# The Multiferroic System $FeTe_2O_5Br$

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***Christian Balz, 20th July 2010***

# Outline

1. Introduction
   i. Multiferroics
   ii. Microscopic origin of thermal expansion
   iii. Methods for measuring thermal expansion

2. The multiferroic system $FeTe_2O_5Br$
   i. Structure
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   iii. Thermal expansion
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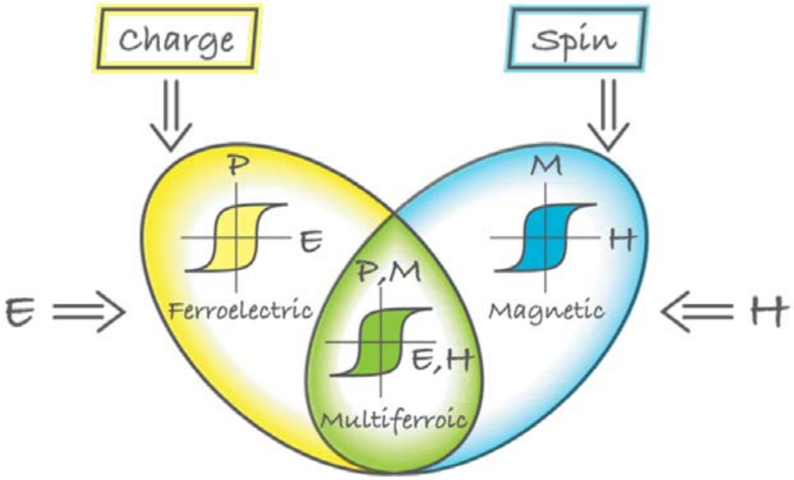
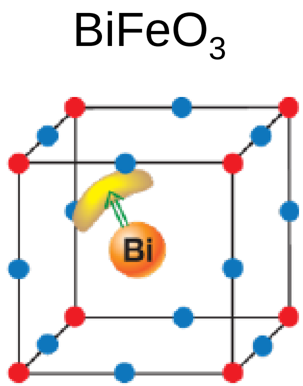
# Multiferroics

- Materials that exhibit more than one ferroic order parameter simultaneously and exhibit coupling between the order parameters (e.g. $BiFeO_3$, $TbMnO_3$)




- ➢ Magnetic response to an electric field
- ➢ Modification of polarization by magnetic field
- ➢ Multifunctional materials

# Multiferroics

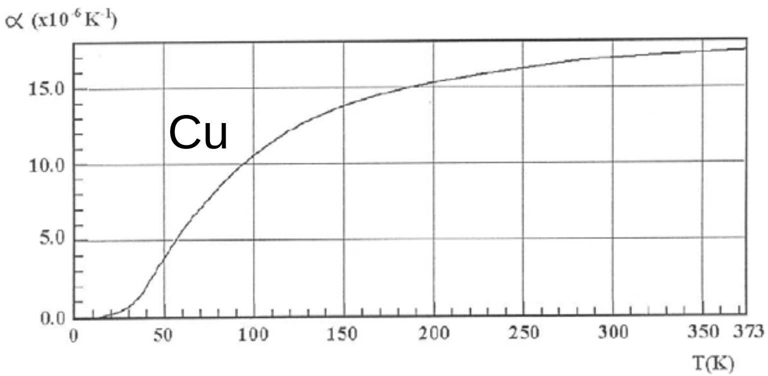



- <u>Types of multiferroics</u>
  - Charge ordered multiferroics
  - Geometrically frustrated multiferroics
  - Magnetically driven multiferroics
  - <u>Lone pair multiferroics</u>
    - Induce both magnetic order and electric polarization

- <u>Potential for applications as</u>:
  - Switches
  - New types of electronic memory devices (multiple state memory elements, where data are stored both in the electric and the magnetic polarizations)
  - Novel spintronic devices

# Microscopic origin of thermal expansion

- According to Debye model: vibrations of the atomic lattice are quantized




Grüneisen-relation:

