

# Lone pairs in the solid state: Visualization, relativistic effects, structural coherence, and frustration





# Lone pairs in the solid state:

Cation centered lone pairs – the important cations (note the valence is 2 below the group valence):

	1+	2+	3+	4+	5+	6+
$3d^{10} 4s^2$	Ga	Ge	As	Se	Br	
$4d^{10} 5s^2$	In	Sn	Sb	Te	I	Xe
$5d^{10} 6s^2$	Tl	Pb	Bi	Po		

The sub-valent state is particularly important in the last row.

# Lone pairs in the solid state:

Hyde and Andersson, *Inorganic Crystal Structures*, Wiley (1988):

In many crystalline solids with cation-centered lone pairs, the lone pair occupies the same volume as an oxide or fluoride ion. However the cation-lone pair distances (in Å) is much shorter than typical cation-anion distances:

	1+	2+	3+	4+	5+	6+
$3d^{10} 4s^2$	Ga 0.95	Ge 1.05	As 1.26	Se 1.22	Br 1.47	
$4d^{10} 5s^2$	In 0.86	Sn 0.95	Sb 1.06	Te 1.25	I 1.23	Xe 1.49
$5d^{10} 6s^2$	Tl 0.69	Pb 0.86	Bi 0.98	Po 1.06		

Polyhedra of anions and lone pairs must have off-centric cations.



# Lone pairs in the solid state: Applications

Cation-centered lone pairs (often with  $\text{Pb}^{2+}$  as the central cation, but also  $\text{Sn}^{2+}$  and  $\text{Bi}^{3+}$ ) are important for applications requiring off-centered polyhedra and their associated dipoles:

- **Ferroelectric and piezoelectric materials, actuators**
- High-refractive index materials (lead crystal)
- Ionic conductors
- **Multiferroic materials**
- Non-linear optical materials
- Phosphors
- Semiconductor/semimetal to insulator transitions





# Lone pairs in the solid state: Visualization

Visualization: DFT based on the Stuttgart TB-LMTO-ASA program

[O. K. Andersen, O. Jepsen etc.]

Electron localization functions (ELFs): An orbital independent measure of electron localization based on the pair probability of electrons [Becke, Edgecombe J. Chem. Phys. 92 (1990) 5397; Silvi, Savin, Nature 371 (1994) 683.]

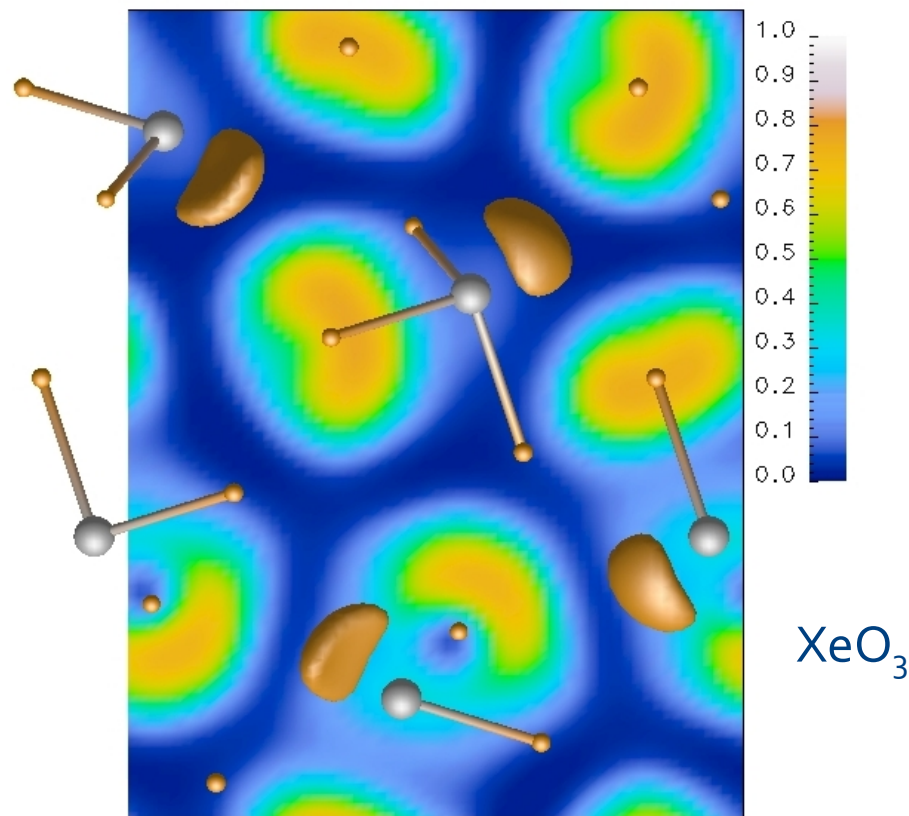
$$\text{ELF} = \frac{1}{1 + \left(\frac{D}{D_H}\right)^2} \in (0, 1)$$

