Physicist's view on structural phase transitions

Alexander Tsirlin

Experimental Physics VI, Center for Electronic Correlations and Magnetism
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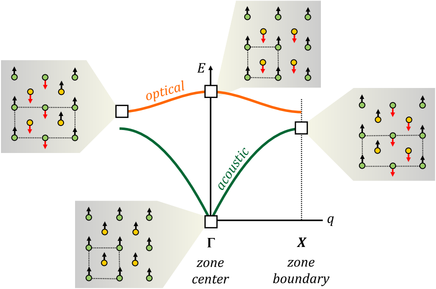
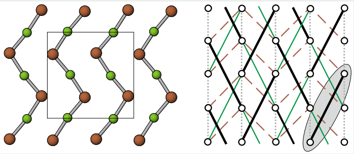


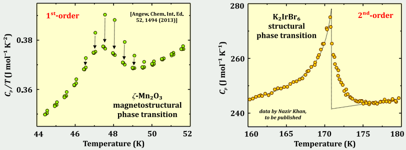
Alexander von Humboldt Stiftung/Foundation

University of Lille, France
November 26, 2018



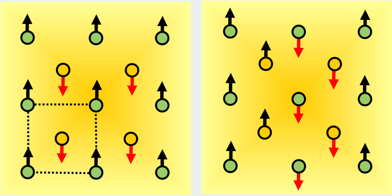
Prelude

on the importance of phase transitions and accurate structure determination



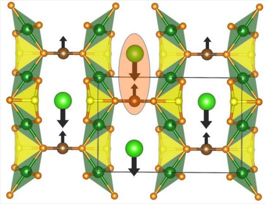
Classification and thermodynamics

first-order, second-order, and how to identify them?



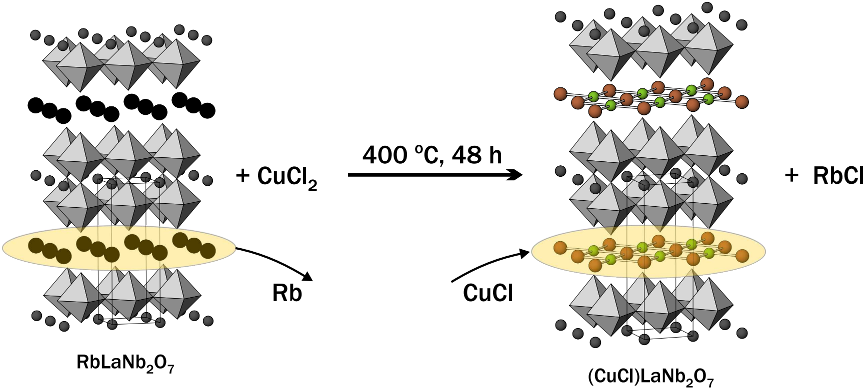
Soft modes

and beyond (order-disorder)



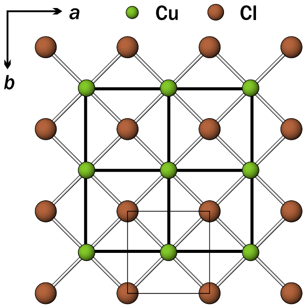
Practical example

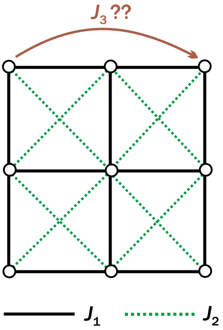
francisite: ferro- or antiferroelectric?



- Low-temperature ion-exchange reaction leads to a highly crystalline product that **can't be obtained by high-temperature solid-state synthesis**
- Other transition metals work too: $(MnCl)LaNb_2O_7$, $(FeCl)LaNb_2O_7$, etc.

T. Kodenkandath et al. JACS 121, 10743 (1999)
T. Kodenkandath et al. Inorg. Chem. 40, 710 (2001)





- **Theory:** Long-standing interest in spin-$\frac{1}{2}$ (Cu-based) square-lattice antiferromagnets that evade magnetic order (precursor of high-T_c states?)
- **Experiment:** no long-range magnetic order in (CuCl)$LaNb_2O_7$ indeed [H. Kageyama *et al.* J. Phys. Soc. Jpn. 74, 1702 (2005)]

Interest from theory

PRL **96,** 027213 (2006) PHYSICAL REVIEW LETTERS week ending 20 JANUARY 2006

Nematic Order in Square Lattice Frustrated Ferromagnets

Nic Shannon,[1,2] Tsutomu Momoi,[3] and Philippe Sindzingre[4]

[1]*Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Strasse 40, 01187 Dresden, Germany*

[2]*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8-1TL, United Kingdom*

[3]*Condensed Matter Theory Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*

[4]*Laboratoire de Physique Théorique de la Matière Condensée, UMR 7600 of CNRS, Université P. et M. Curie, case 121, 4 Place Jussieu, 75252 Paris Cedex, France*

(Received 15 September 2005; published 19 January 2006)

PRL **96,** 027213 (2006) PHYSICAL REVIEW LETTERS week ending 20 JANUARY 2006

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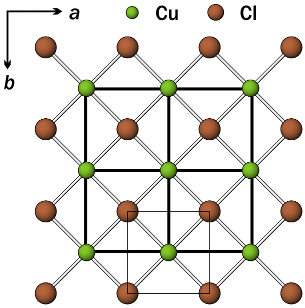
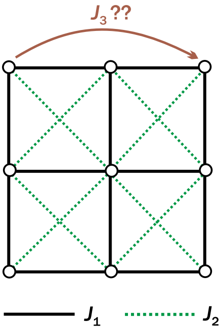
PHYSICAL REVIEW B **76**, 214428 (2007)

Ground-state phase diagram and magnetic properties of a tetramerized spin-1/2 J_1-J_2 model: BEC of bound magnons and absence of the transverse magnetization

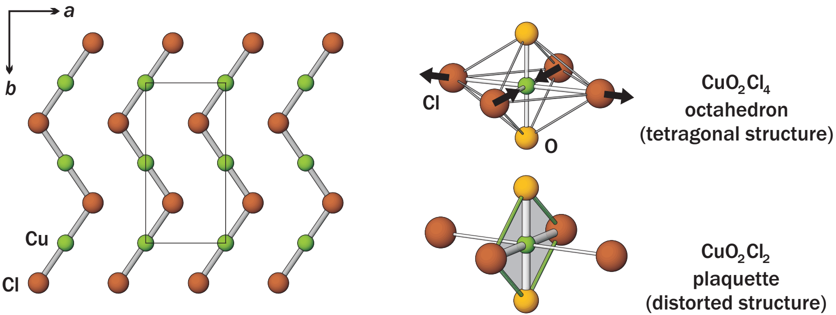
Hiroaki T. Ueda and Keisuke Totsuka
Yukawa Institute for Theoretical Physics, Kyoto University, Kitashirakawa Oiwake-Cho, Kyoto 606-8502, Japan
(Received 1 October 2007; published 26 December 2007)





- **Theory:** Long-standing interest in square-lattice antiferromagnets that evade magnetic order (precursor of high-T_c states?)
- **Experiment:** no long-range magnetic order in $(CuCl)LaNb_2O_7$ indeed

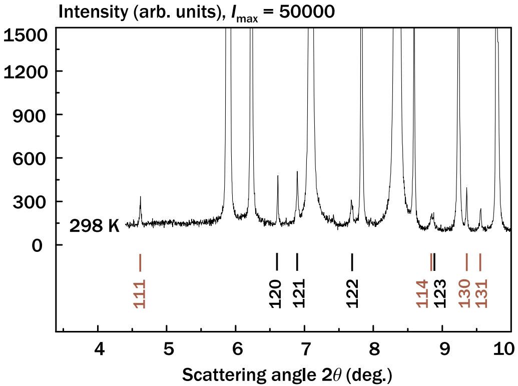
U_{iso}**(Cl)** $= 0.133$ **Å**^{2} **??! – something must be wrong here**



- **Crystal structure optimization in DFT:**
  arbitrary supercell, random guess of U...

