Cation reorientation and octahedral tilting in the metal-organic perovskites MAPI and FAPI

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Collaborations

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anelastic spectroscopy

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Giovanna Pennesi,
Gloria Zanotti — CNR-ISM - Roma — sample preparation, DSC

Amanda Generosi — X-ray

Summary

- Metallorganic lead-halide perovskites:
  - MAPI - $MAPbI_3$ [MA = CH_3NH_3]
  - FAPI - $FAPbI_3$ [FA = $HC(NH_2)_2$]

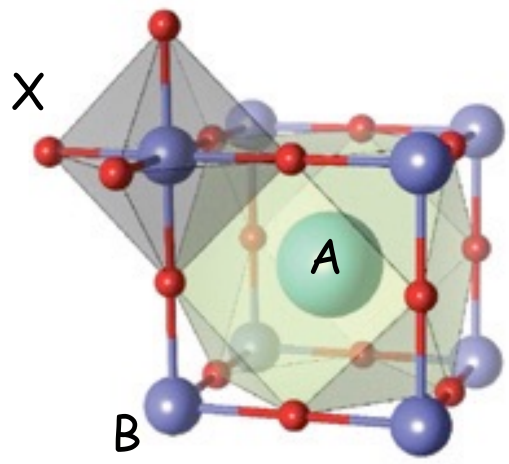
- Anelastic spectra of MAPI and FAPI: structural transitions and relaxation due to cation reorientation and octahedral tilting

- Competition between polar and antiferrodistortive modes and correlated dynamics of the methylammonium molecules in MAPI

- Instability of cubic FAPI and influence of temperature, pressure, and humidity on the transition kinetics among the various polymorphs

  J. Phys. Chem. Lett. 10, 2463 (2019); J. Phys. Chem. C 124, 22972 (2020)

Hybrid metal-organic halide perovskites



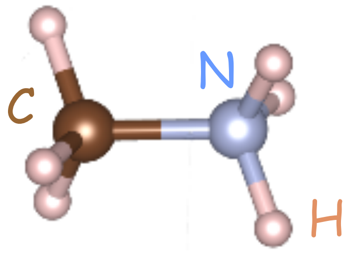
ABX_3

A = organic molecules (**methylammonium**, **formamidinium**, …)

B = $\mathbf{Pb^{2+}}$, Sn^{2+}, Mn^{2+}, Cd^{2+};

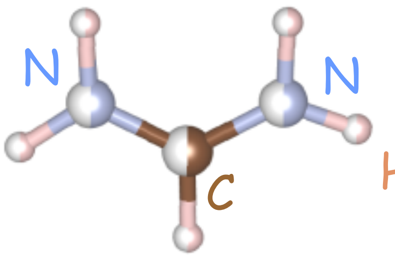
X = Cl^-, Br^-, $\mathbf{I^-}$

$MAPbI_3$ (MAPI)



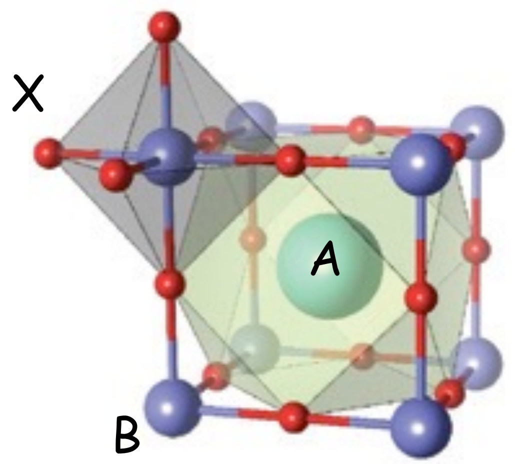
MA = CH_3NH_3

$FAPbI_3$ (FAPI)



FA = $CH(NH_2)_2$

Hybrid metal-organic halide perovskites



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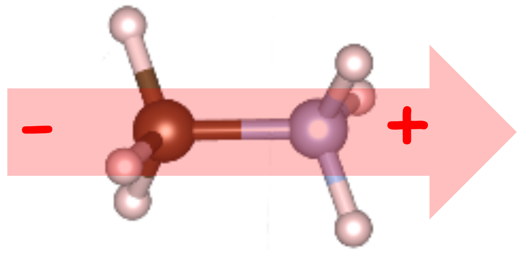
X = Cl^-, Br^-, **I^-**

Goldschmidt's tolerance factor

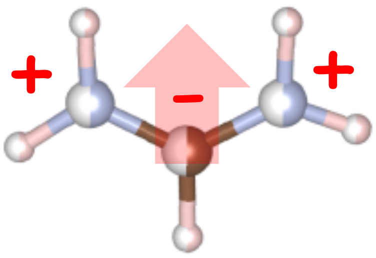
$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \rightarrow t = 1$$

cubic structure

$MAPbI_3$ (MAPI)