with

$$D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}$$

and

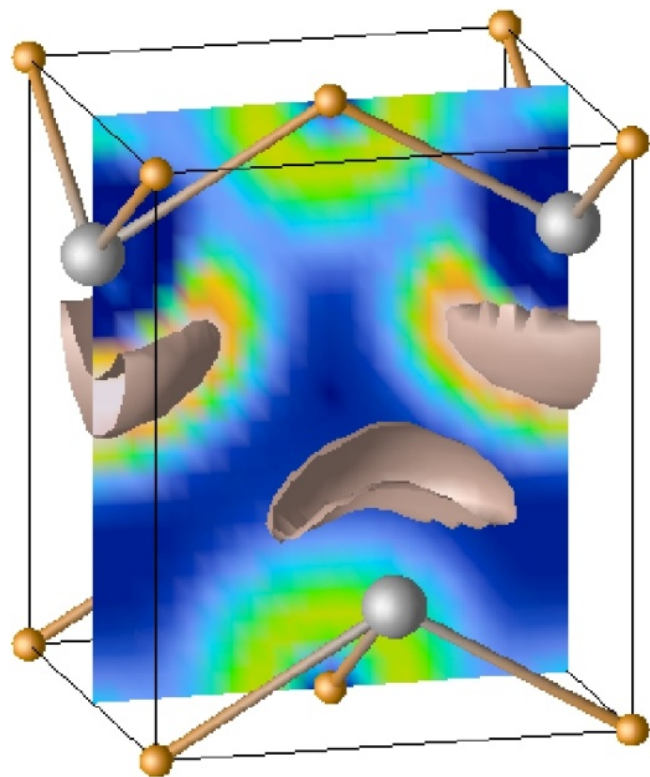
$$D_H = \frac{3}{10} (3\pi^2)^{5/3} \rho^{5/3}$$



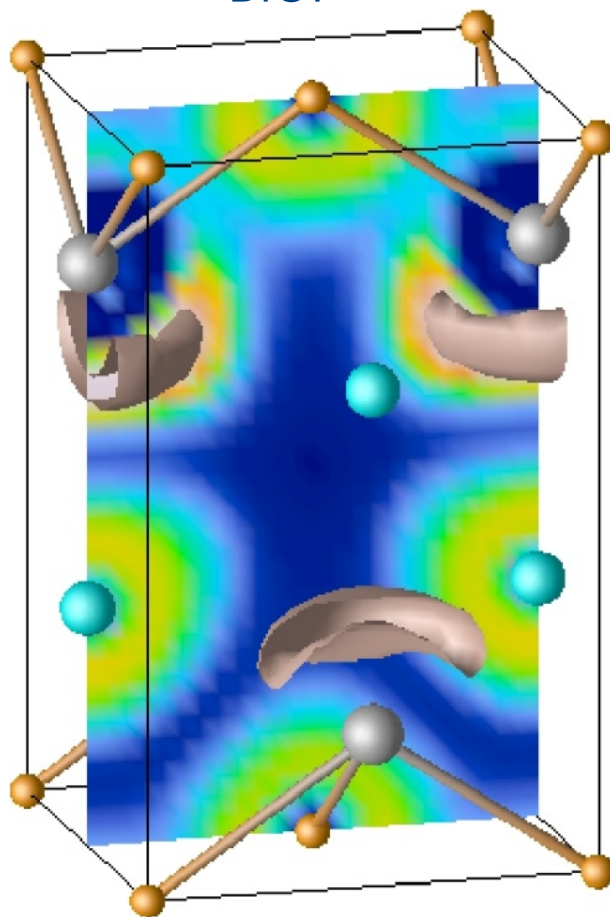
The electron density  $\rho$  does not reveal lone pairs.