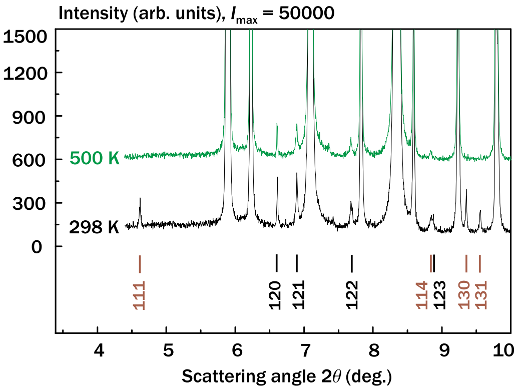
- Cu^{2+} remains **Jahn-Teller-active** and tends to reduce the symmetry from tetragonal to orthorhombic
- **CuO_2Cl_2 plaquettes** form, akin to the CuO_4 squares in Cu^{2+} oxides

AT et al. Phys. Rev. B 79, 214416 (2009)



- Unit cell should be expanded ($2a \times 2a \times c$)
  same superstructure reflections were observed before, but assigned to an (unknown) impurity
- Two structural transitions upon heating
- Above RT, orthorhombic splitting becomes visible (accidentally, $a \simeq b$ at RT)

AT et al. Phys. Rev. B 82, 054107 (2010)



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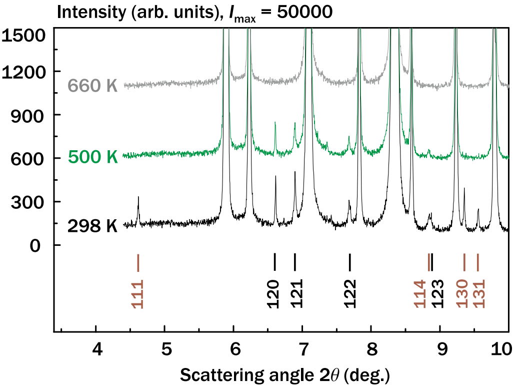

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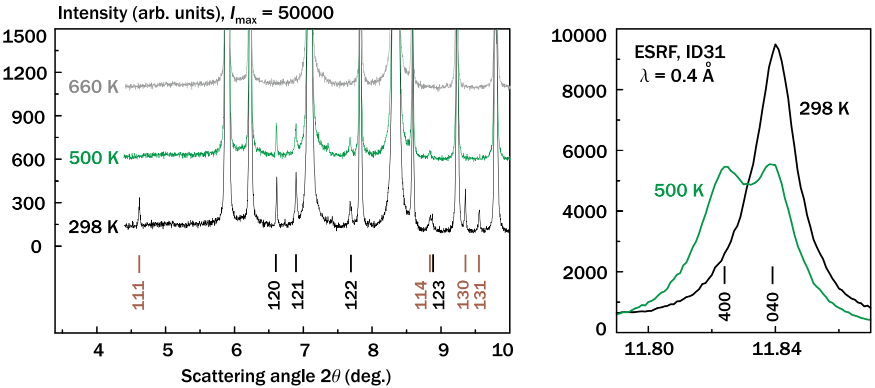

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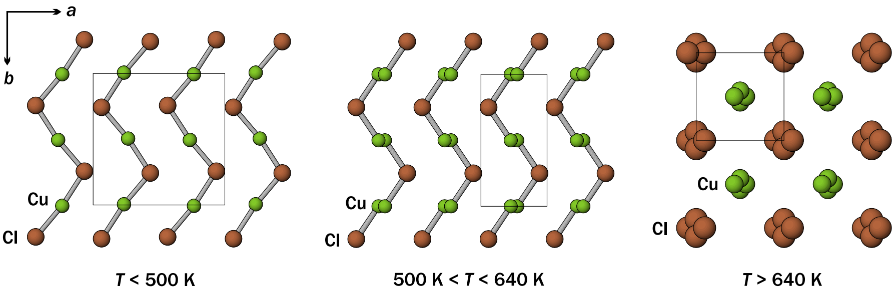

- Fully ordered and orthorhombic **below 500 K**
  confirmed by single-crystal XRD: [Hernandez *et al.* Dalton Trans. 40, 4605 (2011)]
- Disorder of Cu **above 500 K** (still orthorhombic)
- Disorder of Cu and Cl **above 640 K** $\longrightarrow$ tetragonal symmetry

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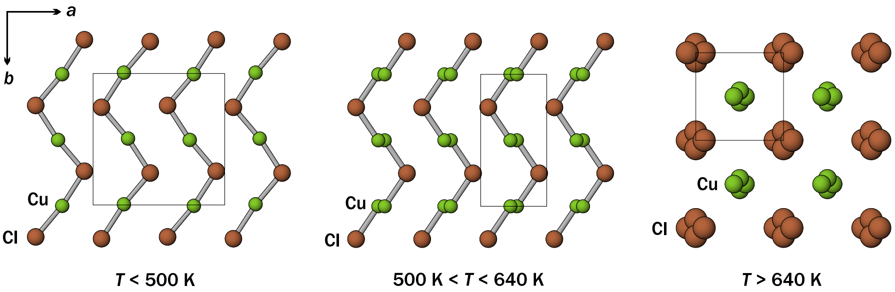

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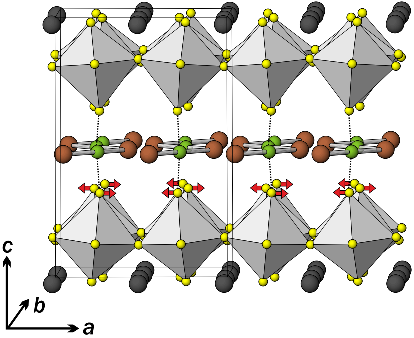
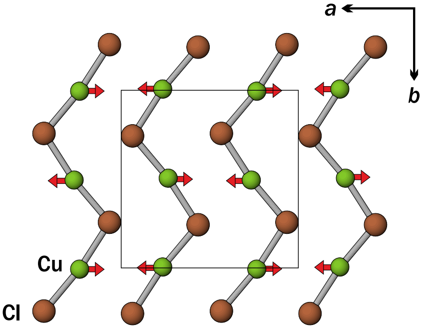
▶ **Phase transitions are of order-disorder type**

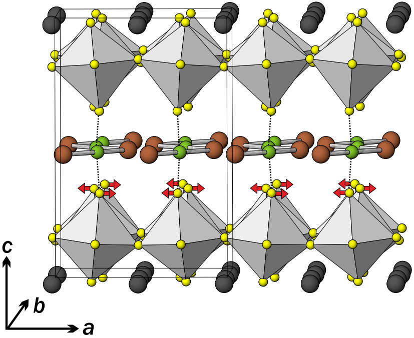
AT et al. Phys. Rev. B 82, 054107 (2010)