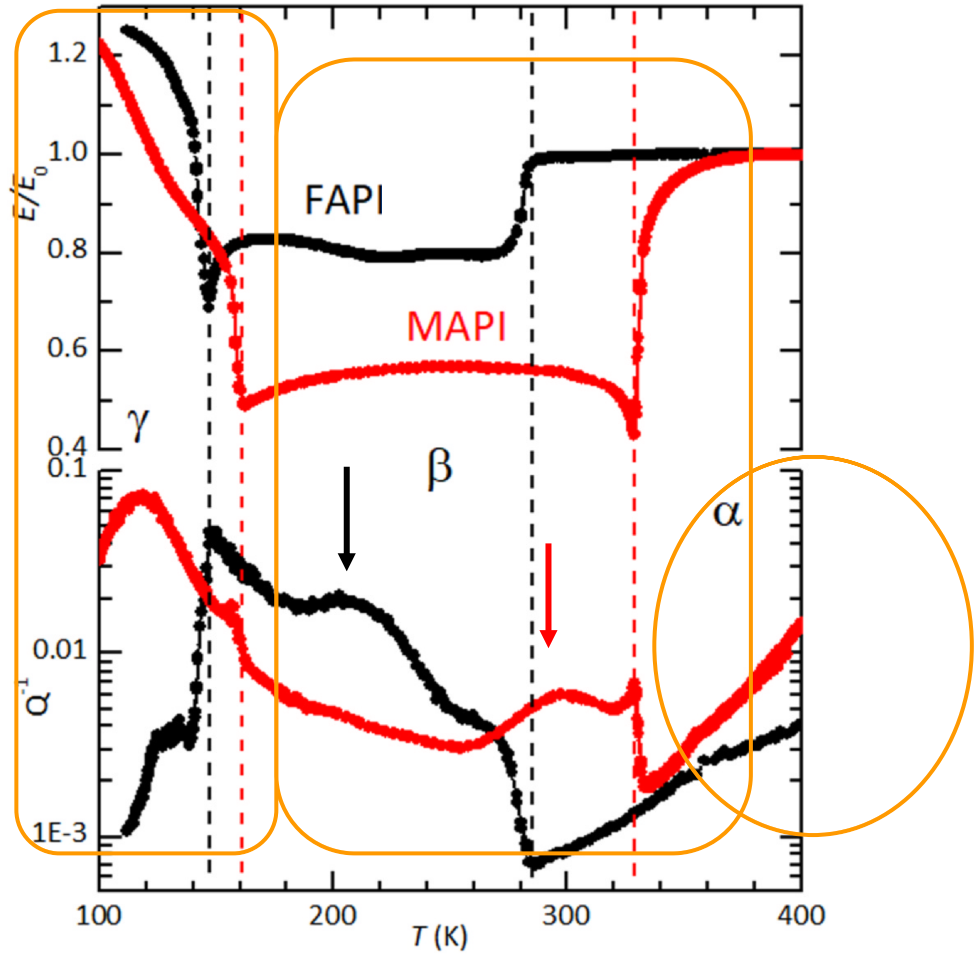


$FAPbI_3$ (FAPI)



Anelastic spectra and dielectric permittivity of MAPI and FAPI

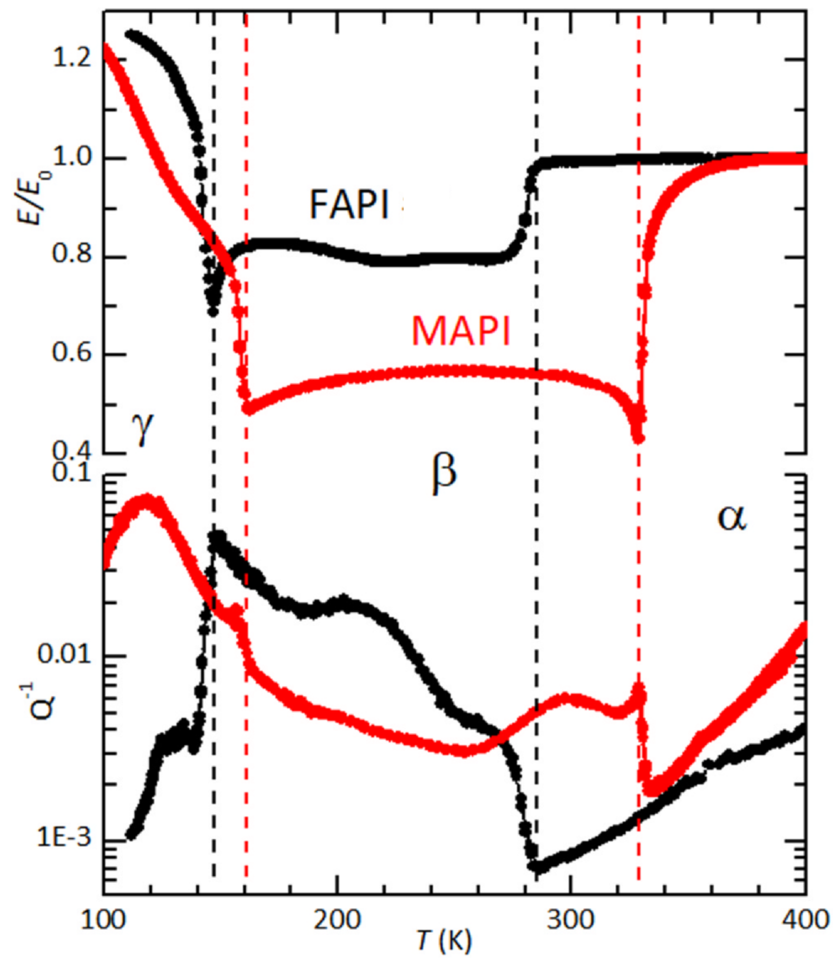
(~1 kHz) Anelastic spectra



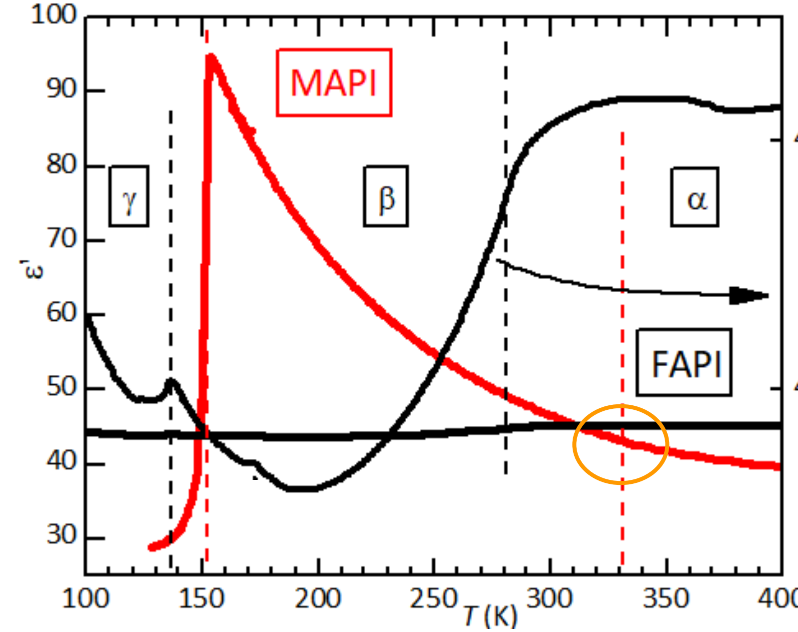
J. of All. and Comp. 867, 158210 (2021)