$$\beta = \gamma_G \frac{C_V \kappa}{V}$$

$$\beta = \sum_{i=1}^{3} \alpha_i$$

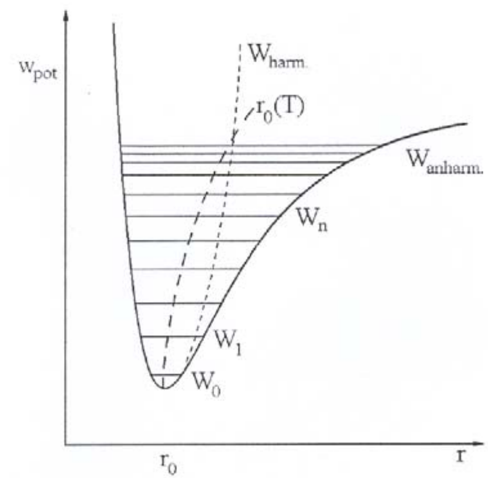
- Linear thermal expansion coefficient

$$\alpha = \frac{1}{L}\left(\frac{dL}{dT}\right)$$

- Oscillation of the atoms is not harmonic

$$U(x) = cx^2 - gx^3 - fx^4$$

$$< x >= \frac{3g}{4c^2} k_B T$$



# Methods for measuring thermal expansion

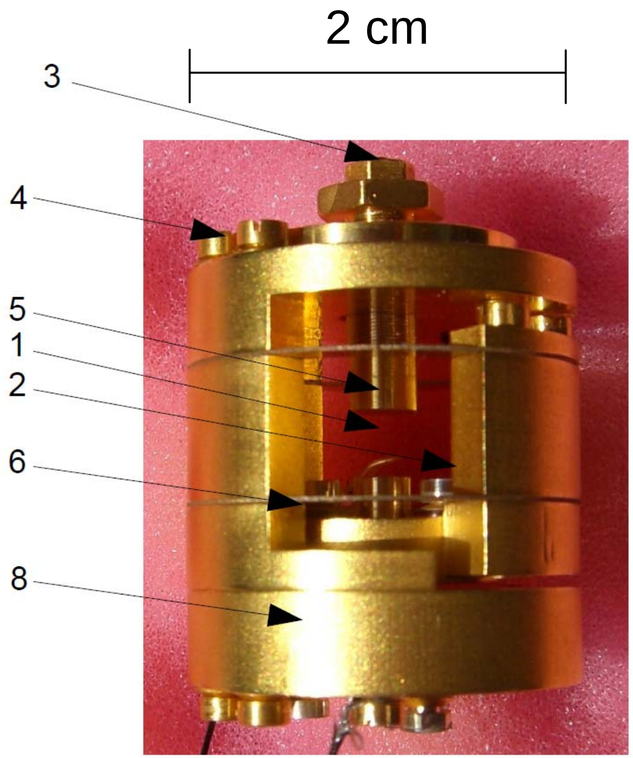
- X-ray diffractometer
  - Single crystals or polycrystalline samples
  - Changes of the lattice parameters
  - Sensitivity $\Delta a/a \sim 10^{-5}$

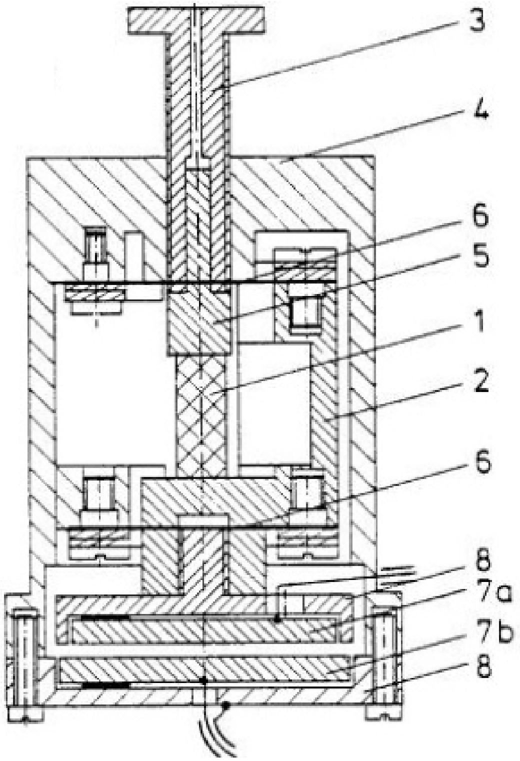
- Interferometer
  - Sensitivity $\Delta l/l \sim 10^{-7}$-$10^{-8}$

- Capacitive dilatometer
  - Sensitivity $\Delta l/l = 10^{-10}$
  - Resolves length changes $\Delta l \geq 0.01$ Å
  - ➢ Sensitive probe for studying lattice effects (expected at ferroelectric phase transitions)