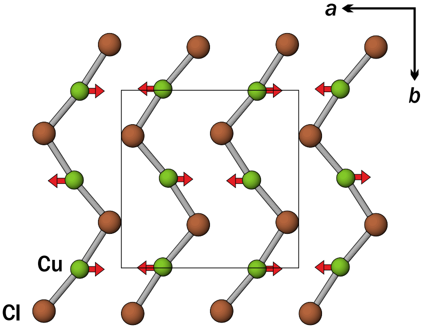




- Displacements of Cu and Cl are not random, because Cu is linked to the oxygens of the $[LaNb_2O_7]$ layers
- Suppression of the tilting distortion leads to a progressive disorder in the [CuCl] planes; one part of the structure facilitates the ordering in the other

AT et al. Phys. Rev. B 82, 054107 (2010)





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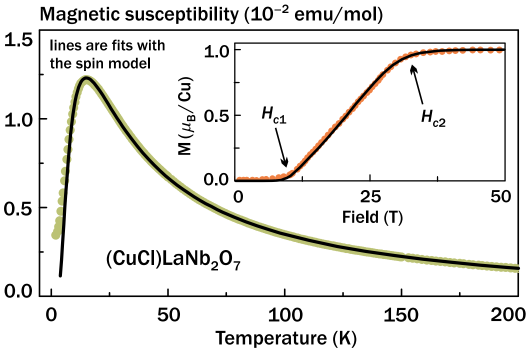
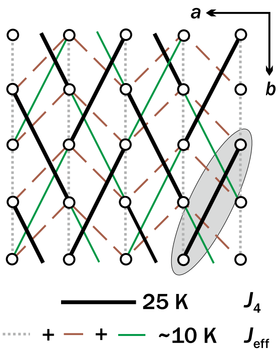
▶ **The occurrence of phase transitions confirms the low-T crystal structure**

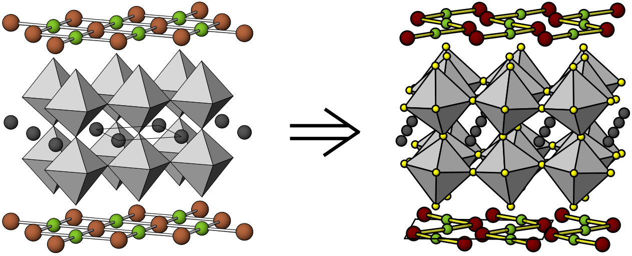
AT et al. Phys. Rev. B 82, 054107 (2010)

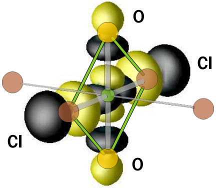




- **Magnetic model is a mess**
- It's consistent with the experiments, but has nothing to do with the square-lattice geometry and high-T_c's
- Absence of magnetic order is completely normal in this case and would be well anticipated, **should the correct crystal structure be available from the beginning**

AT et al. Phys. Rev. B 82, 060409(R) (2010)

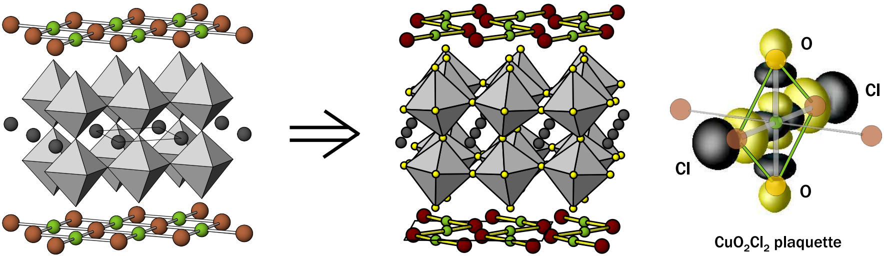




CuO_2Cl_2 plaquette

- Pay attention to superstructure reflections
- Beware of high atomic displacement parameters
- Structural transitions help one to identify the correct type of ordering
- **In physicists' hands, wrong crystal structures may lead to bad consequences**

Take-home messages



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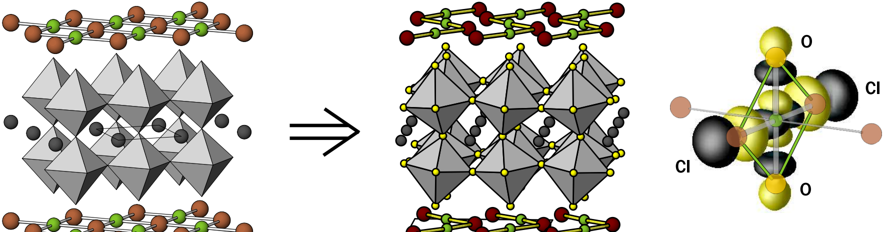

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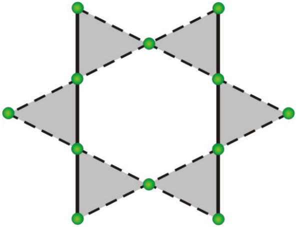
Volborthite, $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$, is an interesting frustrated magnet with the *time-dependent* crystal structure



Anisotropic kagome lattice

Z. Hiroi *et al.*
JPSJ 70, 3377 (2001)

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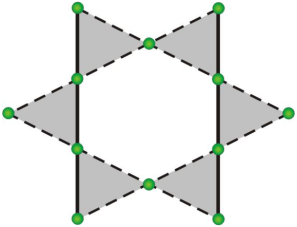

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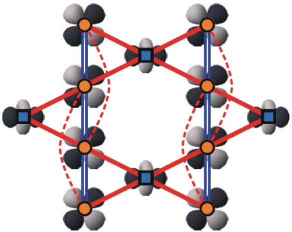

Coupled frustrated spin chains

Structure:
M. Lafotaine *et al.*
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Model: O. Janson *et al.*
PRB 82, 104434 (2010)

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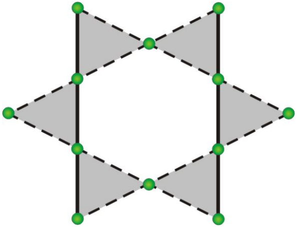

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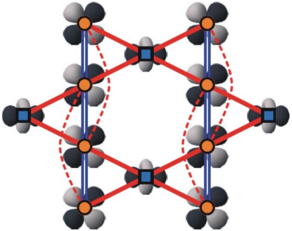

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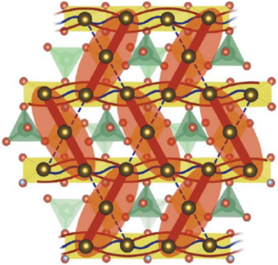


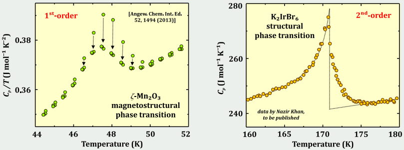
Frustrated trimers

Structure:
H. Yoshida *et al.*
Nat. Comm. 3, 860 (2012)

Model: O. Janson *et al.*
PRL 117, 037206 (2016)

Prelude

on the importance of phase transitions
and accurate structure determination



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Practical example

francisite: ferro- or antiferroelectric?