Anelastic spectra and dielectric permittivity of MAPI and FAPI

(~1 kHz) Anelastic spectra



Dielectric permittivity (1 MHz)



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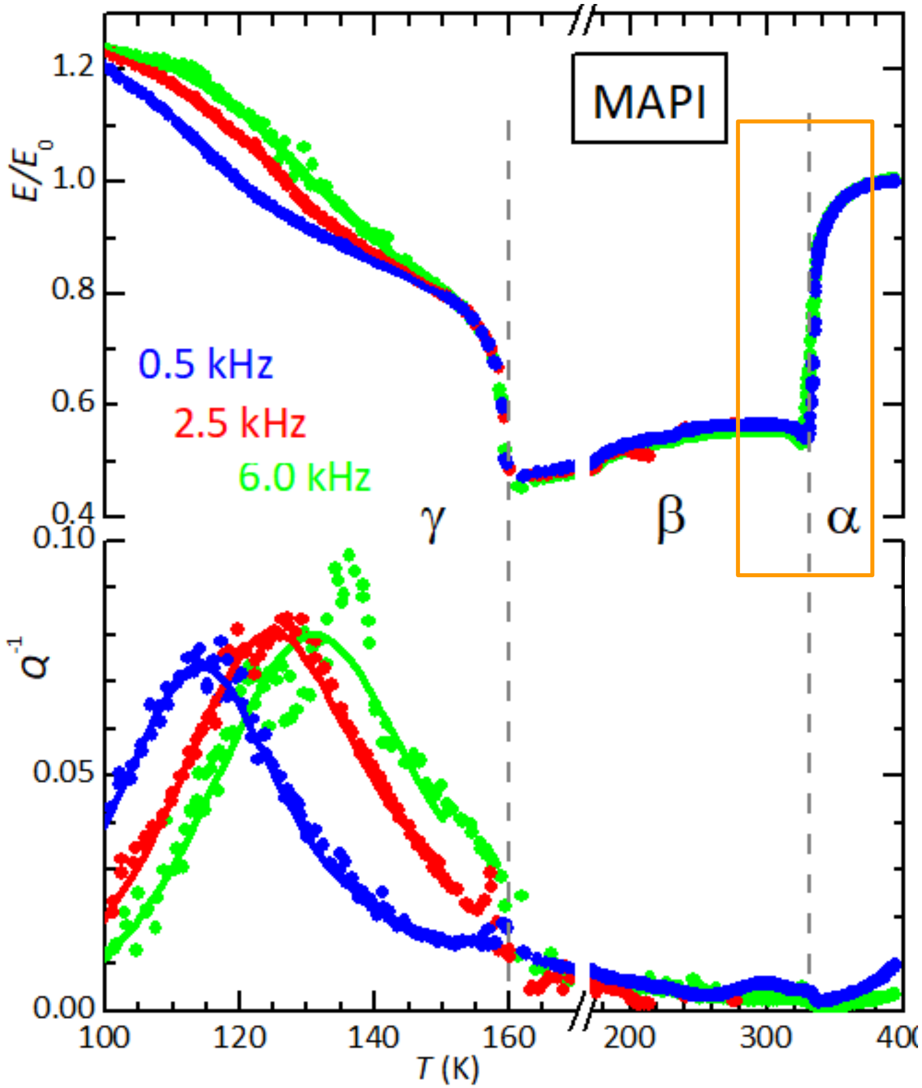
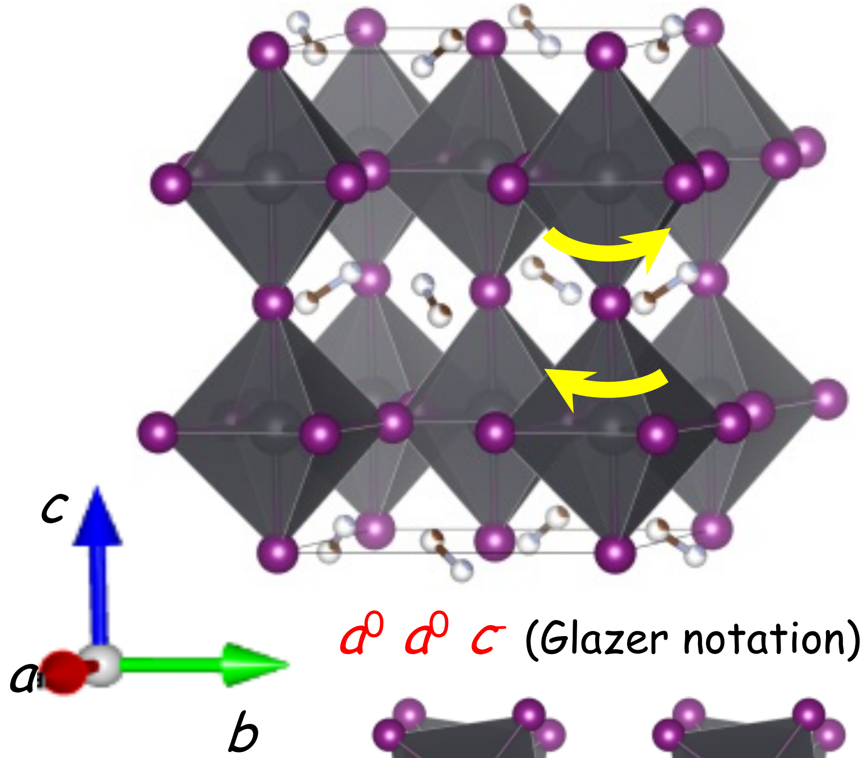
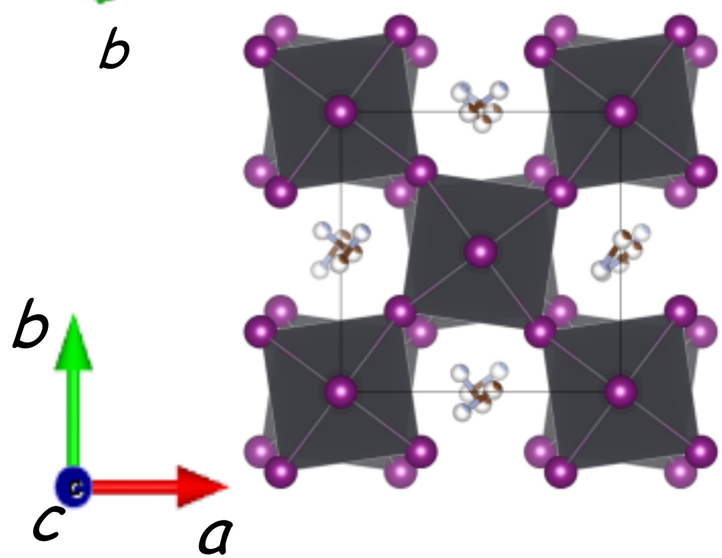
- both perovskites in cubic α–phase above RT
  (freely rotating MA and FA cations)
- two tilt transition of the PbI_6 octahedra into a tetragonal β and orthorombic γ phase
  (loss of orientational degrees of freedom of the MA and FA cations)