# Capacitive dilatometer

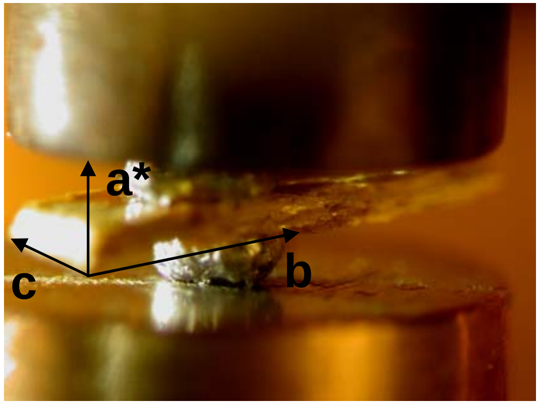
capacitor plate



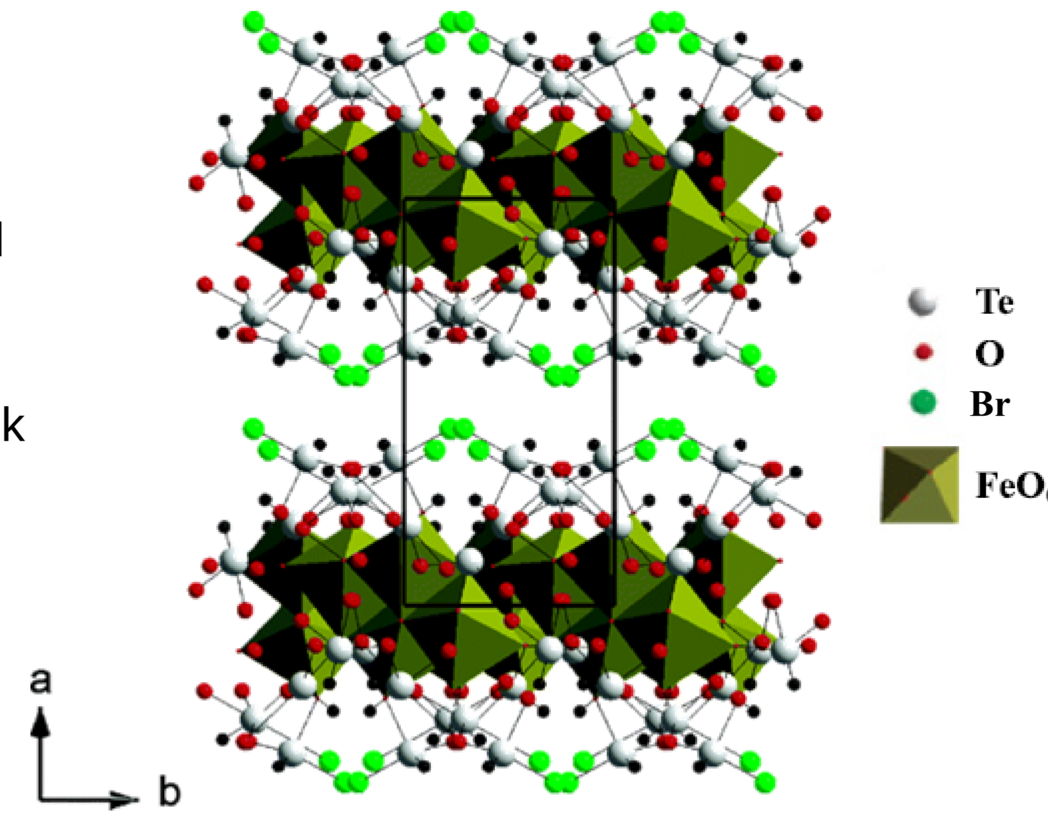




(1) sample, (2) movable part, (3) screw, (4) frame, (5) piston, (6) springs, (7) capacitor plates (not visible), (8) guard ring

# $FeTe_2O_5Br$

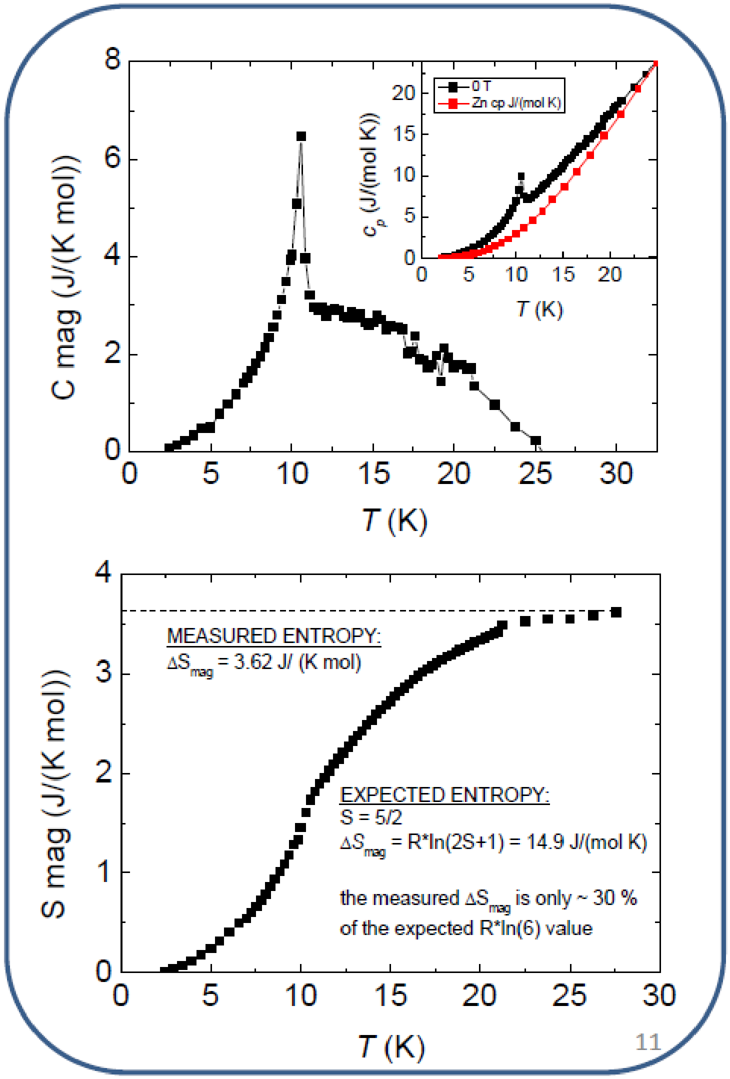



- layered crystal structure stacked along the *a*-axis
- halide anions and Lone pair electrons of the $Te^{4+}$ cations stick out of the layers
- $[Fe_4O_{16}]^{20-}$ units sandwiched by $[Te_4O_{16}Br_2]^{6-}$ groups
- groups are connected via oxygens to build up the layers
- layers have no net charge
  - ➢ weakly connected via VdW forces