Image credit: Andreas Weith, Fir0002 (Wikimedia Commons)

- In daily life, phase transitions are typically accompanied by:
  - Phase coexistence
  - Heat released or absorbed upon the transition (**latent heat**)

Image credit: Andreas Weith, Fir0002 (Wikimedia Commons)

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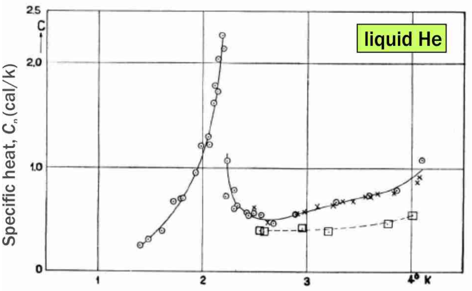
Paul Ehrenfest
1880–1933

first theory of phase transitions



Superfluid transition of helium (λ-transition)
first example of a second-order transition

W.H. Keesom and K. Clusius,
KNAW Proceedings 35, 307 (1932)

- **First order:** latent heat, discontinuity in $dG/d\alpha$
- **Second order:** no latent heat, discontinuity only in $d^2G/d\alpha^2$

$$\frac{\partial G}{\partial p} =$$

$$\frac{\partial G}{\partial p} = V$$

Volume

1^{st} order: cell volume changes abruptly
2^{nd} order: volume changes continuously

$$\frac{\partial G}{\partial p} = V$$

Volume

$1^{\rm st}$ order: cell volume changes abruptly
$2^{\rm nd}$ order: volume changes continuously

$$\frac{\partial G}{\partial T} =$$

$$\frac{\partial G}{\partial p} = V$$

Volume

1^{st} order: cell volume changes abruptly
2^{nd} order: volume changes continuously

$$\frac{\partial G}{\partial T} = S$$

Entropy

latent heat, $Q = T\Delta S$

1^{st} order: latent heat released
2^{nd} order: no latent heat

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1^{st} order: cell volume changes abruptly
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$$\frac{\partial^2 G}{\partial p\,\partial T} = \frac{\partial V}{\partial T} \sim \alpha$$

Thermal expansion coefficient

1^{st} order: ill-defined
2^{nd} order: anomaly (hump)

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Volume

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$2^{\rm nd}$ order: volume changes continuously

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Thermal expansion coefficient

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$$\frac{\partial^2 G}{\partial T^2} \sim$$

Derivatives of the free energy

$$\frac{\partial G}{\partial p} = V$$

Volume

1^{st} order: cell volume changes abruptly
2^{nd} order: volume changes continuously

$$\frac{\partial G}{\partial T} = S$$

Entropy

latent heat, $Q = T\Delta S$

1^{st} order: latent heat released
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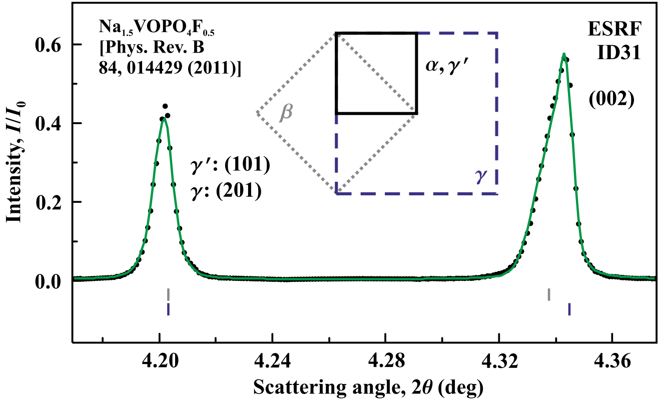
Thermal expansion coefficient

1^{st} order: ill-defined
2^{nd} order: anomaly (hump)

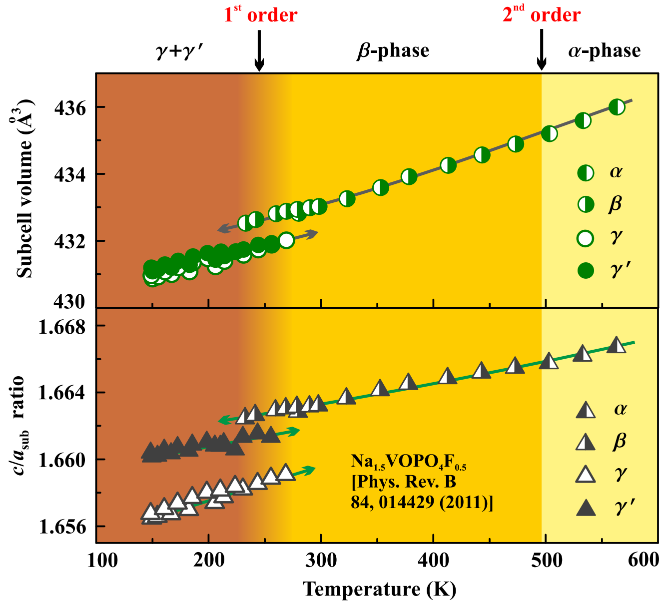
$$\frac{\partial^2 G}{\partial T^2} \sim C_p$$

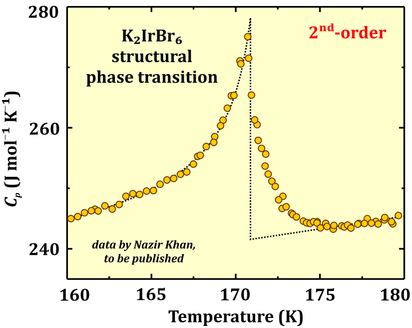
Heat capacity

1^{st} order: ill-defined
2^{nd} order: λ-type anomaly

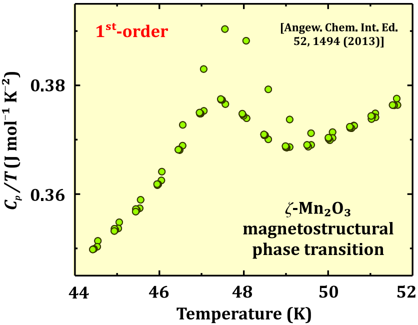


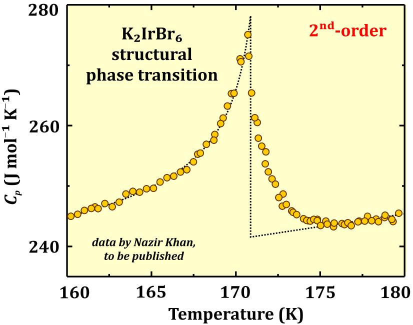
Coexistence of the high-T and low-T phases (or phase separation) marks a first-order transition

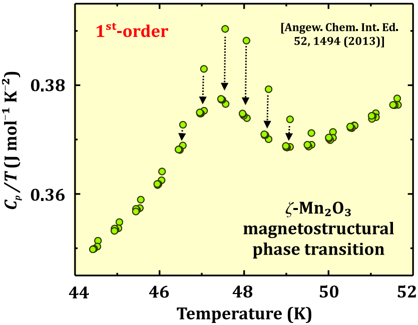

1st order
2nd order
γ+γ′
β-phase
α-phase
Subcell volume (Å3)
436
434
432
430
α
β
γ
γ′
c/a_sub ratio
1.668
1.664
1.660
1.656
Na1.5VOPO4F0.5
[Phys. Rev. B
84, 014429 (2011)]
100
200
300
400
500
600
Temperature (K)

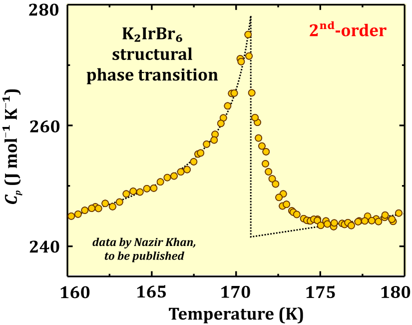


K_2IrBr_6
structural
phase transition
2^{nd}-order
data by Nazir Khan,
to be published
C_p (J mol^{-1} K^{-1})
280
260
240
160
165
170
175
180
Temperature (K)