Anelastic spectra of MAPI: cubic-tetragonal transition





$a^0\ a^0\ c^-$ (Glazer notation)



Expansion of the free energy in powers of Q (OP) and σ

$$G = F - \varepsilon\sigma \qquad \varepsilon = -\frac{\partial G}{\partial \sigma}$$

$$G = \frac{a(T-T_C)}{2}Q^2 + \frac{B}{4}Q^4 + \frac{C}{6}Q^6 - \frac{s_0}{2}\sigma^2 - g\sigma Q - h\sigma Q^2 + \cdots$$

$g = 0$

if Q is the tilt angle or polarization

second order transition

$(B > 0, C = 0)$

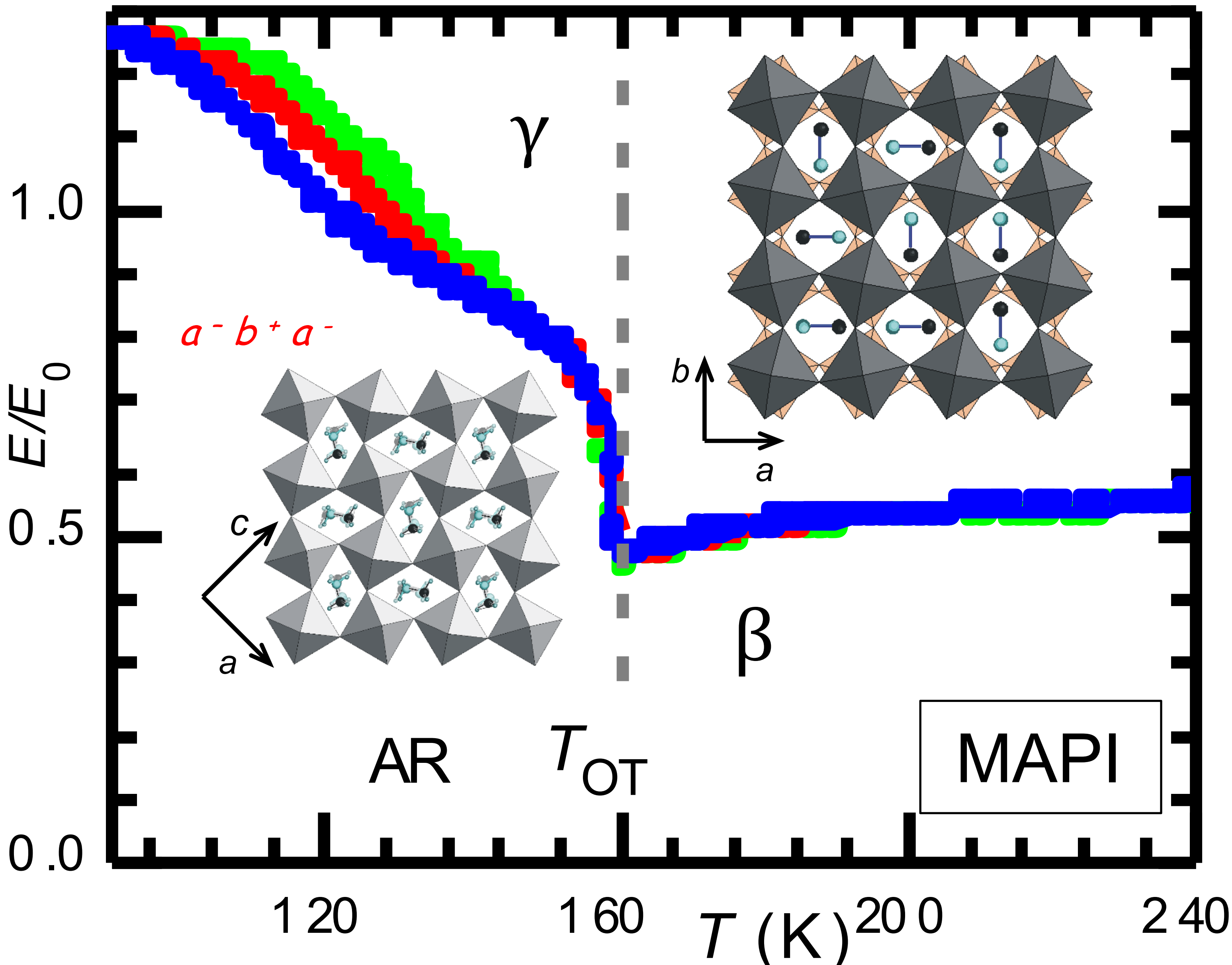
$$\left(s = \frac{d\varepsilon}{d\sigma}\right)$$

$$s = \begin{cases} s_0 & T > T_C \\ s_0 + \dfrac{2h^2}{B} & T < T_C \end{cases}$$