R. Becker *et al.*, J. Am. Chem. Soc. **128**, 15469 (06)

# Specific heat

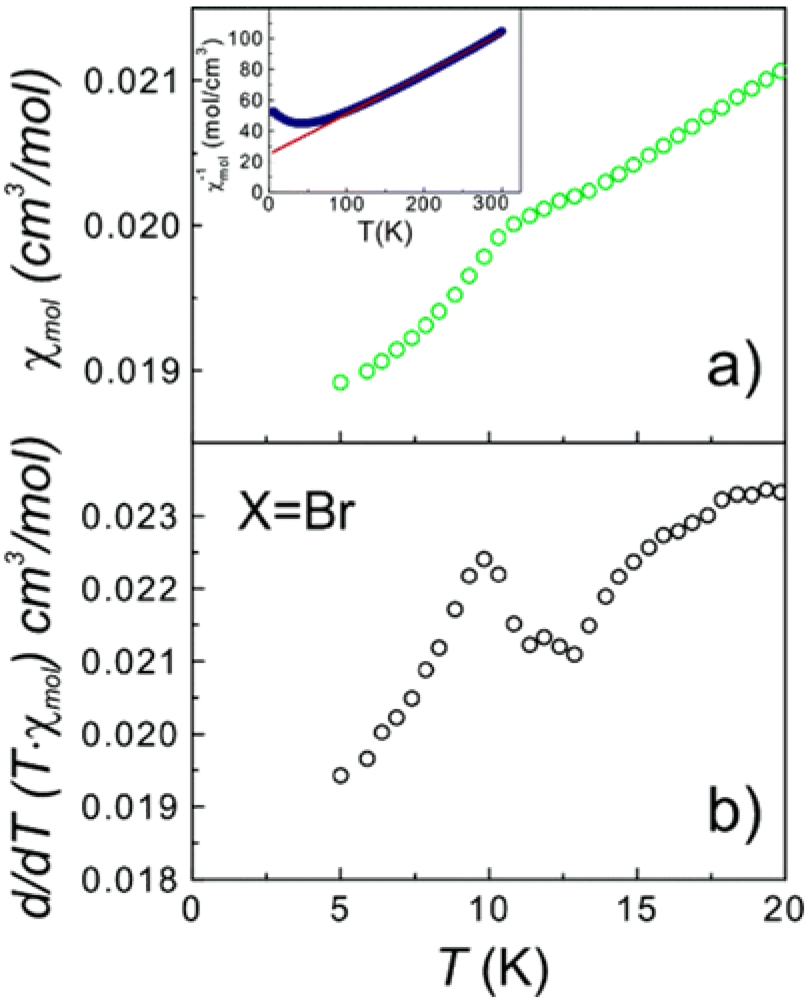


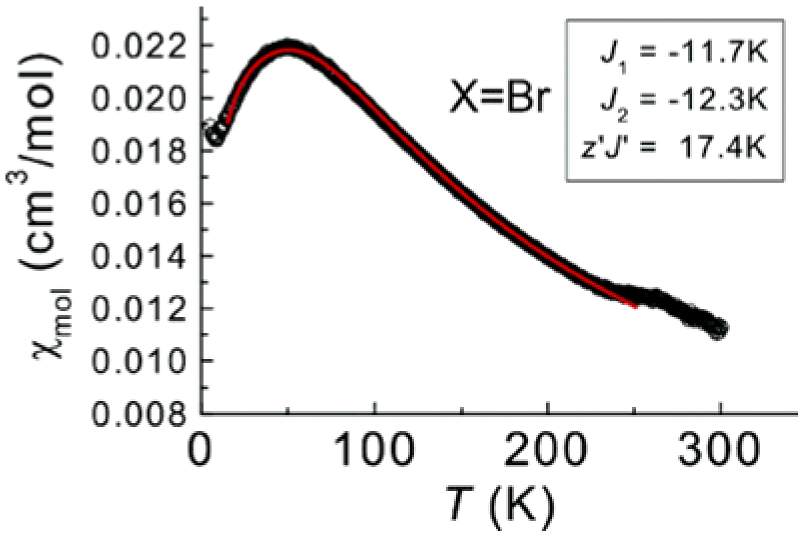

D. Arčon, presentation (09)

- λ-type anomaly at $T_N \approx 10.6$ K due to the onset of long-range afm order
- reduced inter-cluster exchange may be the reason for the small ordering temperature

- measured entropy considerably smaller than expected
- short-range ordering at ~ 50 K involved

