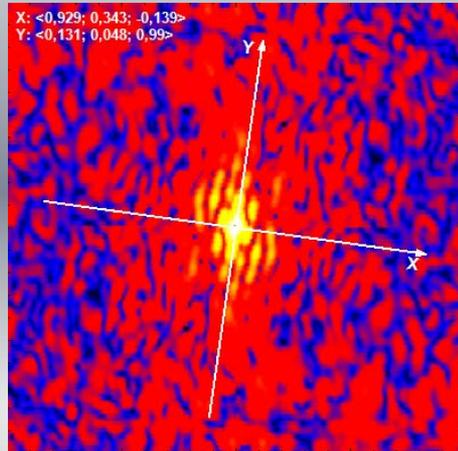


T=300 K

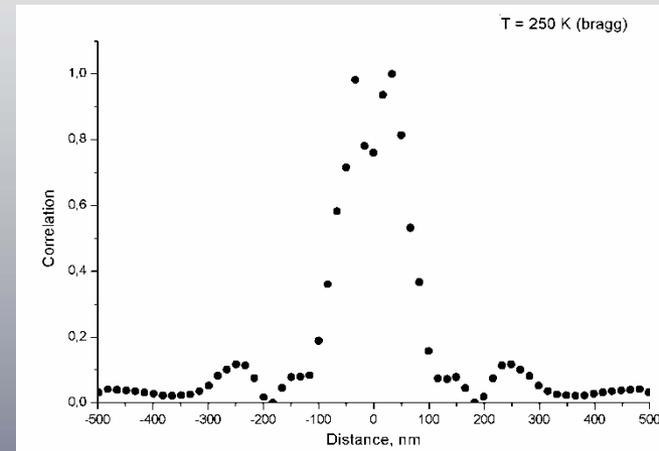
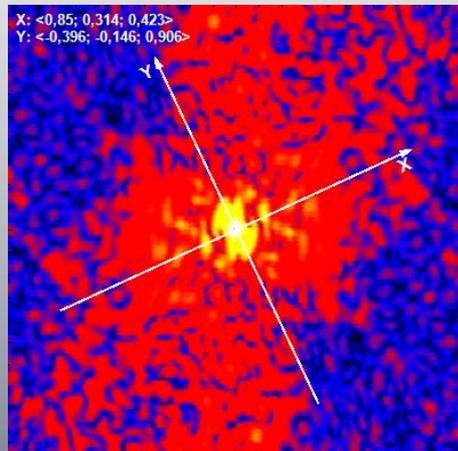


Брэгговское рассеяние.

T=270 K

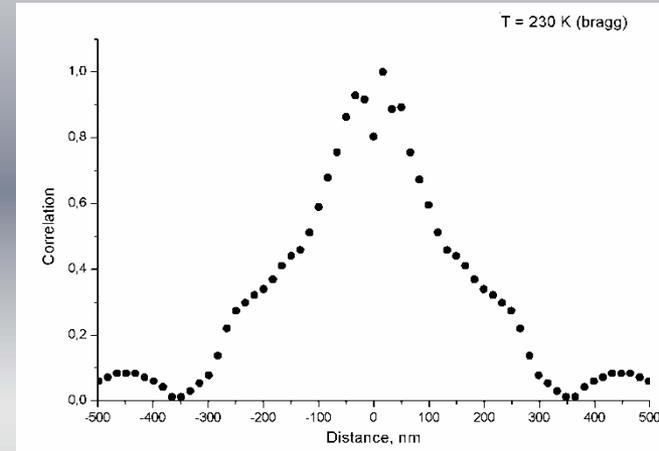
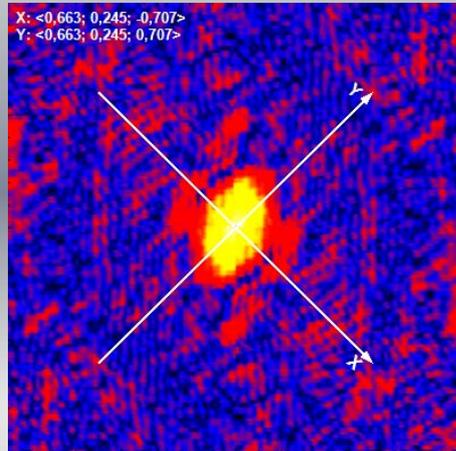


