An Antipolar-driven Ferroelectric

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An Antipolar Driven ferroelectric: Phase Transition of Cu-Cl Boracite

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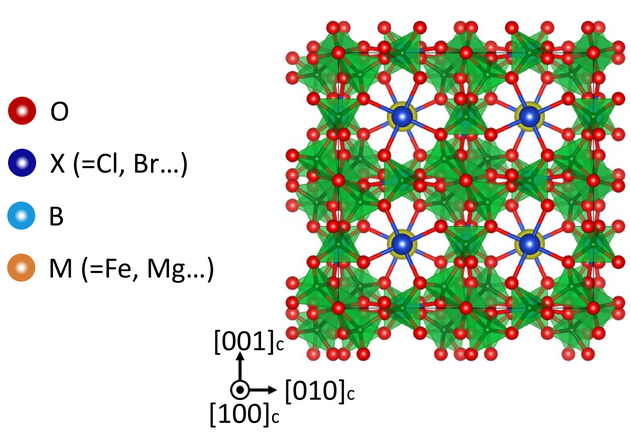
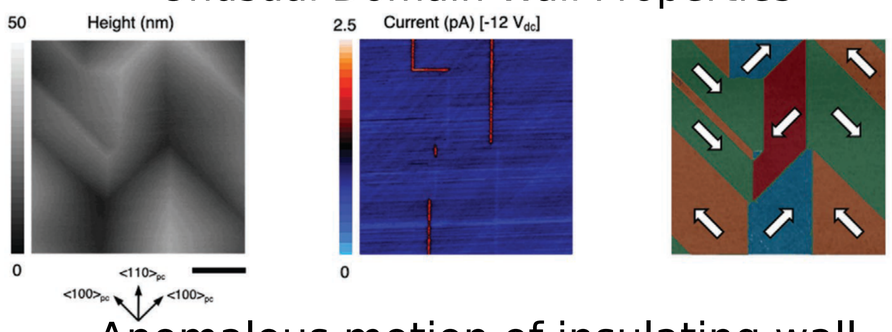
Boracite



- Discovered in the XVIII century: "Lünenburger Diamanten"
- Dispute about its polarity for a long time
- Revival as class I multifefroic
- Strong potential for pyroelectricty

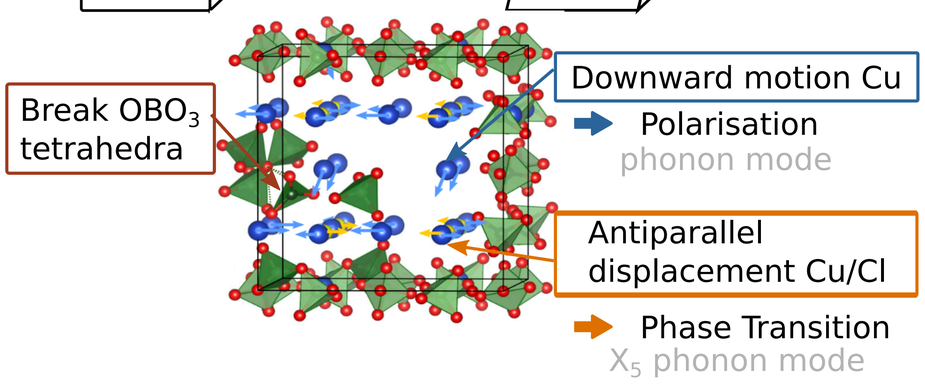
Unusual Domain Wall Properties



Anomalous motion of insulating wall consistent with negative capacitance [1]

Phase transition

Mechanism



Landau expansion

Phase transition $\bar{4}3m \longrightarrow mm2$

$$G = \frac{1}{2}a(T-T_c)q^2 + \frac{1}{4}bq^4 + \frac{1}{6}cq^6$$

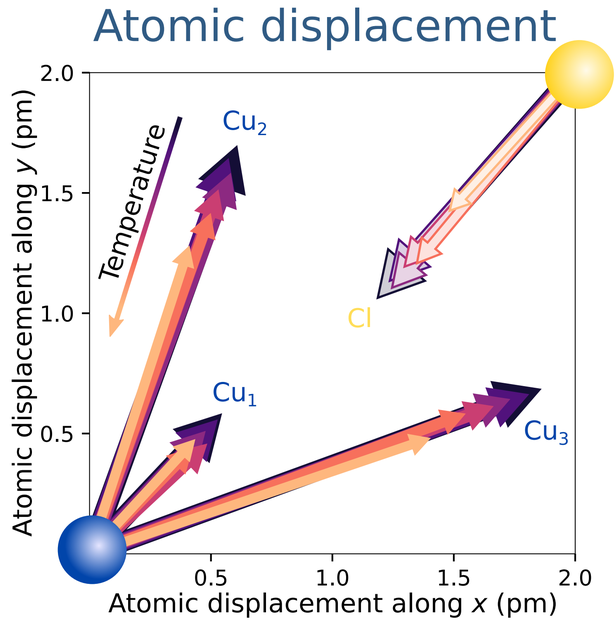
$$+\lambda_1 e_v q^2 + \lambda_2 e_t q^2 + \lambda_3 e_6 q^2 + \lambda_4 e_o^2 q^2 + \lambda_5\left(e_4^2 + e_5^2\right)q^2 + \lambda_6 e_4 e_5 q^2$$

$$+\lambda_7 e_6 P + \lambda_8 e_v P^2 + \lambda_9 e_t P^2 + \lambda_{10} e_4 e_5 P + \lambda_{11} e_0 P^2 + \lambda_{12} q^2 P$$

$$+\frac{1}{4}(C_{11}{}^0 - C_{12}{}^0)(e_o^2 + e_t^2) + \frac{1}{6}(C_{11}{}^0 - 2C_{12}{}^0)e_v^2 + \frac{1}{2}C_{44}{}^0(e_4^2 + e_5^2 + e_6^2) - EP$$