# Magnetic susceptibility

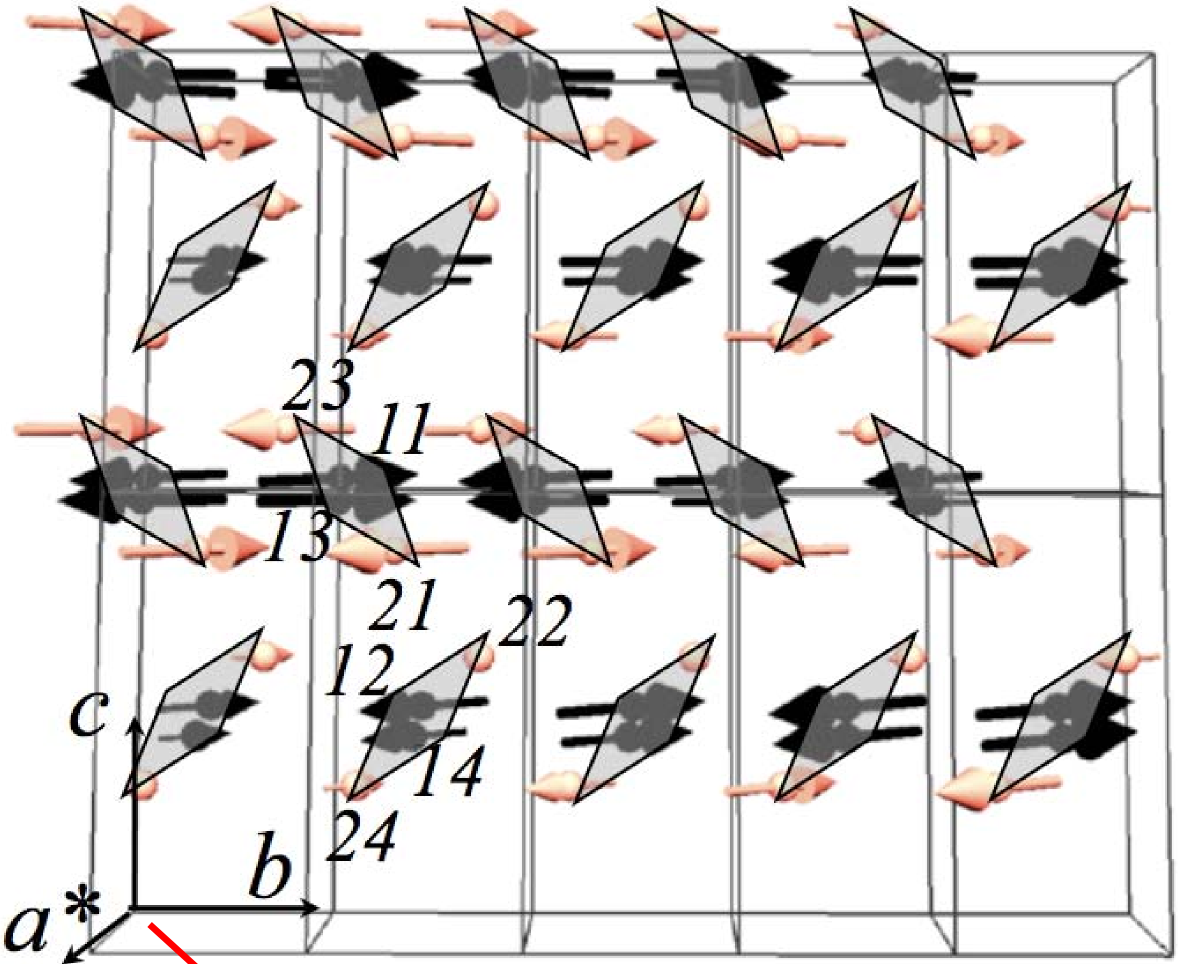



- kink at $T_N \approx 10.6$ K
- broad maximum at 48.4 K
- Curie-Weiss behaviour above 100 K
- $\Theta_{CW}$ = - 98 K → afm
- no hysteresis → 2nd order p.t.

R. Becker *et al.*, J. Am. Chem. Soc. **128**, 15469 (06)

# Magnetic structure



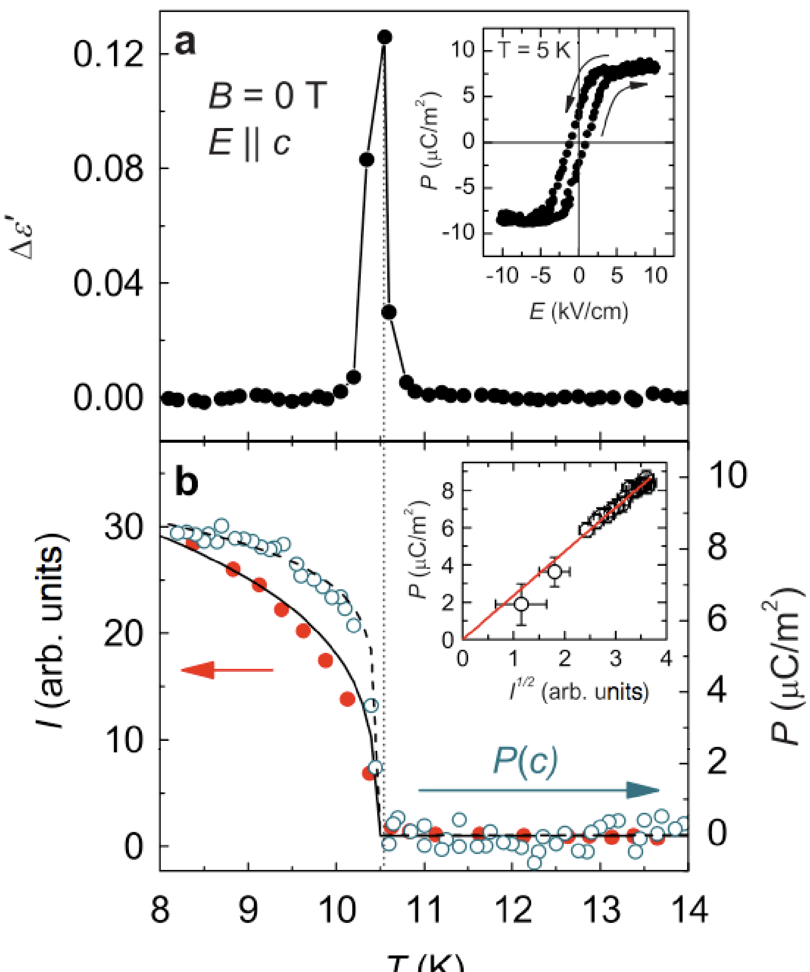

$\mathbf{q}$ = (1/2, 0.463, 0)