T=250 K

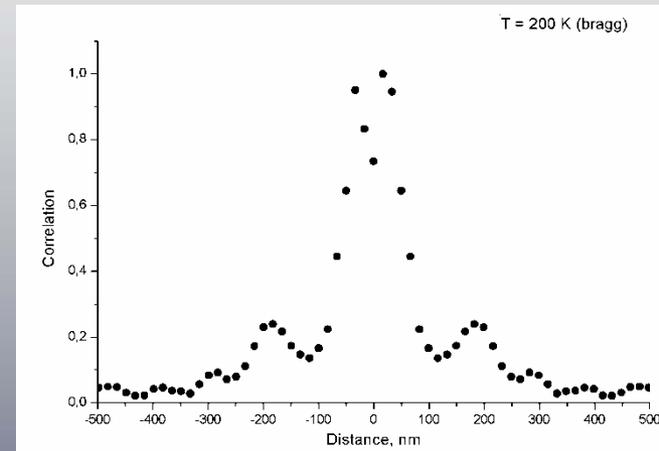
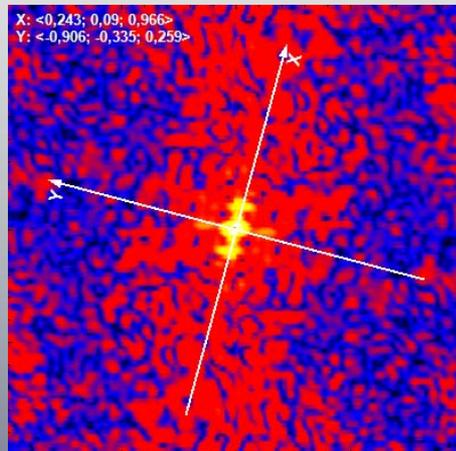


Брэгговское рассеяние.

T=230 K

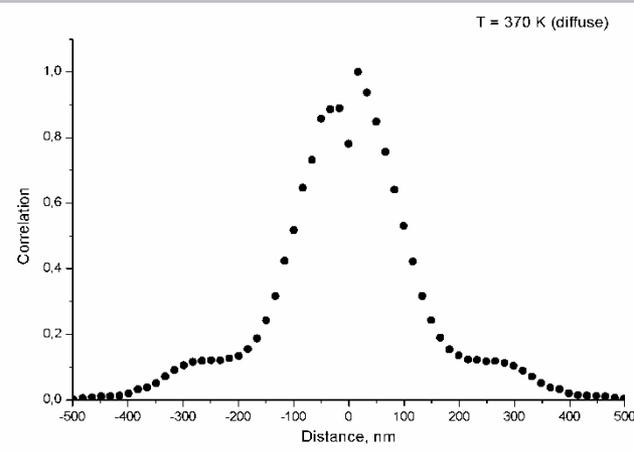
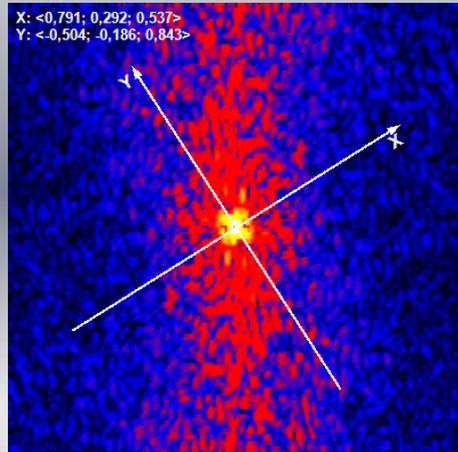