Towards probing directly the order parameter

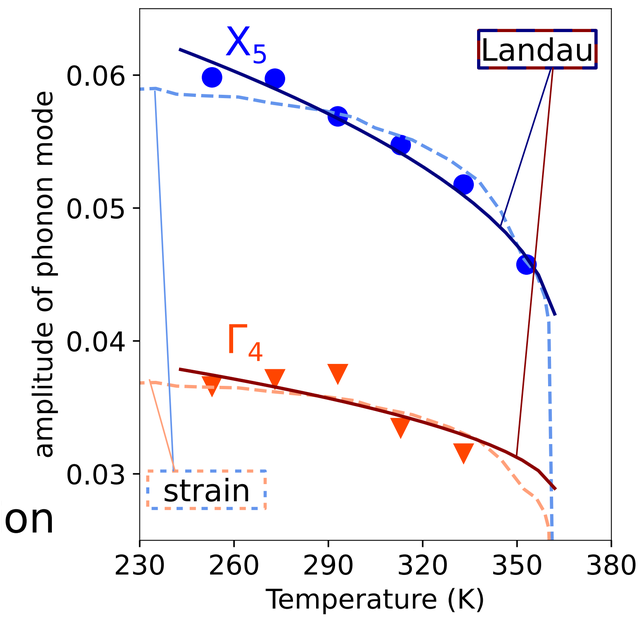
Atomic displacement



Not full agreement between strain and phonon amplitude

Displacements ↗ with temperature ↘

Separate the contribution of each phonon

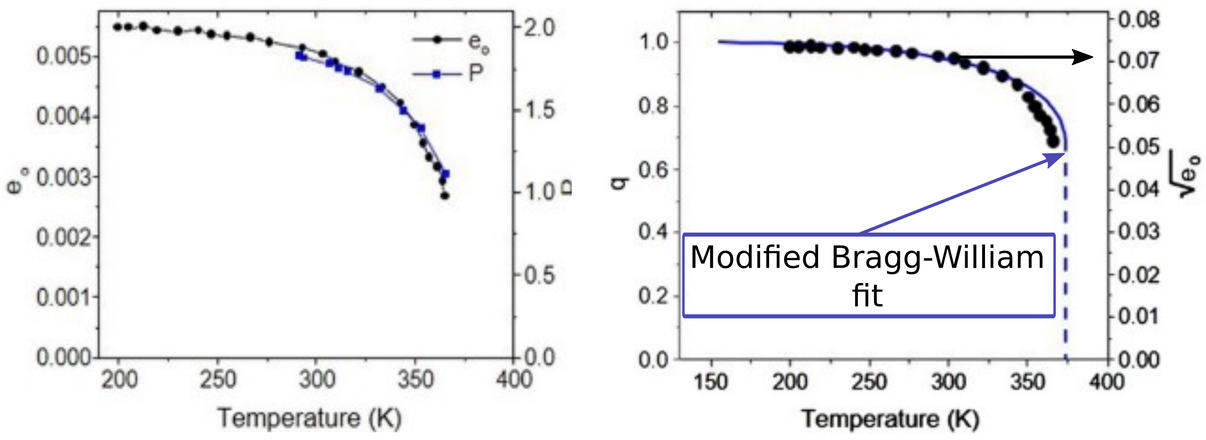


Suggest displacive phase transition

Phase transition- Macroscopic quantities

Strain

Good agreement between order-parameter and strain [2]

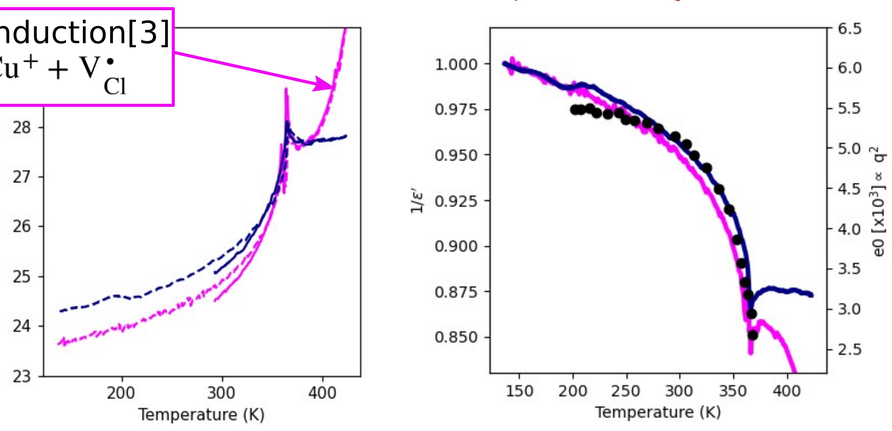


Dielectric permittivity

Unusual temperature dependence ⟶ ~~Curie-Weiss~~

Relaxation+conduction[3]

$$Cu^{2+} + O \rightarrow Cu^{+} + V_{Cl}^{\bullet}$$



Suggest order-disorder phase transition

Conclusion

Ferroelectric phase transition driven by **antipolar** phonon modes

Attempt to **directly** probe the thermal evolution of the **order parameter**

References

[1] Guy, J. G. M. et al. Adv. Mater. 33, 2008068 (2021).
[2] Fernandez-Posada, et al. J. Phys. Condens. Matter 33, 095402 (2021).
[3] Cochard, C. et al. Appl. Phys. Lett. 119, 202904 (2021).

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