($s_0 \rightarrow$ cubic phase)

steplike softening

Coupling between FE and tilt modes



Coupling between two modes (within Landau theory of p. t.).

coupling part

$$F = \frac{\alpha_2}{2}P^2 + \frac{\alpha_4}{4}P^4 + \frac{\beta_2}{2}Q^2 + \frac{\beta_4}{4}Q^4 + \boxed{\frac{\gamma}{2}P^2Q^2}$$

$\alpha_2 = \alpha_0(T - T_C)$ $\rightarrow$ FE transition below T_C

if $\gamma = 0$

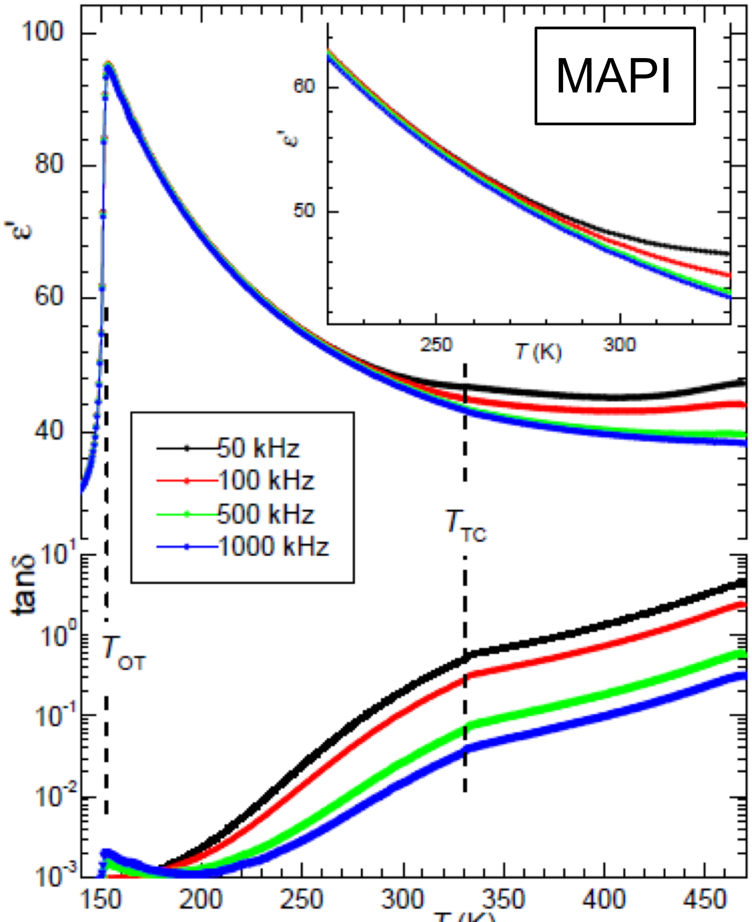
$\beta_2 = \beta_0(T - T_T)$ $\rightarrow$ tilt transition below T_T

$$B = \frac{\beta_0}{\beta_2}\gamma$$

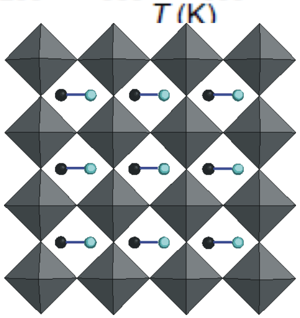
$$\epsilon = \epsilon_\infty + \frac{C}{T - T_C + BC(T_T - T)}$$

J. Phys. Chem. Lett. 9, 4401 (2018)

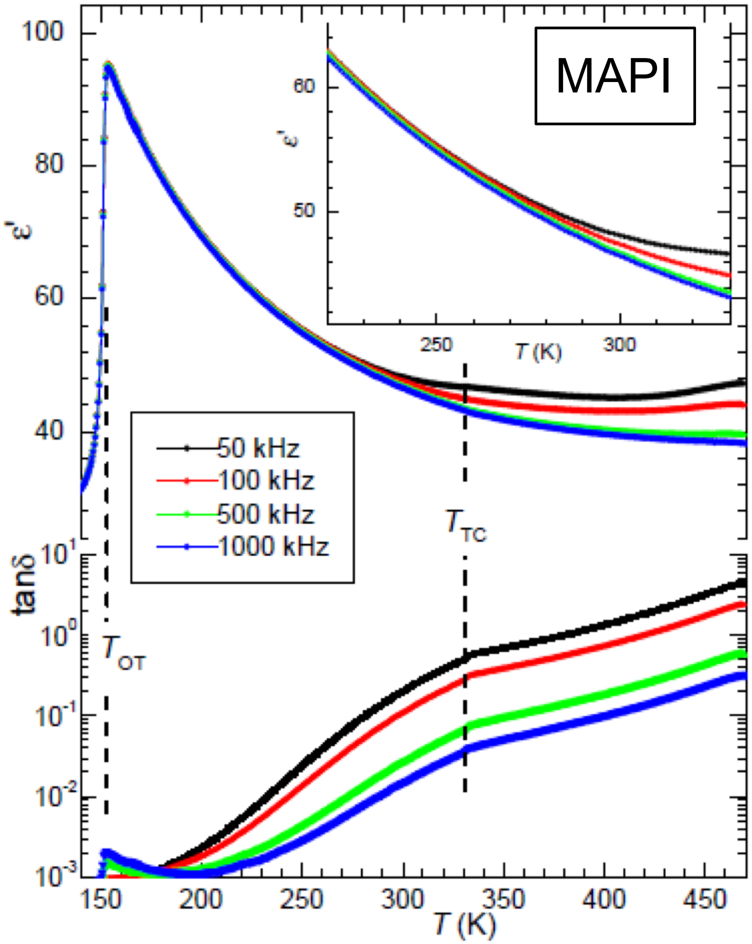
Competition between polar and antiferrodistortive modes