# Lone pairs in the solid state: Visualization

$\alpha$ -PbO



BiOF



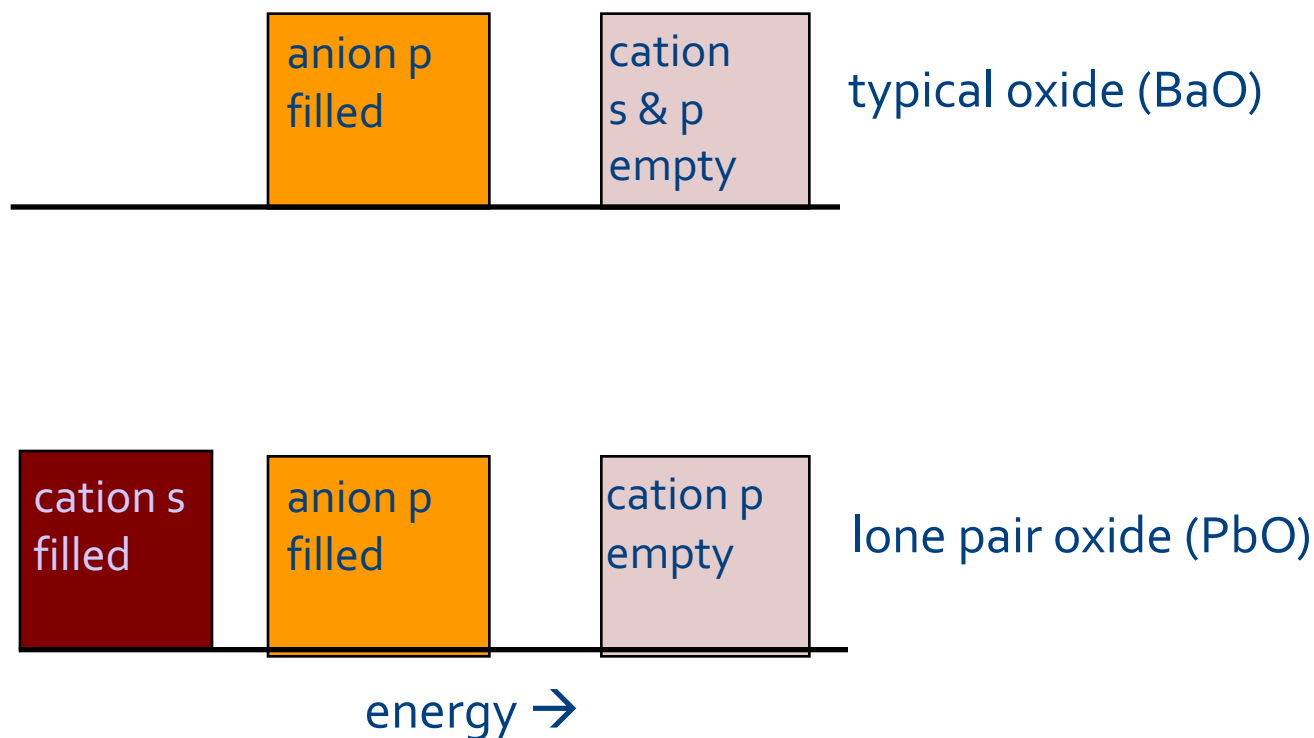
Lone pairs typically visualized with ELF values between 0.65 and 0.9

# Lone pairs in the solid state: Chemistry

Composition of the lone pair

Orgel (1959): The lone pair cannot have purely s character when it is stereochemically active; it must admix with p.

