Origin of negative electrocaloric effect in *Pnma*-type antiferroelectric perovskite

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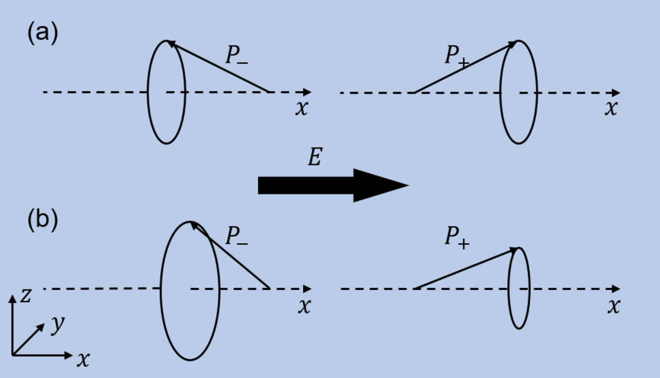
Introduction

Electrocaloric effect (ECE): future cooling technology

Positive and negative ECE can be utilized in combination to improve the performance of cooling/heating devices

Negative ECE in antiferroelectrics (AFE)

- Dipole canting model[1]: only taken the dipolar degrees of freedom into account

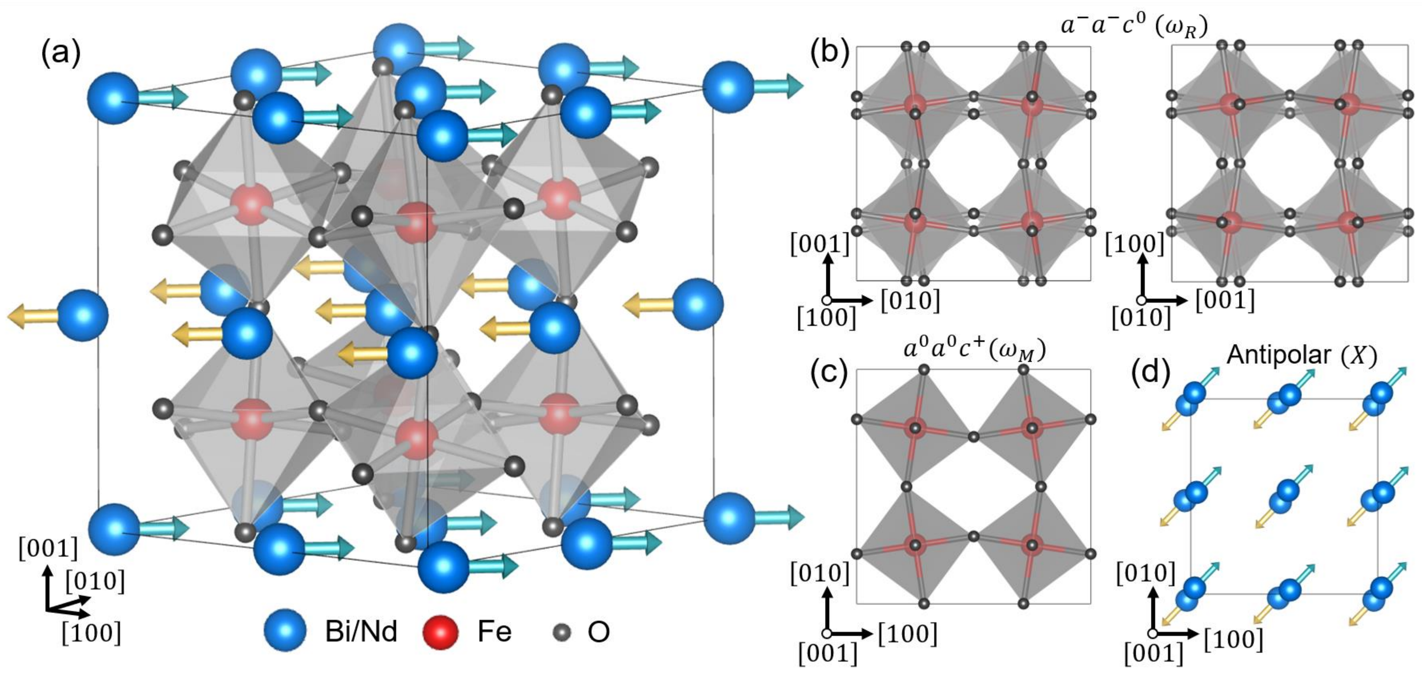


- Most AFE perovskites have octahedral tilting as primary order parameter[2-3]

Questions:

- Can the dipole canting model explain negative ECE for AFE with antiferrodistortion as primary order parameter?
- Contribution to ECE from each important degree of freedom?
- Effect of electric field direction to ECE?