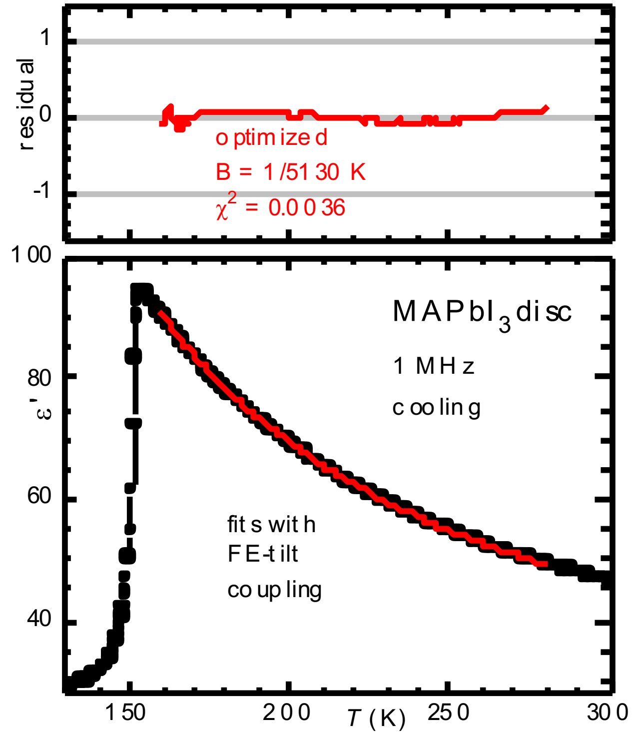


hypothetical
FE mode



Competition between polar and antiferrodistortive modes





$$\epsilon = 1 + \chi = \epsilon_\infty + \frac{C}{T - T_C + BC(T_T - T)}$$

χ diverges at $T_{FE} = \dfrac{T_C - BCT_T}{1 - BC}$

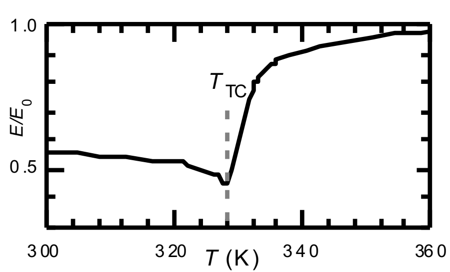
from best fit ($T_T = 328$ K):