T=200 K

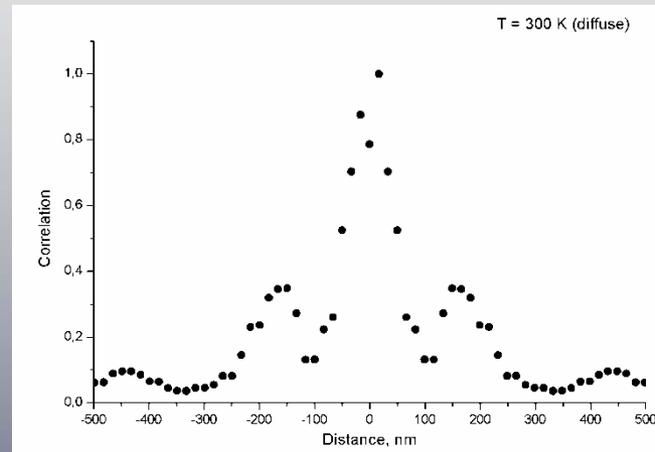
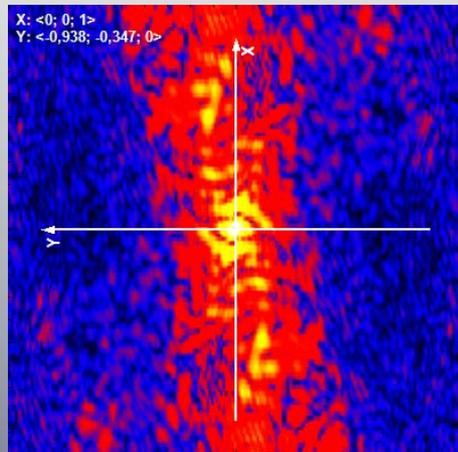


Диффузное рассеяние.

T=370 K

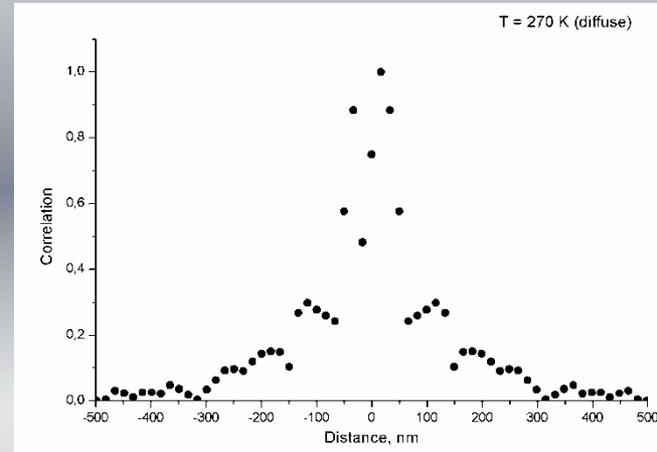
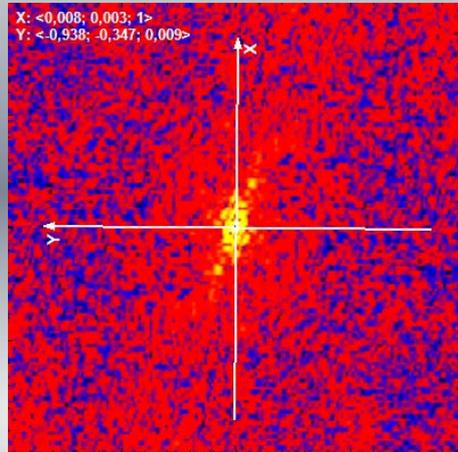