1st-order
[Angew. Chem. Int. Ed.
52, 1494 (2013)]
ζ-Mn2O3
magnetostructural
phase transition
Cp/T (J mol−1 K−2)
0.38
0.36
44
46
48
50
52
Temperature (K)

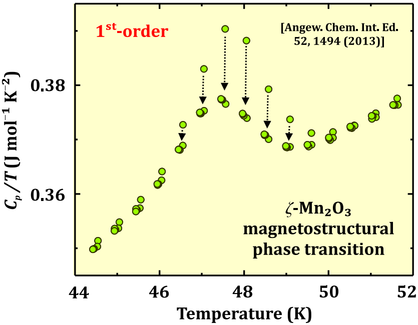

K2IrBr6
structural
phase transition
2nd-order
data by Nazir Khan,
to be published
Cp (J mol−1 K−1)
280
260
240
160
165
170
175
180
Temperature (K)

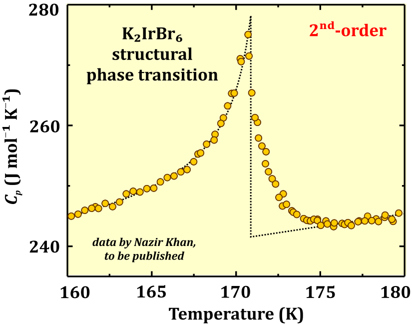




- Latent heat manifests itself in heat-capacity measurements
  always do several measurements at each temperature and check it out
- For a *magnetic transition*, the presence of latent heat could imply:
  - a structural component
  - appearance of a second propagation vector
  - transformation between magnetic structures with the same symmetry
  - any other change in magnetic order inconsistent with the symmetry rules

Specific heat





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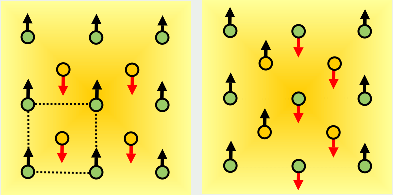
Prelude

on the importance of phase transitions
and accurate structure determination

Classification and thermodynamics

first-order, second-order,
and how to identify them?



Soft modes

and beyond (order-disorder)

Practical example

francisite: ferro- or antiferroelectric?

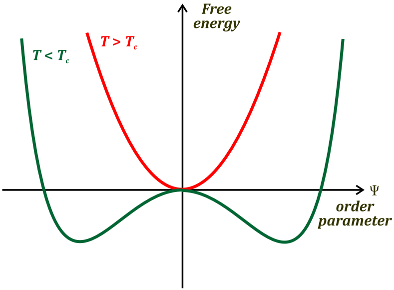
For a second-order phase transition:

- **Order parameter** Ψ can be introduced, such that $\Psi = 0$ above T_c and $\Psi \neq 0$ below T_c

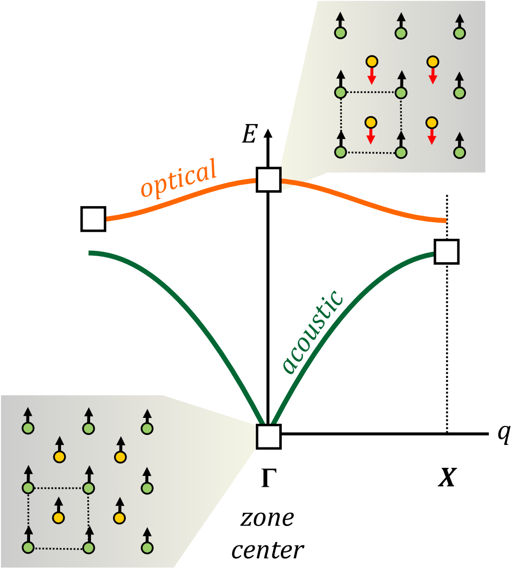
  Order parameter can be:
  – atomic displacement (structural transitions)
  – ordered magnetic moment
  – wavefunction of the superconducting state

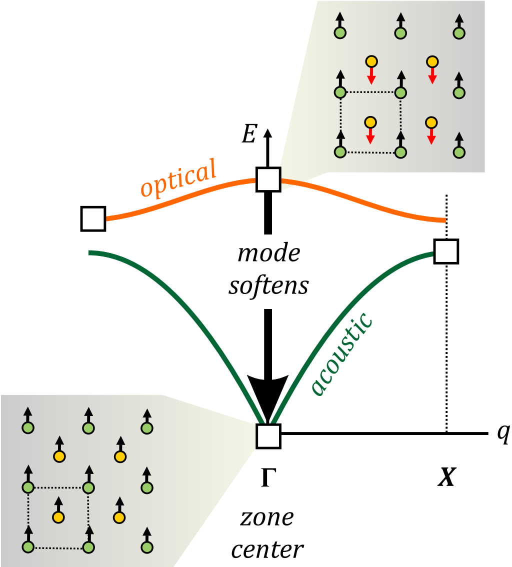
- **Free energy**
  can be expanded in even powers of Ψ,

$$F = F_0 + a\Psi^2 + b\Psi^4 + \dots$$



- Symmetry of the low-temperature phase follows an **irreducible representations of the symmetry group of the high-temperature phase**
- Symmetry analysis helps in identifying the transition
- **For 2^{nd}-order structural phase transitions, look at soft phonon modes**


E
optical
acoustic
q
Γ
X
zone
center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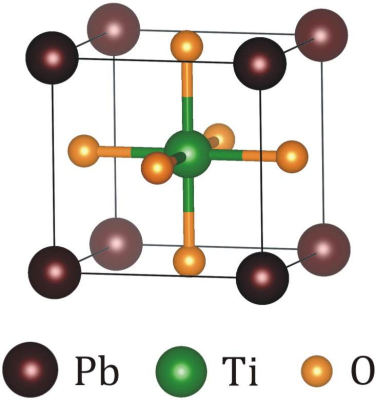
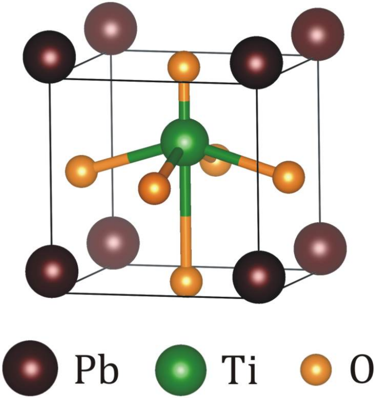


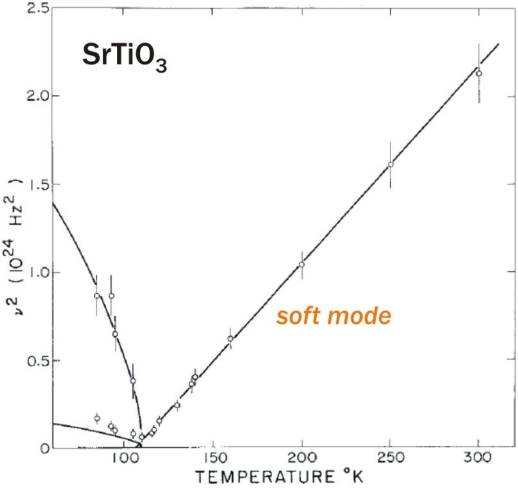


Cubic structure

paraelectric

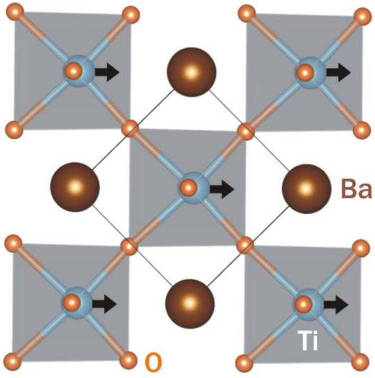
Tetragonal structure

ferroelectric



Condensation of a soft mode triggers a structural phase transition that can give rise to ferroelectricity