$B = 1.95 \cdot 10^{-4}$ K

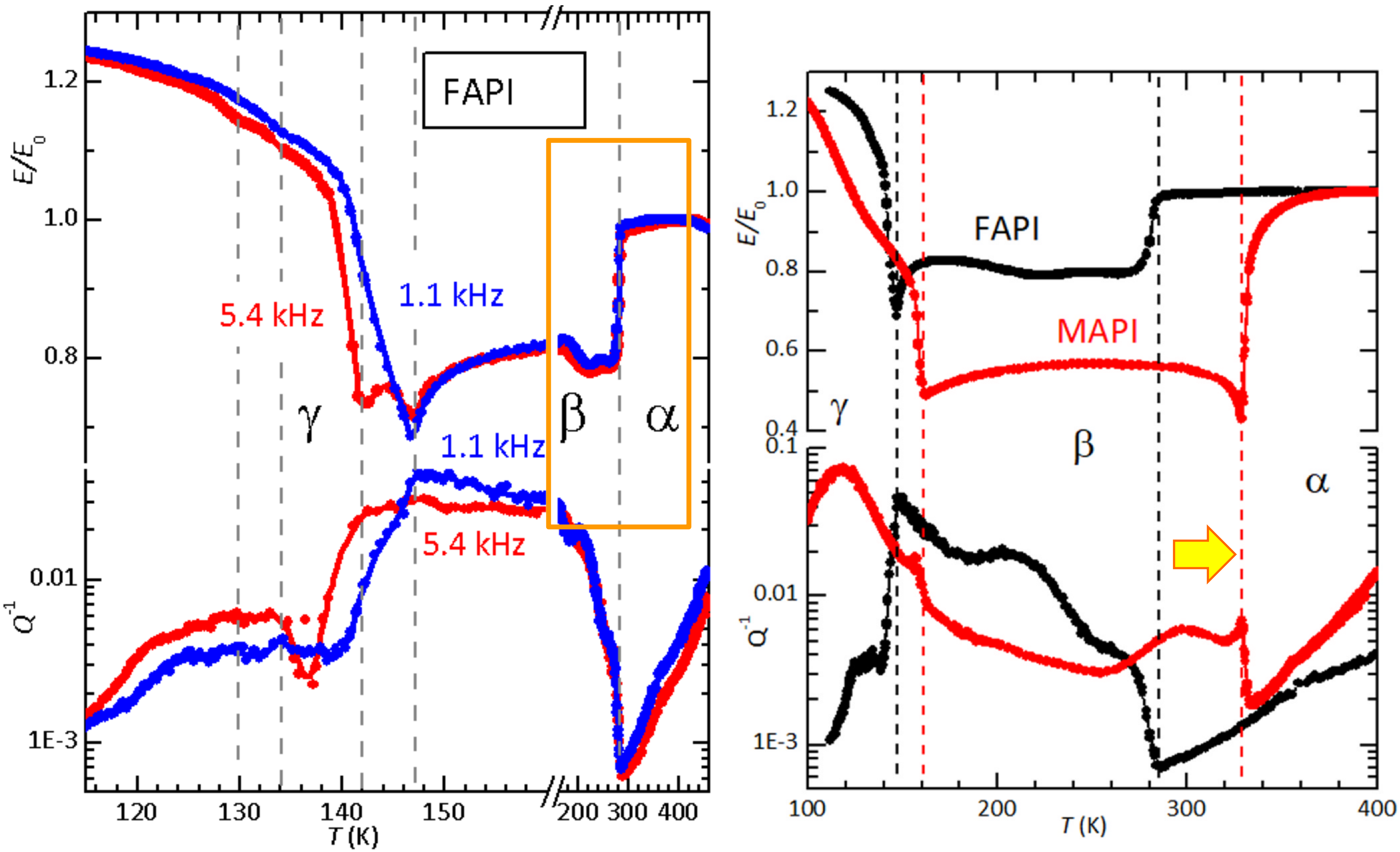
$C = 3190$ K

$T_C = 223$ K

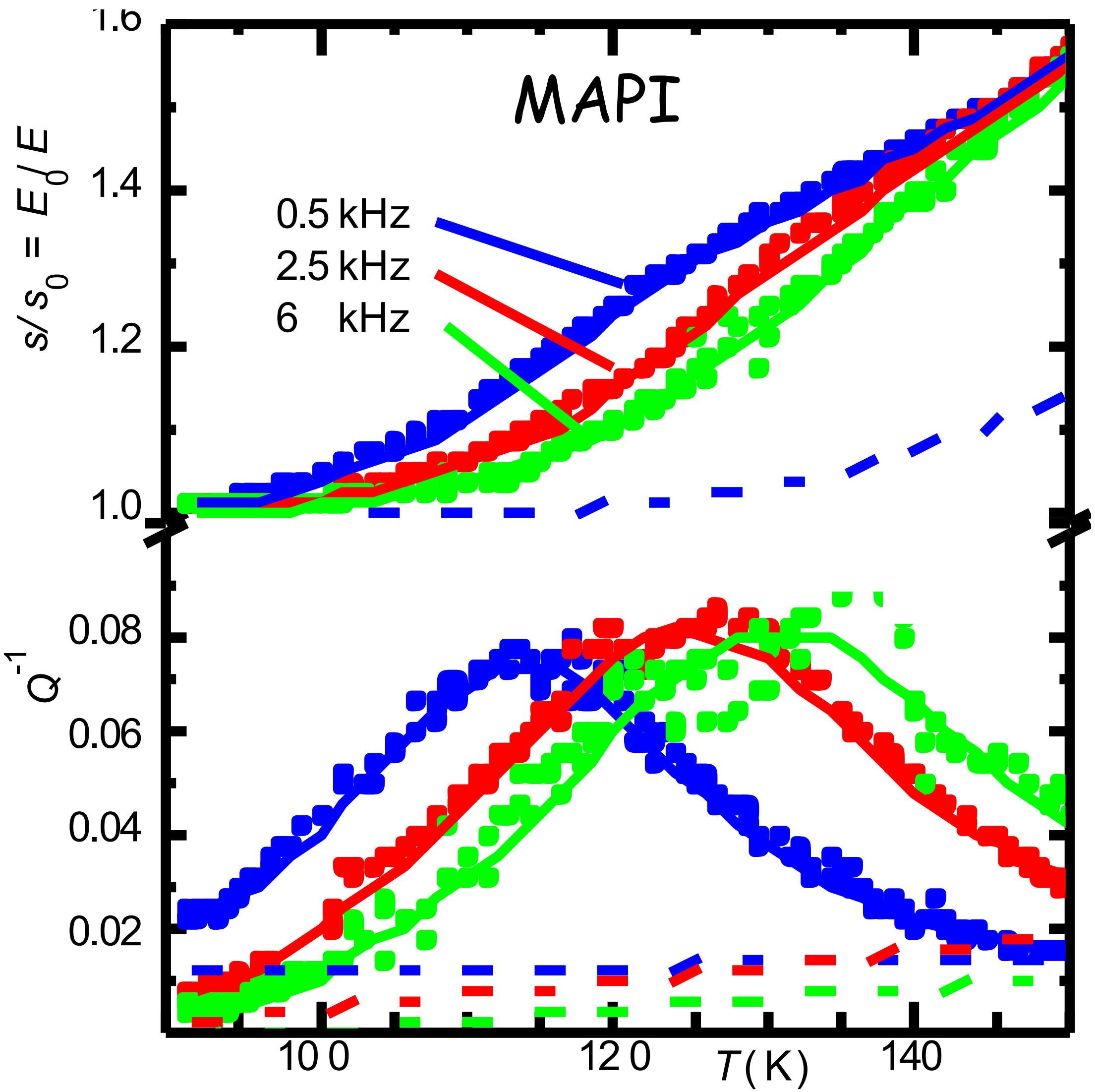
$T_{FE} = 50$ K



FAPI: $\alpha \rightarrow \beta$ transition



Anelastic relaxation due to cation reorientation (MAPI)