T=300 K

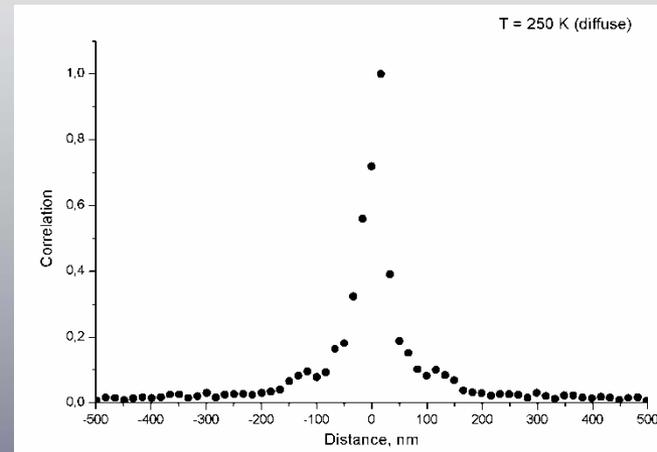
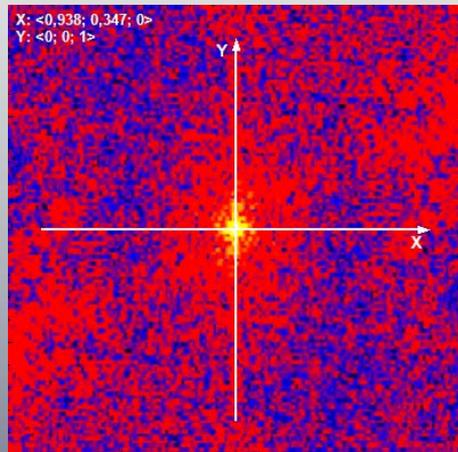


Диффузное рассеяние.

T=270 K

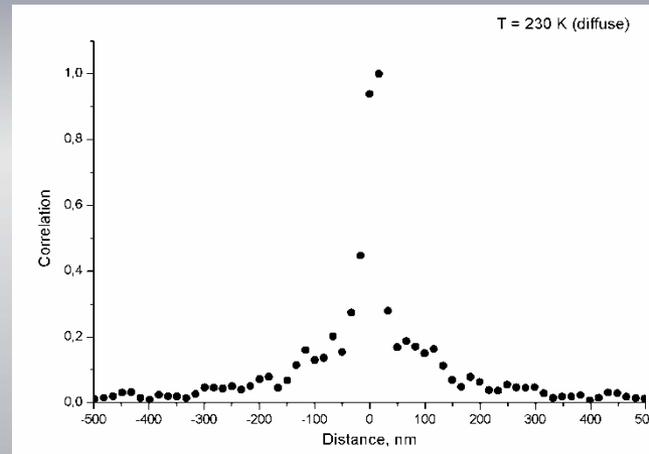
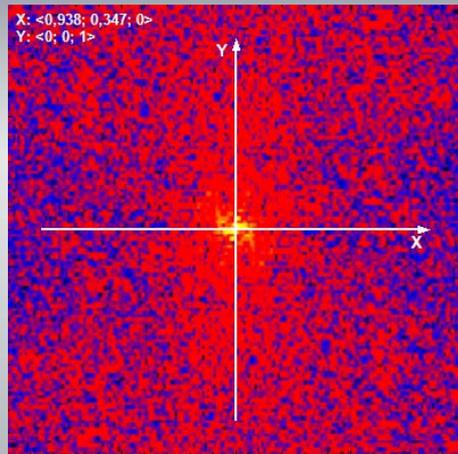