- measured with neutron diffraction
- incommensurate amplitude modulated magnetic order below $T_N$
- magnetic moments of $Fe^{3+}$ almost orthogonal to **q**
- no inversion centre
- ➢ electric polarization is allowed

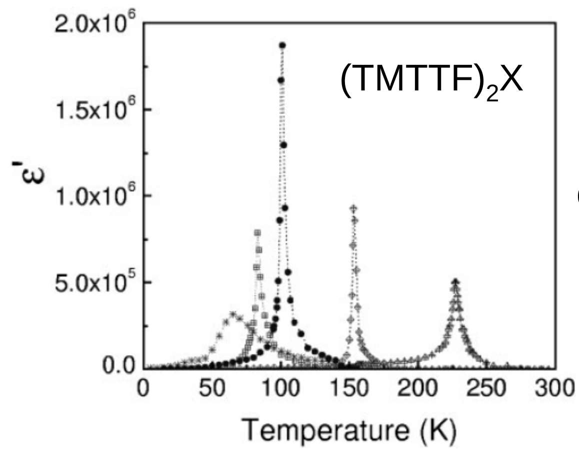
M. Pregelj *et al.*, Phys. Rev. Lett. **103**, 147202 (09)

# Dielectric measurements

$FeTe_2O_5Br$



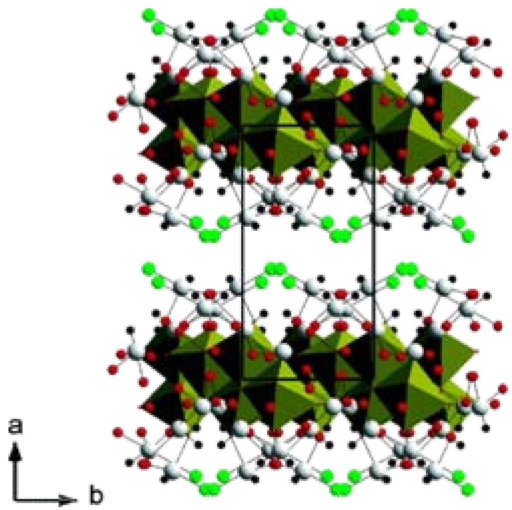

M. Pregelj *et al.,* Phys. Rev. Lett. **103**, 147202 (09)

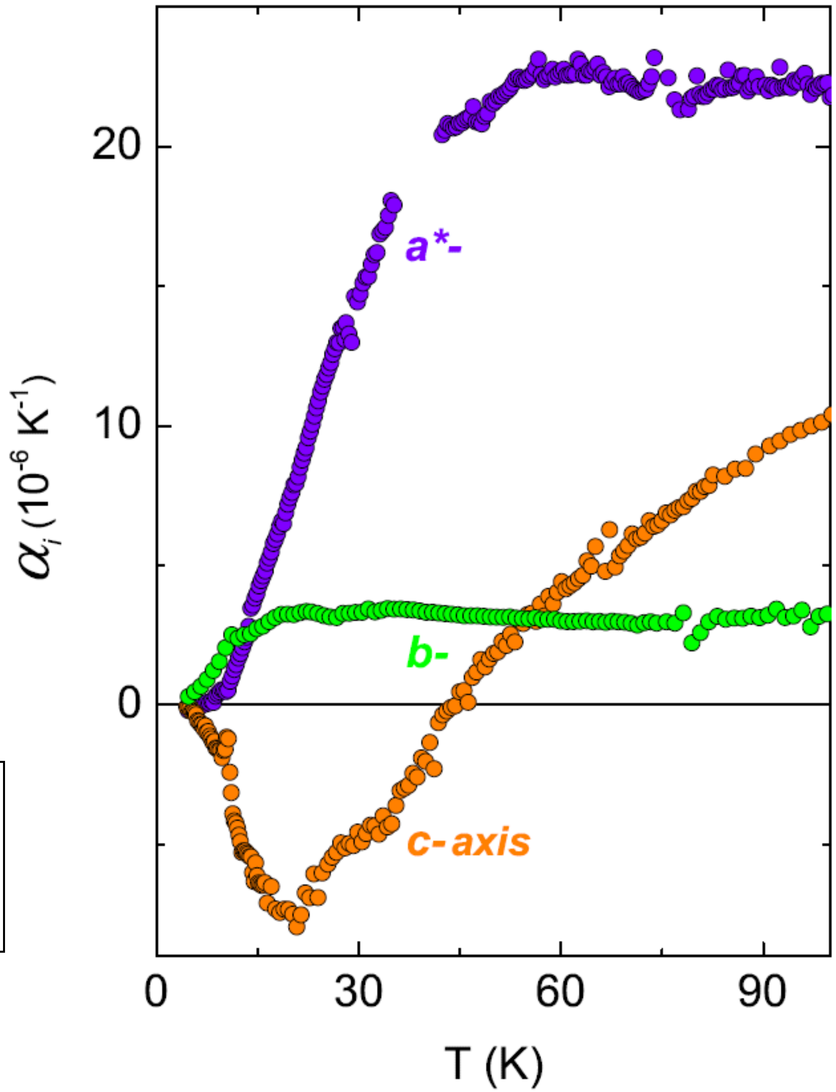



F. Nad *et al.*, J. Phys. Soc. **75**, 051005 (06)

- sharp peak in **ε′** → FE transition
- spontaneous electric polarization (// *c*-axis) appears simultaneously with the long-range magnetic order
- ferroelectric order perpendicular to **q** and to $Fe^{3+}$ magnetic moments
- ascribed to the polarization of $Te^{4+}$ Ions