$$s = s_{bg} + \frac{\Delta s}{[1 + (i\omega\bar{\tau})^{-\alpha}]^{\gamma}}$$

$$\bar{\tau} = \tau_0 e^{W/T} \cosh^{-1}(A/2T)$$

$$\Delta s = \frac{\Delta}{T\cosh^2(A/2T)}$$

$\tau_0 = 2.0 \cdot 10^{-12}$ s

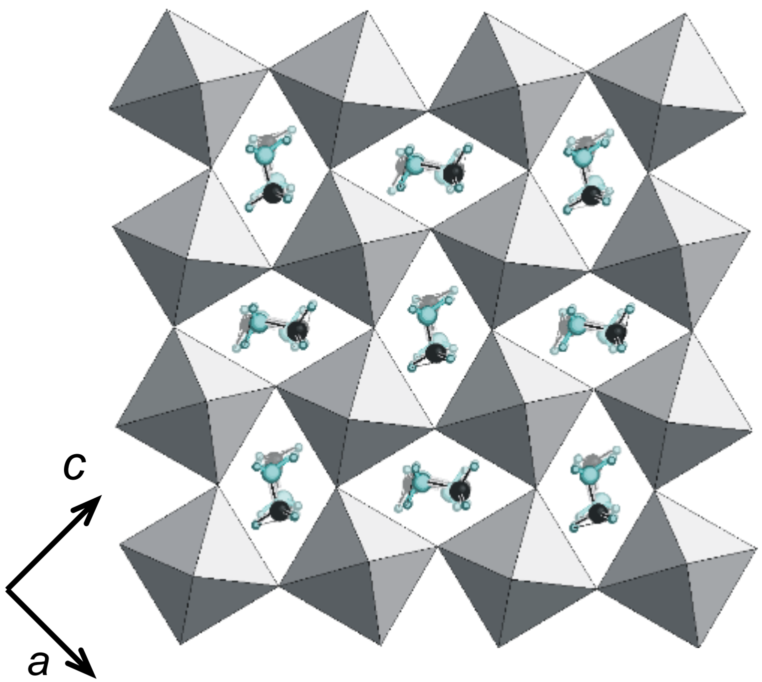
$W = 2340$ K

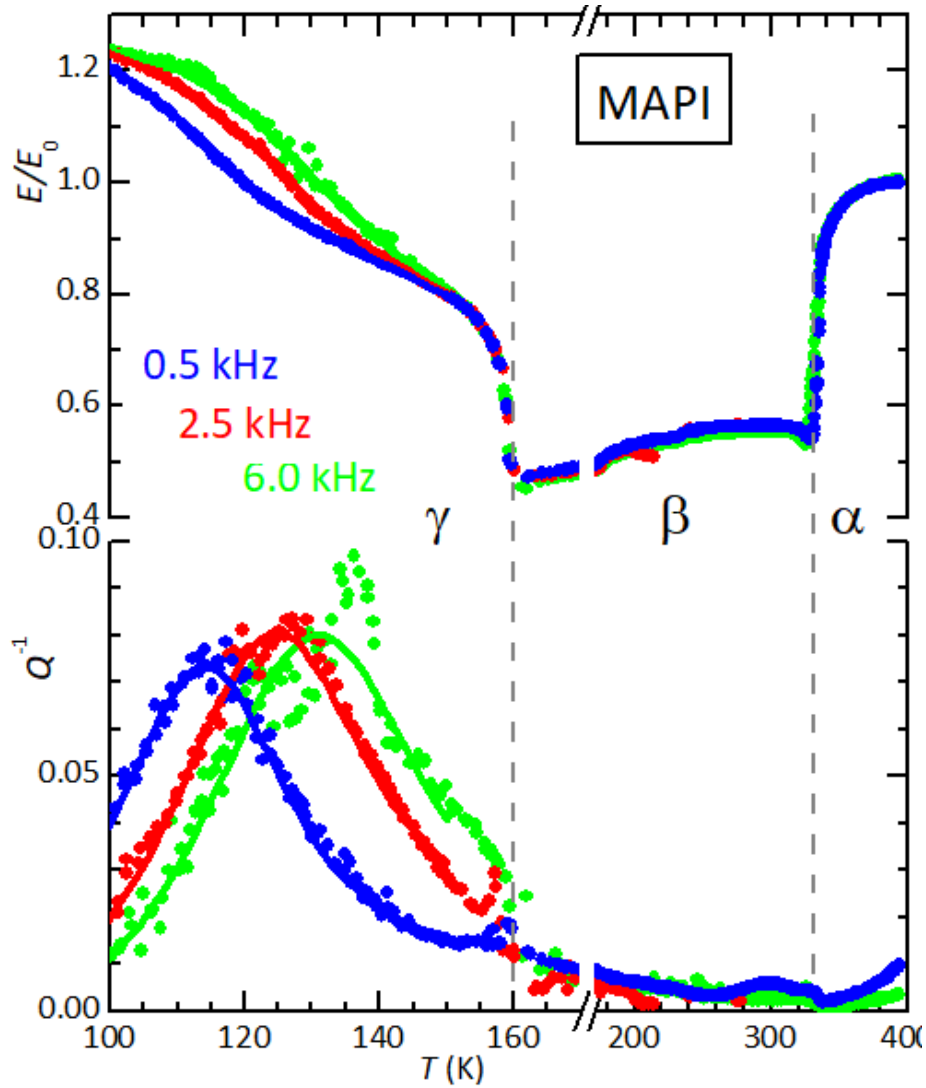
$A = 366$ K

$\alpha = 0.797$

$\gamma = 0.498$

MAPI: β → γ transition





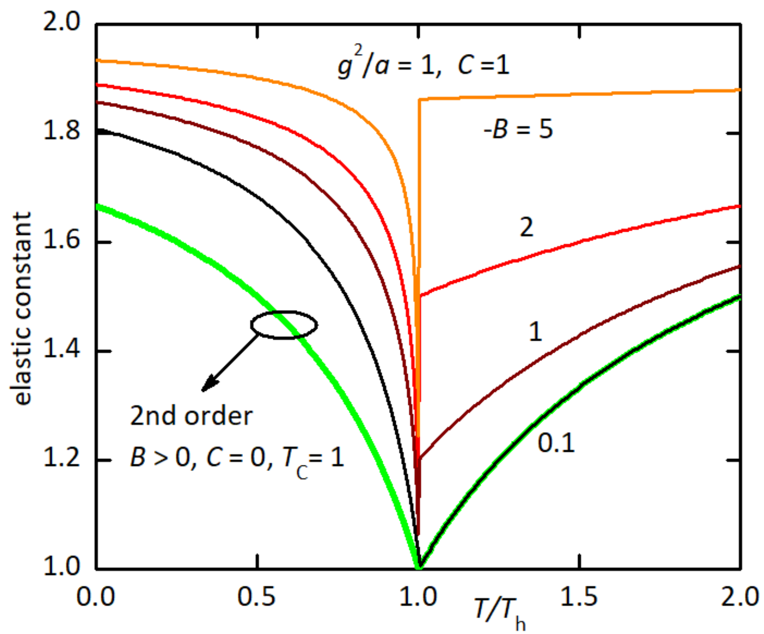
First order transition

$$G = \frac{a(T-T_C)}{2}Q^2 + \frac{B}{4}Q^4 + \frac{C}{6}Q^6 - \frac{s_0}{2}\sigma^2 - g\sigma Q - h\sigma Q^2 + \cdots$$

first order transition $(B < 0)$

$g \neq 0, h = 0$ if Q is a symmetrized coordinate

$$T_h = T_C + \frac{B^2}{4aC} \qquad s - s_0 = \begin{cases} \dfrac{g^2}{(T - T_C)} & T > T_C \\ \dfrac{g^2}{4a\left[T_h - T + \sqrt{(T_h - T_C)(T_h - T)}\right]} & T < T_C \end{cases}$$



FAPI: β → γ transition