T=250 K

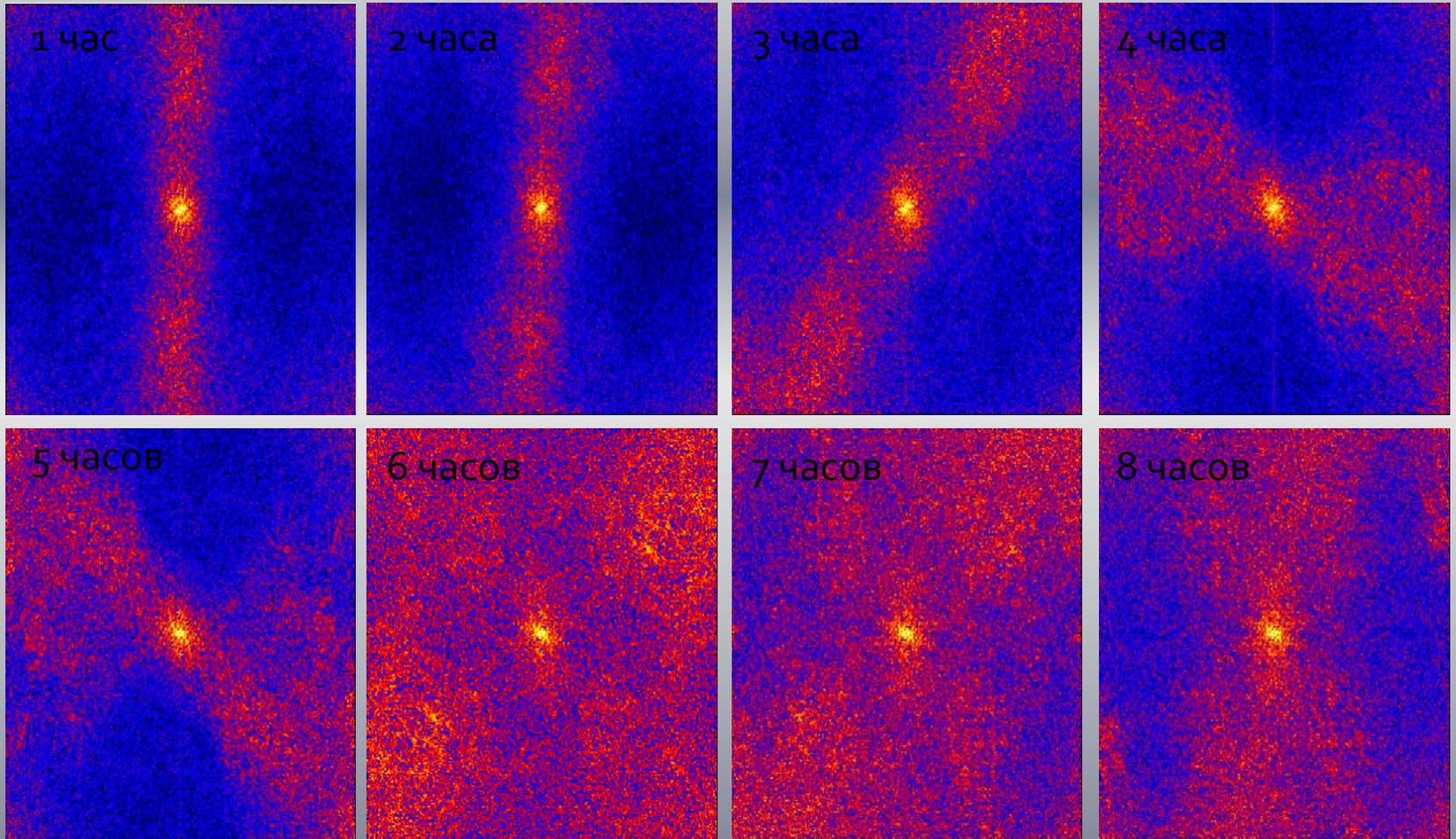


Диффузное рассеяние.

T=230 K



Временная эволюция.