# Thermal expansion

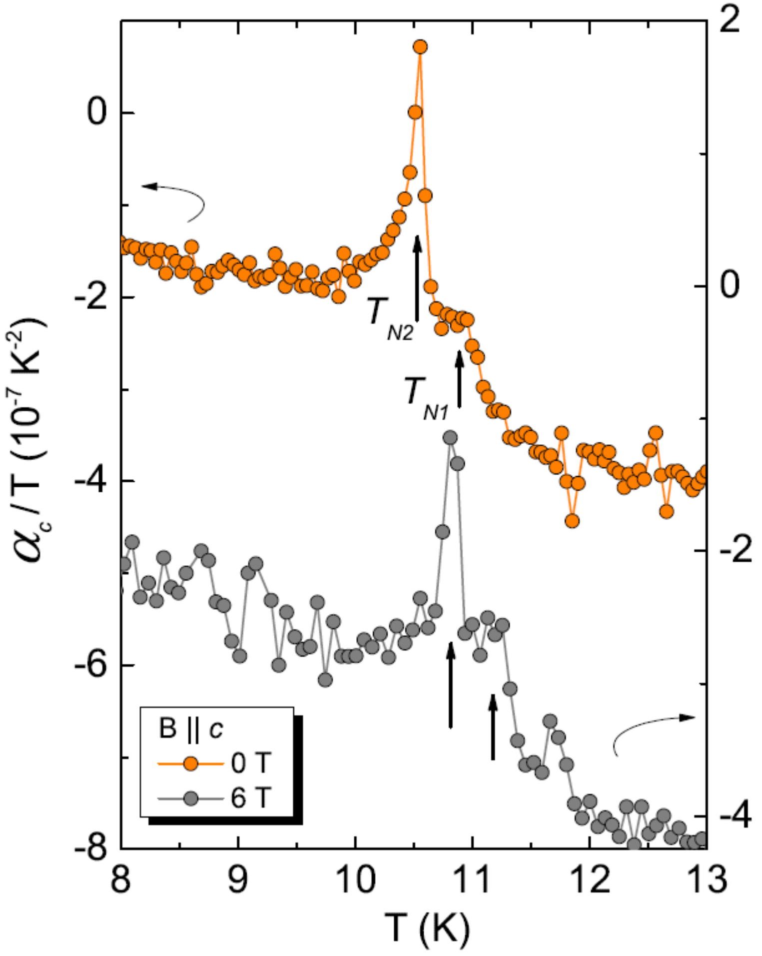


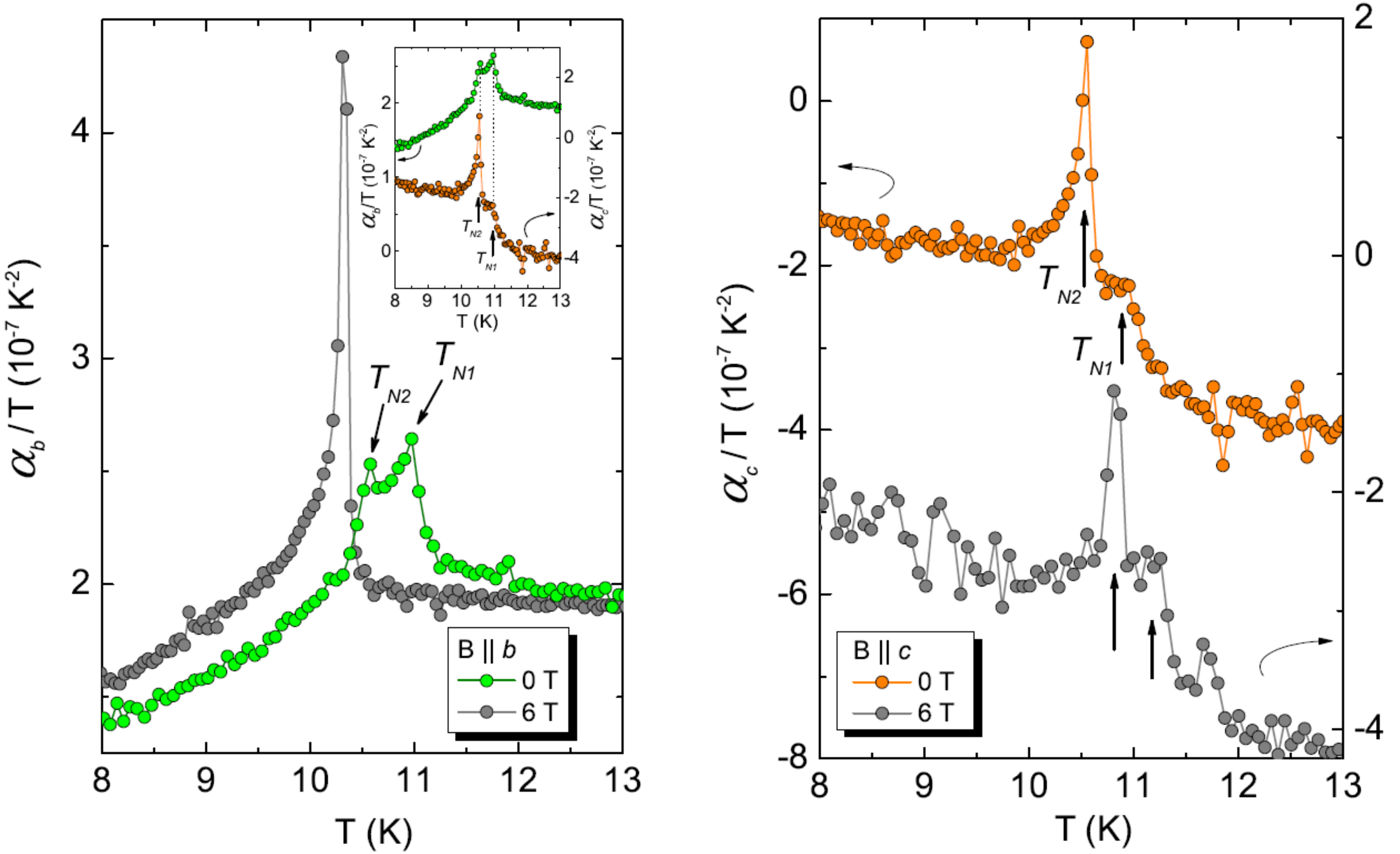

- strongly anisotropic lattice effects
- First sign of short-range order at ~ 50 K

# Thermal expansion

- Phase transition anomalies sit on top of a negative background
- λ-type transition at 10.6 K
- Step-like change at 11 K
- ➢ Mean-field transition

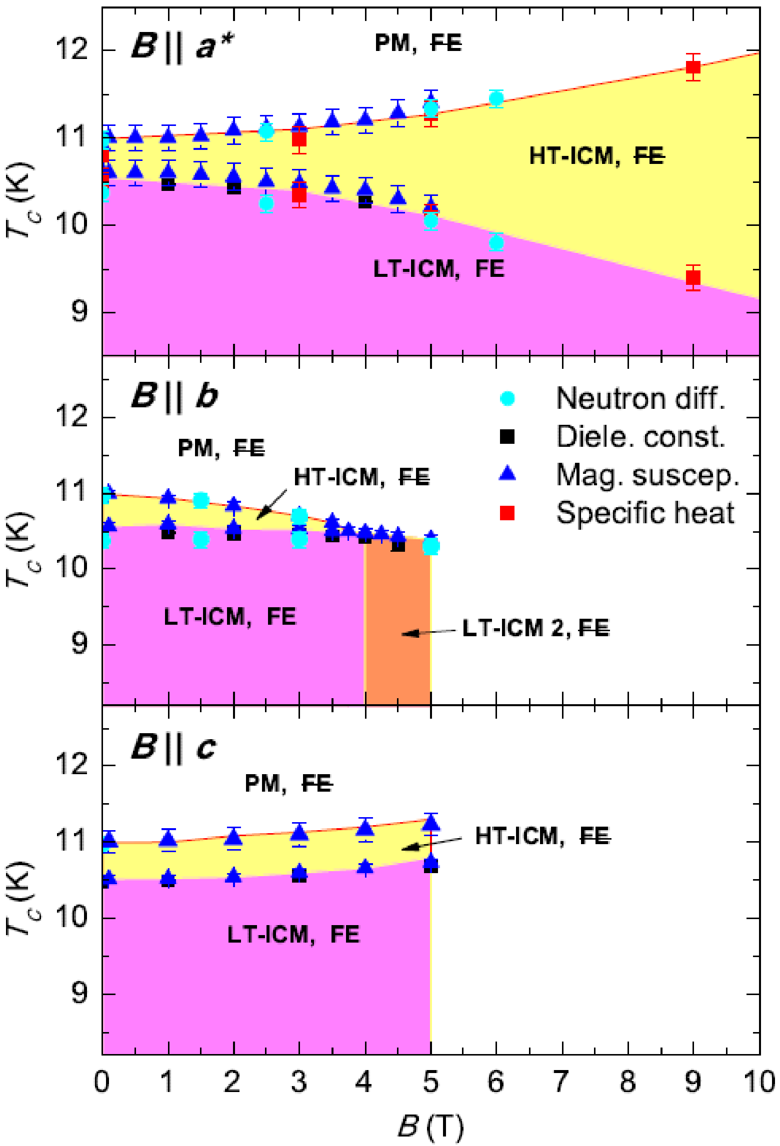


# Thermal expansion




- negative field dependence of transition temperature along *b* direction
- positive field dependence along *c* direction

# Magnetic phase diagram




## Conclusions

- First sign of short-range magnetic correlations at 50 K
- At $T_{N1}$ = 11.0 K magnetic p.t. into the HT-ICM phase
- Already 0.4 K lower at $T_{N2}$ second p.t. into the LT-ICM phase accompanied with electric polarization
- When magnetic field is applied transition temperatures shift
- For *B* // *b* and *B* > 4.5 T, the HT-ICM phase disappears along with the electric polarization in the LT-ICM phase