System: $Bi_{0.6}Nd_{0.4}FeO_3$ (BNFO) AFE (space group: *Pnma*)



Methods

Computational Details

Effective Hamiltonian method[4-7]

$$E_{\text{tot}} = E_{\text{BFO}}(\{\boldsymbol{u_i}\},\{\eta_H\},\{\eta_I\},\{\boldsymbol{\omega_i}\},\{\boldsymbol{m_i}\}) + E_{\text{alloy}}(\{\boldsymbol{u_i}\},\{\boldsymbol{\omega_i}\},\{\boldsymbol{m_i}\},\{\eta_{\text{loc}}\})$$

Monte-Carlo (MC) simulation

- Supercell: 12×12×12
- Electric field: [001], $[1\bar{1}0]$, [110]
- Temperature: 10 K - 1500 K
- MC sweeps: 20000 + 20000

Landau Model

$$F = \frac{1}{2}a_{\omega_R}(T)\omega_R^2 + \frac{1}{4}b_{\omega_R}\omega_R^4 + \frac{1}{2}a_{\omega_M}(T)\omega_M^2 + \frac{1}{4}b_{\omega_M}\omega_M^4 + \frac{1}{2}a_X(T)X^2 + \frac{1}{4}b_X X^4 + \frac{1}{2}a_P(T)P^2 + \frac{1}{4}b_P P^4 - EP - cX\omega_R\omega_M + \frac{1}{2}d_1P^2\omega_R^2 + \frac{1}{2}d_2P^2\omega_M^2$$

$$\Delta S = -A_{\omega_R}[\omega_R^2(T,E_2) - \omega_R^2(T,E_1)] - A_{\omega_M}[\omega_M^2(T,E_2) - \omega_M^2(T,E_1)] - A_X[X^2(T,E_2) - X^2(T,E_1)] - A_P[P^2(T,E_2) - P^2(T,E_1)]$$

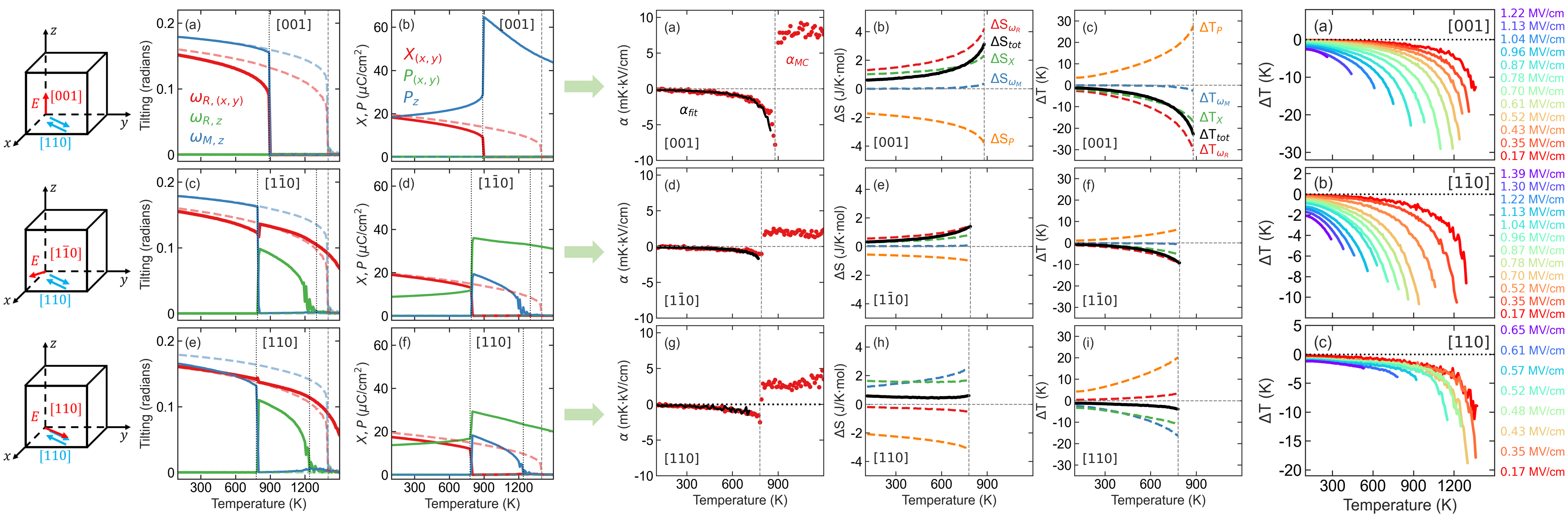
$$\Delta T = -\frac{T}{C_{ph}}\Delta S = \Delta T_{\omega_R} + \Delta T_{\omega_M} + \Delta T_X + \Delta T_P$$

$$\alpha = \frac{\Delta T}{\Delta E} = -\frac{T}{\Delta E \cdot C_{ph}}\Delta S$$