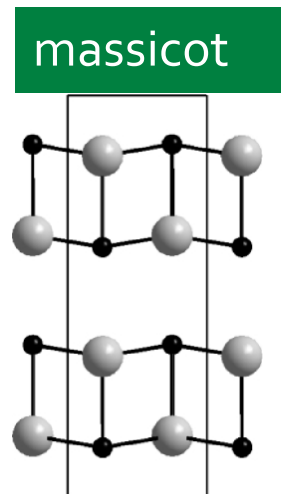
Bersuker (1984): Filled anion p states must play a role.



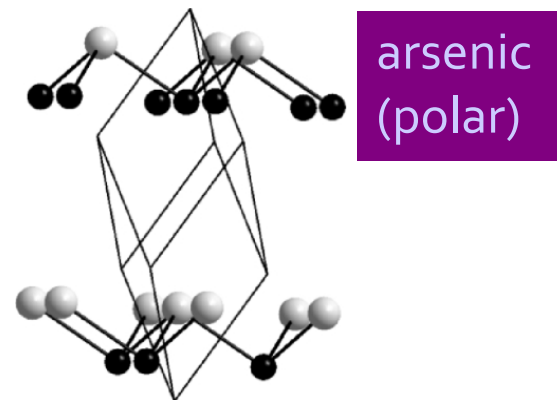


# Lone pairs in the solid state: Chemistry

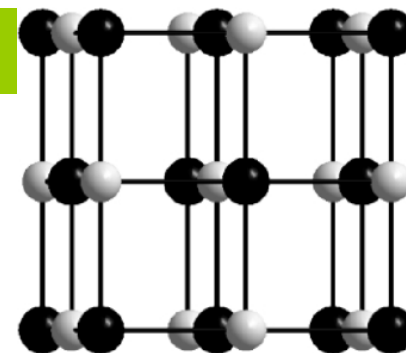
A lone pair sorted structural field AQ (IV-VI semiconductors): The lone pair is not always active!