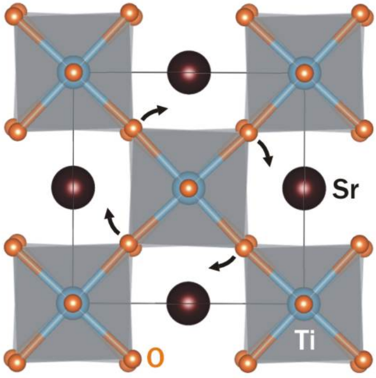
Adv. Phys. 29, 1 (1980)



$BaTiO_3$

parallel displacements of the Ti^{4+} ions

ferroelectric

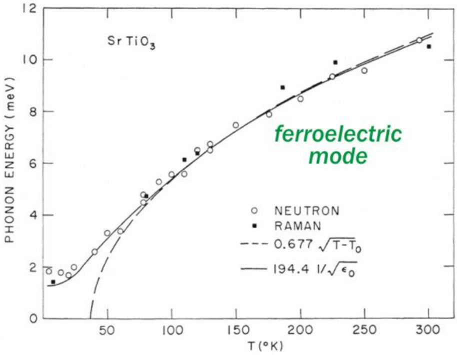


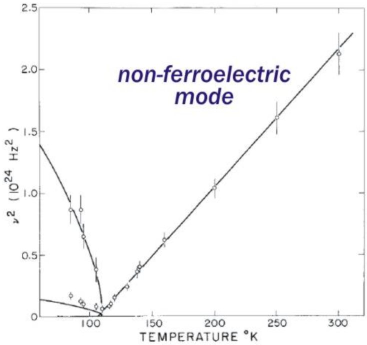
$SrTiO_3$

counter-rotations of the TiO_6 octahedra

paraelectric

Competition between the soft modes

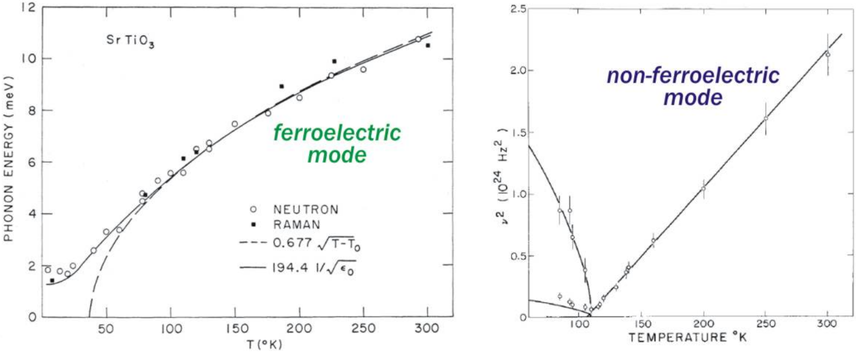




Adv. Phys. 29, 1 (1980); J. Phys. Soc. Jpn. 26, 396 (1969)

Several competing modes are always present, and one of them eventually "wins"

- **$SrTiO_3$:** non-ferroelectric mode
- **$PbTiO_3$:** ferroelectric mode
- **$PbZrO_3$:** antiferroelectric mode
- **$BaTiO_3$:** ferroelectric mode
- **$BaZrO_3$:** neither mode (quantum paraelectric)



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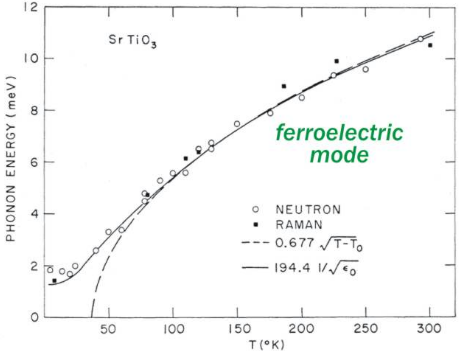

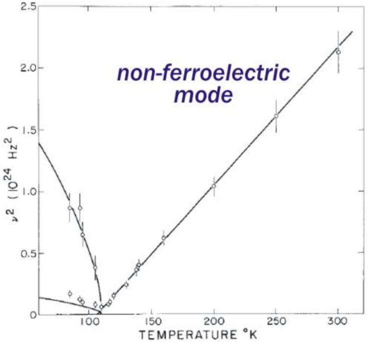

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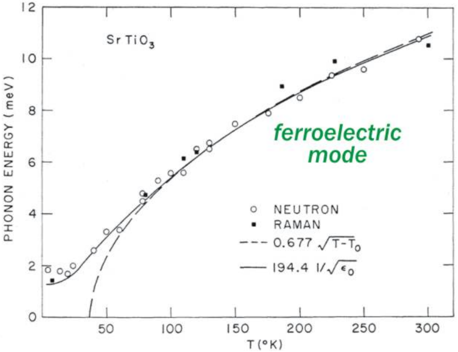

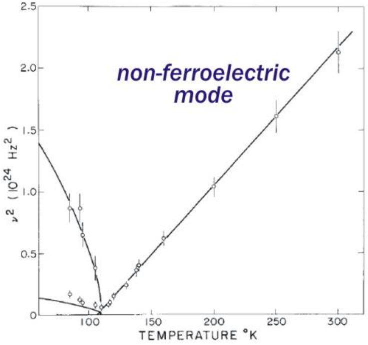

Adv. Phys. 29, 1 (1980); J. Phys. Soc. Jpn. 26, 396 (1969)

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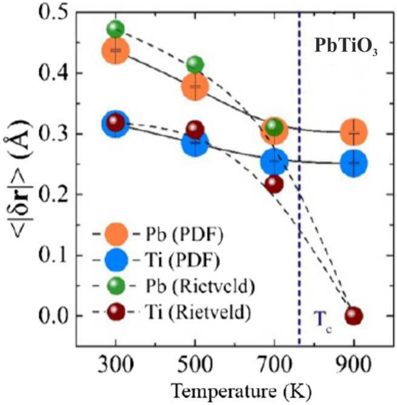
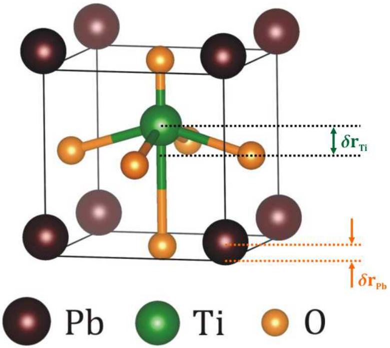
- **$PbTiO_3$:** ferroelectric mode
- ...