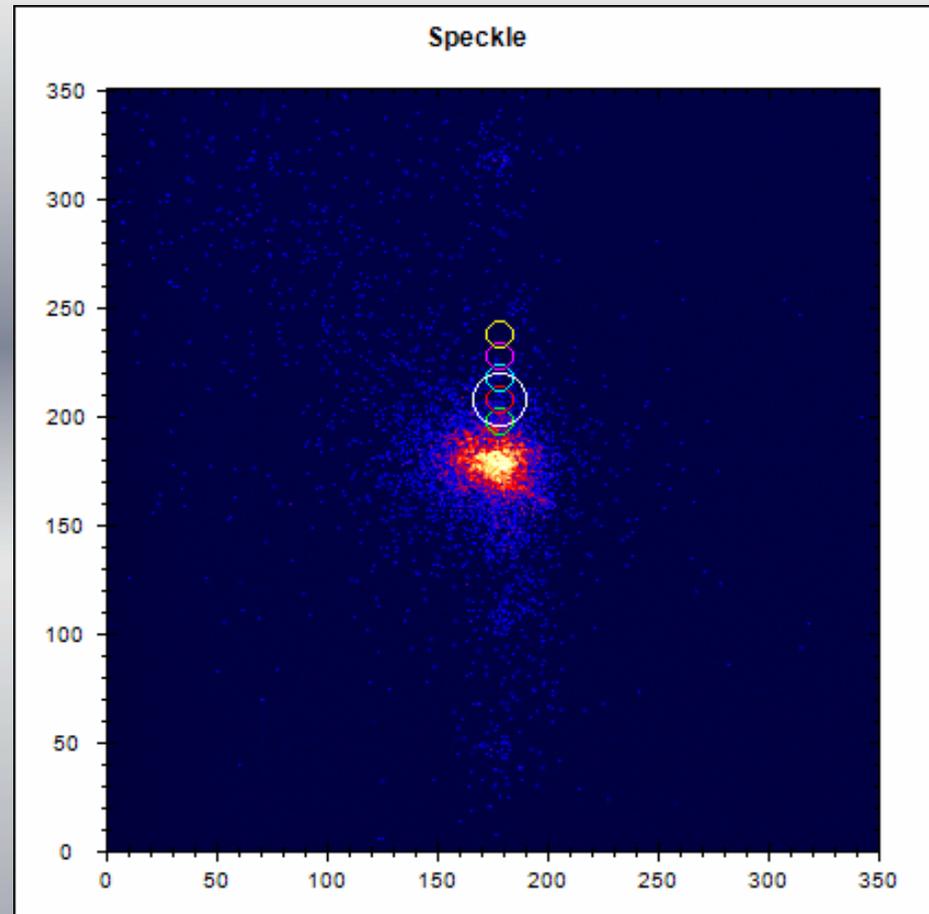


PMNPT10 $T = 230$ К диффузное рассеяние.

Static or Dynamic below T^*

XPCS

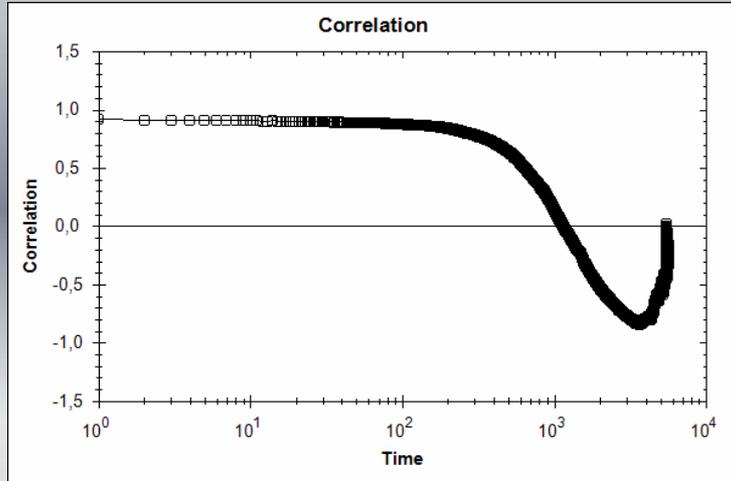
$$\gamma(\mathbf{q}, \tau) = \frac{\langle I(\mathbf{q}, t) \cdot I(\mathbf{q}, t + \tau) \rangle_t}{\langle I^2(\mathbf{q}, t) \rangle_t} \quad (1.1)$$