	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe

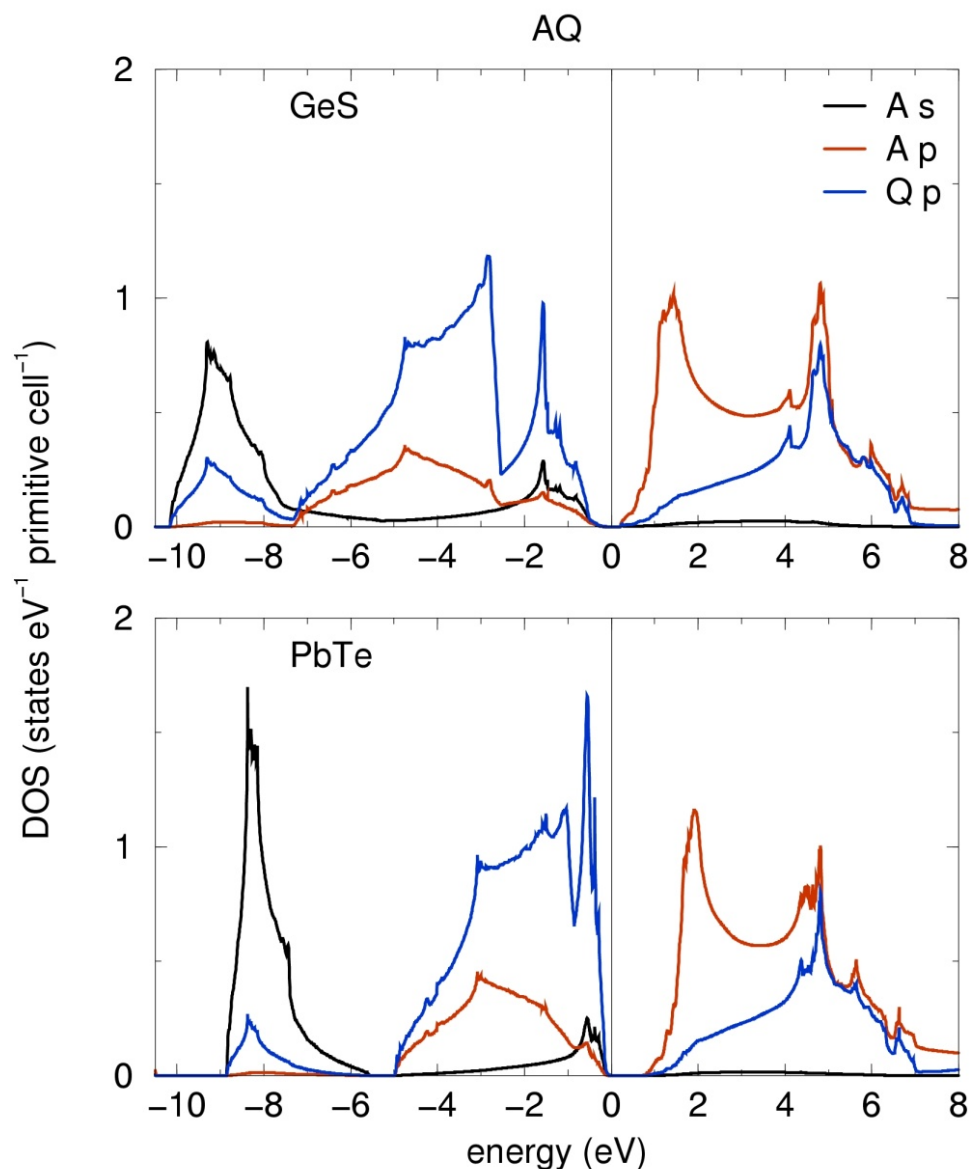


rock salt



Scalar relativistic effects are important !

# Lone pairs in the solid state: Chemistry



	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe

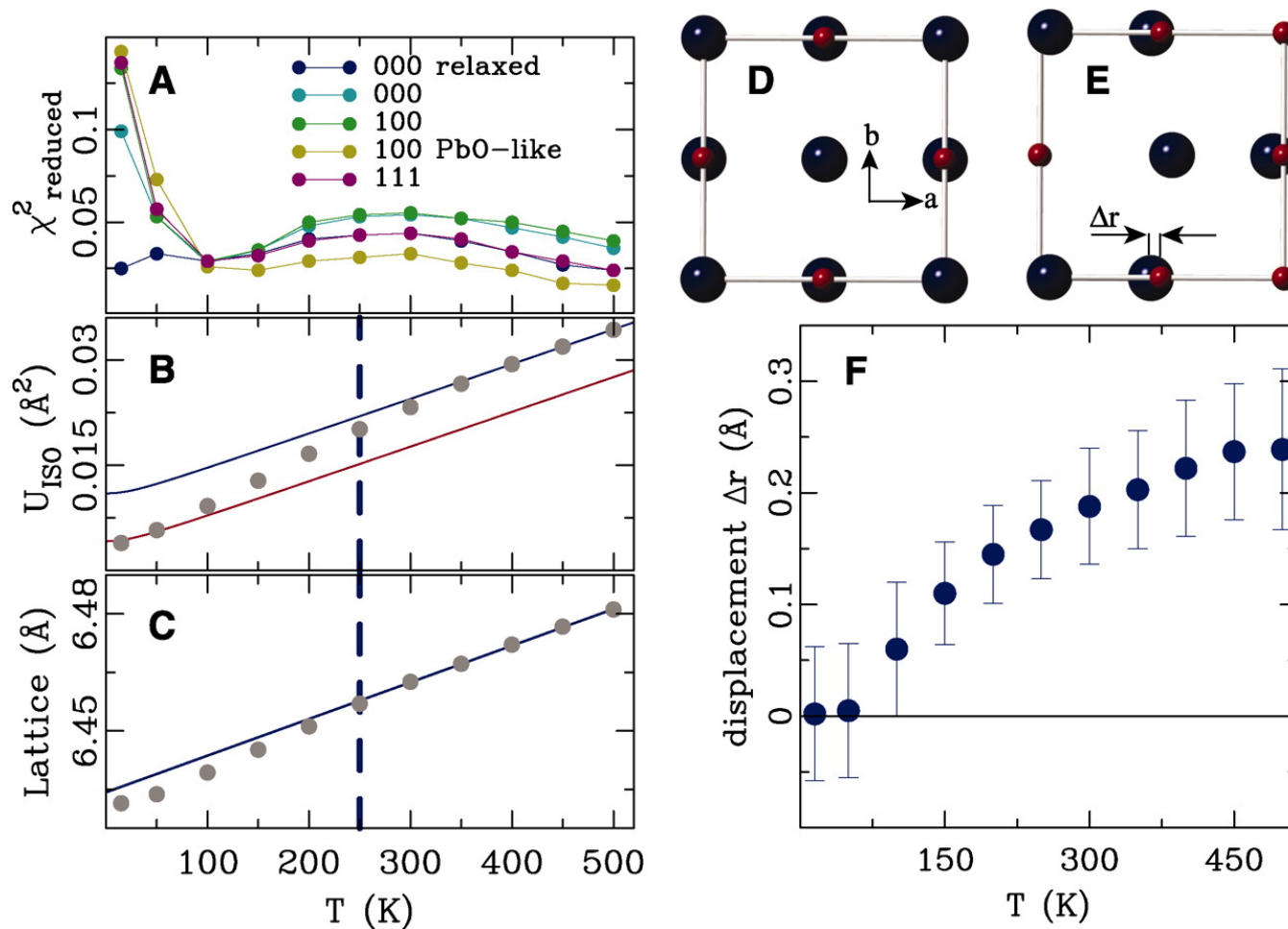
When the lone pair is stereochemically active (as in GeS), cation s states are broader and are better mixed with anion p states. The mixing is intermediated by empty cation p.