Perturbative Approach[8]

$$\Delta T(E_\alpha) \approx -\frac{T^{(0)}}{C_E^{(0)}}\left(\pi_\alpha^{(0)}E_\alpha + \frac{1}{2}\pi_{\alpha\alpha}^{(1)}E_\alpha^2 + \frac{1}{3}\pi_{\alpha\alpha\alpha}^{(2)}E_\alpha^3 + \cdots\right) = \Delta T^{(1)}(E_\alpha) + \Delta T^{(2)}(E_\alpha) + \Delta T^{(3)}(E_\alpha) + \cdots$$

Results



The contribution of the octahedral tilt (ω_R, ω_M) to the EC temperature is related to the direction of the electric field.

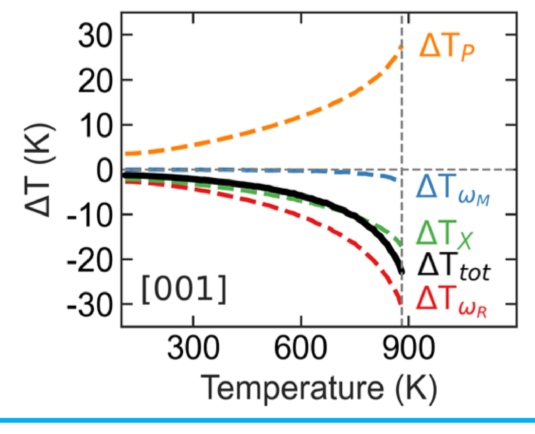
The electric field (direction, magnitude) can be used to regulate the EC temperature.

Dipole Canting Model

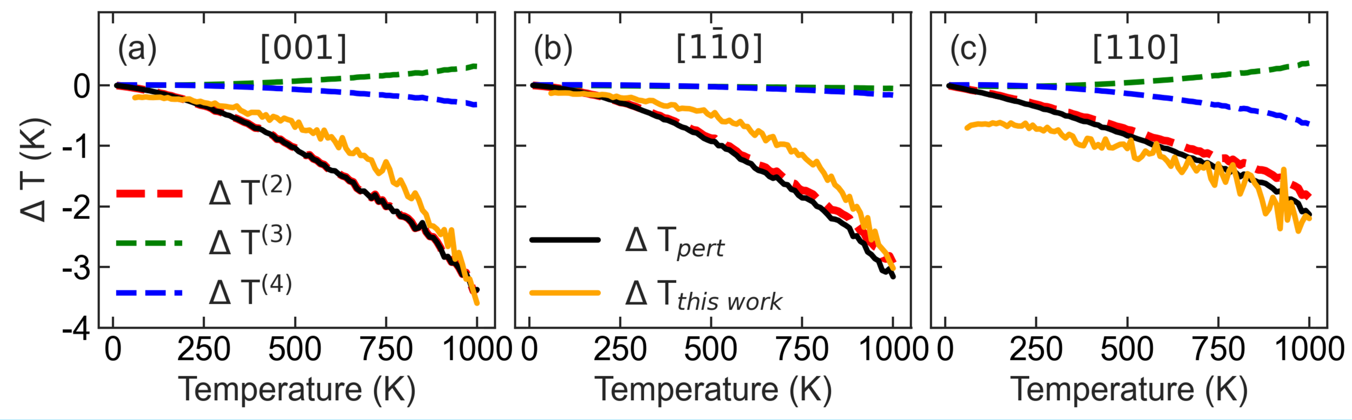
Dipole: X and P

ΔT: $\Delta T_X < 0$, $\Delta T_P > 0$

$\Delta T_X + \Delta T_P > 0$



Perturbative Approach



The sum of the EC temperatures of the dipoles ($\Delta T_X + \Delta T_P > 0$) is always positive, which cannot explain the overall negative ECE.

The perturbative approach solely based on polarization agrees reasonably well with our predictions at low fields.

Summary

- Landau model with multiple important degrees of freedom
- Main contribution: ω_R/ω_M, P and X
- Octahedral tiltings must be considered explicitly
- ω_R/ω_M contribution to ECE sensitive to the direction of the electric field
- Max ΔT = -29 K ([001] 0.70 MV/cm)
- Room temperature ΔT = -4.7 K ([001] 1.13 MV/cm)
- Dipole canting model can not explain the negative ECE in AFE
- Perturbative approach is valid under low electric field

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Acknowledgement:

National Natural Science Foundation of China: No. 12074277
Natural Science Foundation of Jiangsu Province (BK20201404)
Office of Naval Research: No. N00014-21-1-2086

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