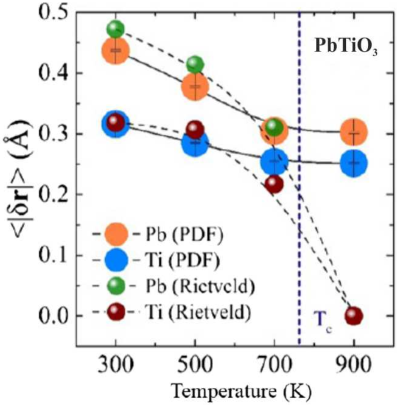
▶ **Identification of potential soft modes helps in predicting a phase transition**

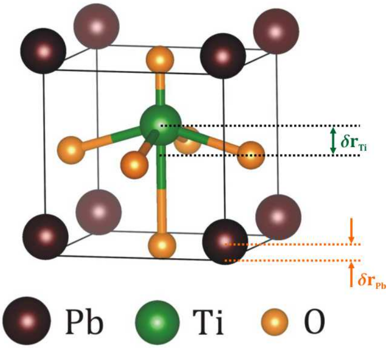




K. Datta et al. Phys. Rev. Lett. 121, 137602 (2018)

- Local displacements survive well above the transition temperature
- Most transitions can be seen as intermediate between **displacive** (softening of a phonon mode) and **order-disorder** (ordering of pre-existing local displacements)





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- Local displacements survive well above the transition temperature
- Most transitions can be seen as intermediate between **displacive** (softening of a phonon mode) and **order-disorder** (ordering of pre-existing local displacements)

► Symmetry arguments are still the same, so **the search for soft modes is very useful**

Prelude

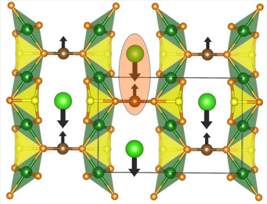
on the importance of phase transitions
and accurate structure determination

Classification and thermodynamics

first-order, second-order,
and how to identify them?

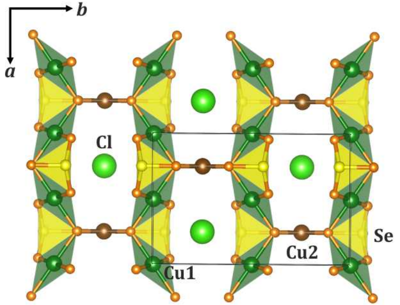
Soft modes

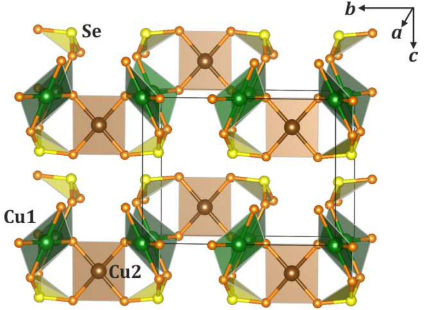
and beyond (order-disorder)



Practical example

francisite: ferro- or antiferroelectric?





Francisite = $Cu_3Bi(SeO_3)_2O_2Cl$:

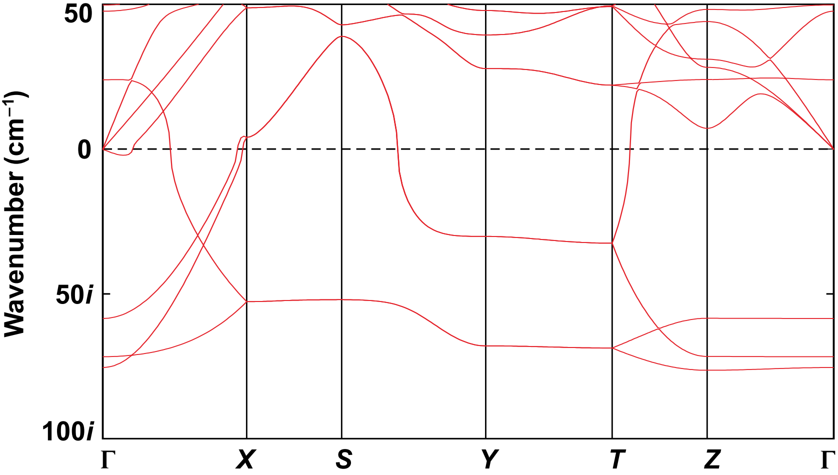
- $U_{\rm iso}$**(Cl)** $= 0.042$ **Å**^{2} at 293 K
- Cl is not part of the CuO_4 units
- Magnetic model OK [Phys. Rev. B 91, 024416 (2015)]
- Still, something is wrong here...

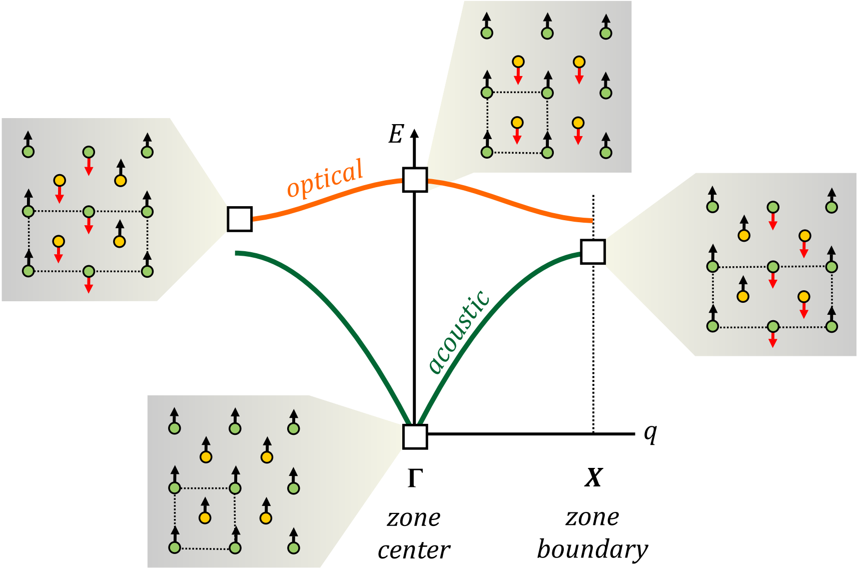
Syntheses, crystal structures and magnetic properties of francisite compounds $Cu_3Bi(SeO_3)_2O_2X$ (X = Cl, Br and I)

P. Millet,*[a] B. Bastide,[a] V. Pashchenko,[b,c] S. Gnatchenko,[c] V. Gapon,[c] Y. Ksari[d] and A. Stepanov[d]

[a] *Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS, 29 rue Jeanne Marvig, BP 4347 Toulouse Cedex 4, France. E-mail: millet@cemes.fr*
[b] *Grenoble High Magnetic Field Laboratory, MPI-FKF and CNRS, 38042 Grenoble Cedex 9, France*