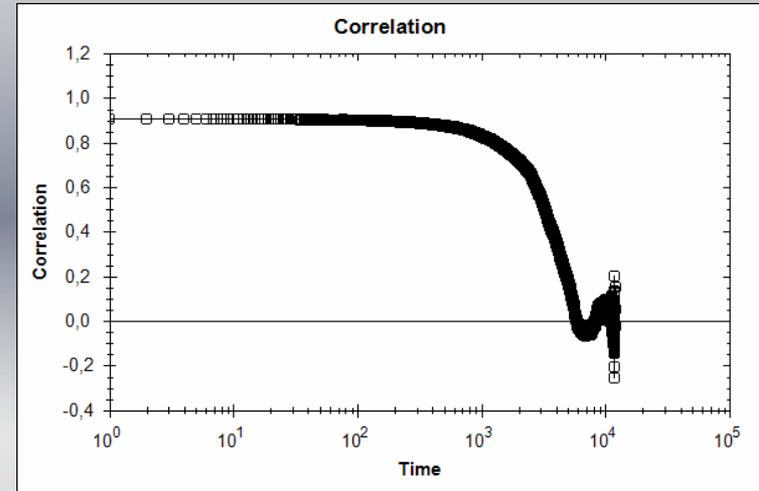
$$\gamma(\mathbf{q}, \tau) = \frac{\langle [I(\mathbf{q}, t) - \langle I(\mathbf{q}) \rangle_t] \cdot [I(\mathbf{q}, t + \tau) - \langle I(\mathbf{q}) \rangle_t] \rangle_t}{\langle [I(\mathbf{q}, t) - \langle I(\mathbf{q}) \rangle_t]^2 \rangle_t} \quad (1.2)$$

XPCS Temperature evolution

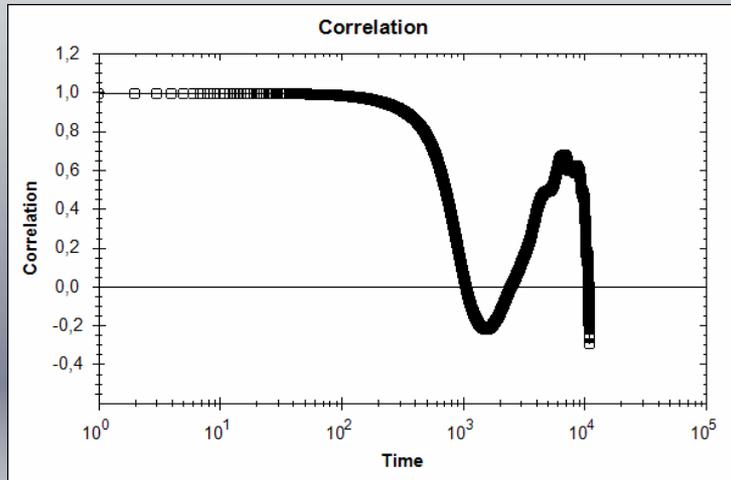
360K



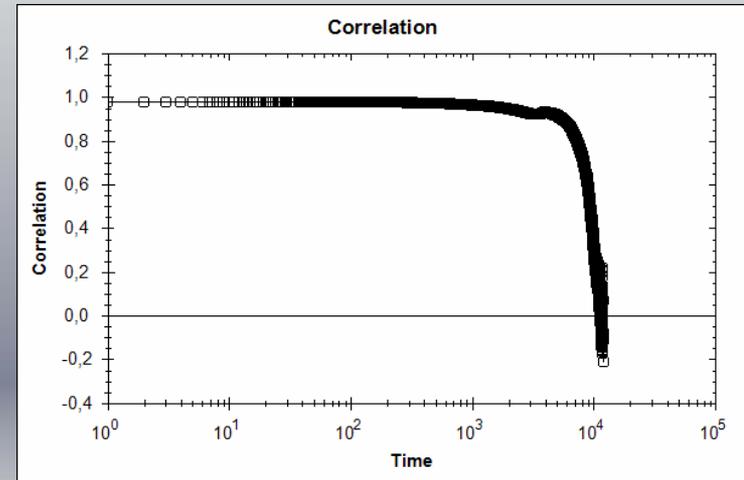
310K



260K



220K



What is probably going on

- $T > T_d$ Phonons (Soft mode (2SM)) + local excitations Pb^{2+} in the oxygen case. No relaxation.
- $T^* < T < T_d$ Coupling of SM with local degree of freedom. Creation of mixed relaxational mode (dynamic PNR, superspins ...). Diffuse scattering: dynamic; weak. Anisotropy follows anisotropy of the SM
- Creation of static distorted regions SDR (probably in the COR). These regions strongly enhance DS. We do not know shape of the SDR, anisotropy of the DS is the same as at higher temperature. Probable 2 components of the DS – static and dynamic.

Our vision of the mesoscopic structure evaluation (*imagination not modeling*)