J. Mater. Chem. 11, 1152 (2001)


50
0
50i
100i
Wavenumber (cm⁻¹)
Γ
X
S
Y
T
Z
Γ


E
optical
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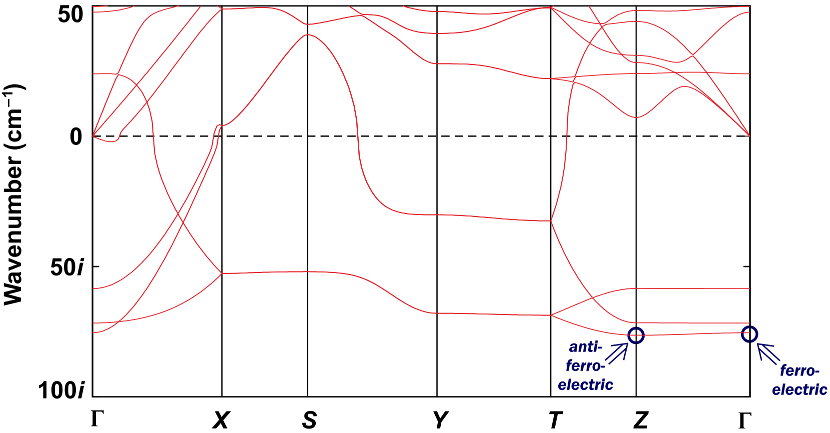
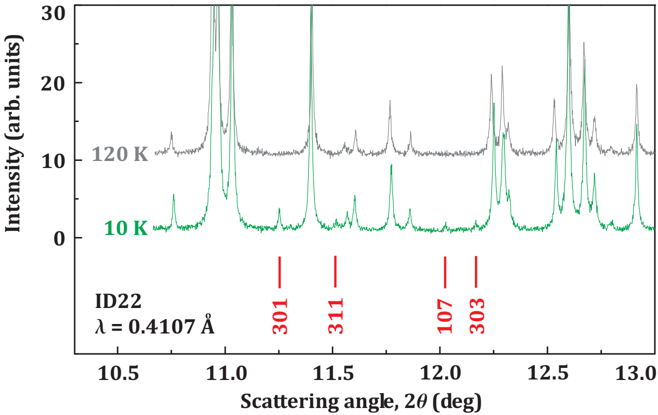
q
Γ
X
zone
center
zone
boundary



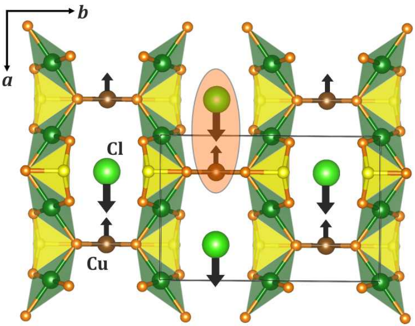
- **Γ-point instability:** ferroelectric structure, $P2_1mn$
- ***Z*-point instability:** antiferroelectric structure, *Pcmn*
- The latter is slightly lower in energy (by 3 meV/f.u.)



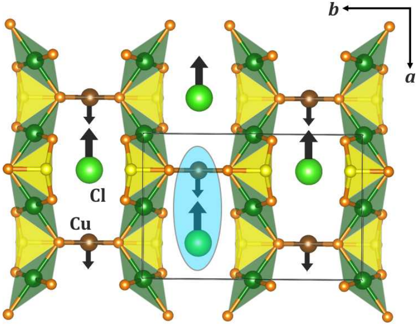
- **New unit cell:** $a_{\rm sub} \times b_{\rm sub} \times 2c_{\rm sub}$
- **New space group:** *Pcmn*, inversion symmetry retained

▶ As predicted by DFT

D. Prishchenko, AT et al. Phys. Rev. B 95, 064102 (2017)



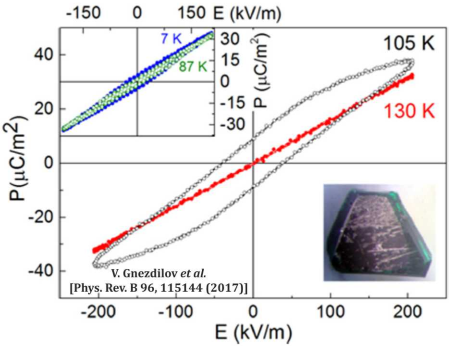
$z = 0$ layer



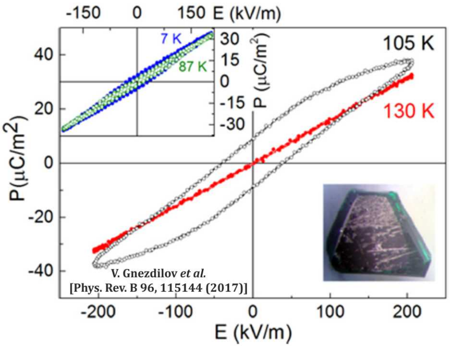
$z = \frac{1}{2}$ layer

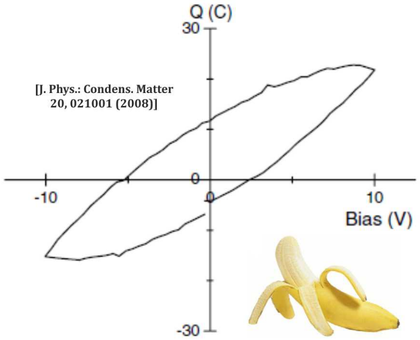
- Cu and Cl displacements create local dipoles
- These dipoles have opposite directions in the adjacent layers, hence an **antiferroelectric structure** is formed

D. Prishchenko, AT et al. Phys. Rev. B 95, 064102 (2017)



- Claim of ferroelectricity based on the hysteresis in $P(E)$
- But the polarization is small ($\sim 10\,\mu C/m^2$), and not confirmed by pyroelectric current measurements





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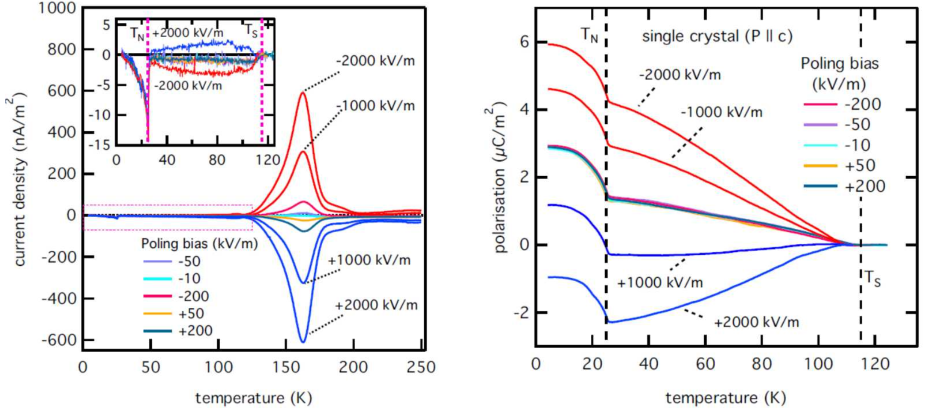
J F Scott

VIEWPOINT

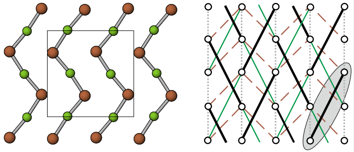
Ferroelectrics go bananas

Francisite: antiferroelectric



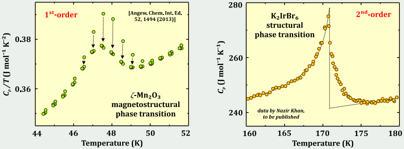
- The polarization from pyroelectric current measurements is even smaller, $\sim 1\,\mu C/m^2$, and clearly extrinsic (defects, grain boundaries...)
  - **Francisite is eventually antiferroelectric, as expected**

E. Constable et al. Phys. Rev. B 96, 014413 (2017)



Prelude

on the importance of phase transitions and accurate structure determination



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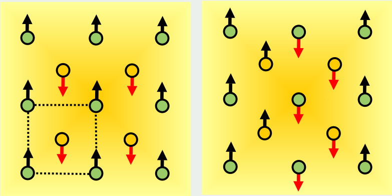

Soft modes

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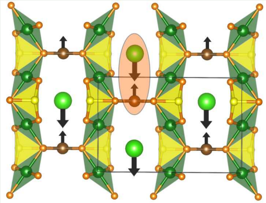

Practical example

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