Cation s states are narrow and largely unmixed with anion p in cases when the lone pair is not stereochemically active (cf. the inert pair effect).



# Lone pairs in the solid state: Dynamics in rock-salt PbS

At low-T, the lone pairs are frozen and stereochemically inactive. As the temperature is raised, they manifest activity:







## Relativity and the Lead-Acid Battery

Rajeev Ahuja,<sup>1,\*</sup> Andreas Blomqvist,<sup>1</sup> Peter Larsson,<sup>1</sup> Pekka Pyykkö,<sup>2,†</sup> and Patryk Zaleski-Ejgierd<sup>2,‡</sup>

<sup>1</sup>*Division of Materials Theory, Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20, Uppsala, Sweden*

<sup>2</sup>*Department of Chemistry, University of Helsinki, Box 55 (A. I. Virtasen aukio 1), FI-00014 Helsinki, Finland*

(Received 30 August 2010; published 5 January 2011)

The energies of the solid reactants in the lead-acid battery are calculated *ab initio* using two different basis sets at nonrelativistic, scalar-relativistic, and fully relativistic levels, and using several exchange-correlation potentials. The average calculated standard voltage is 2.13 V, compared with the experimental value of 2.11 V. All calculations agree in that 1.7–1.8 V of this standard voltage arise from relativistic effects, mainly from PbO<sub>2</sub> but also from PbSO<sub>4</sub>.

DOI: 10.1103/PhysRevLett.106.018301

PACS numbers: 82.47.Cb, 31.15.ae, 31.15.aj, 82.60.Cx

First-principles calculations of the discharge reaction:

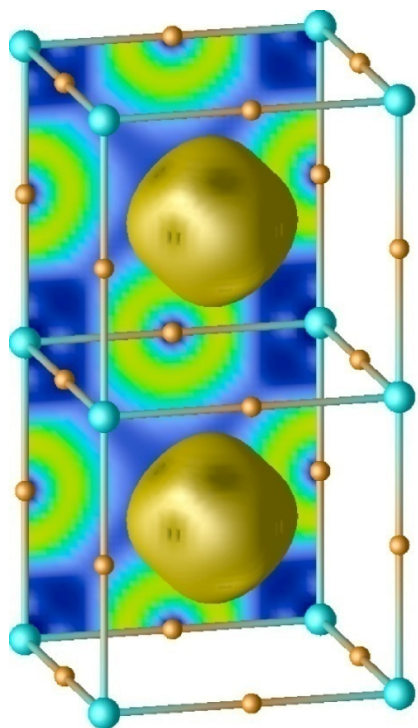


suggest that 1.7 V to 1.8 V of the total 2.1 V are due to relativistic effects.

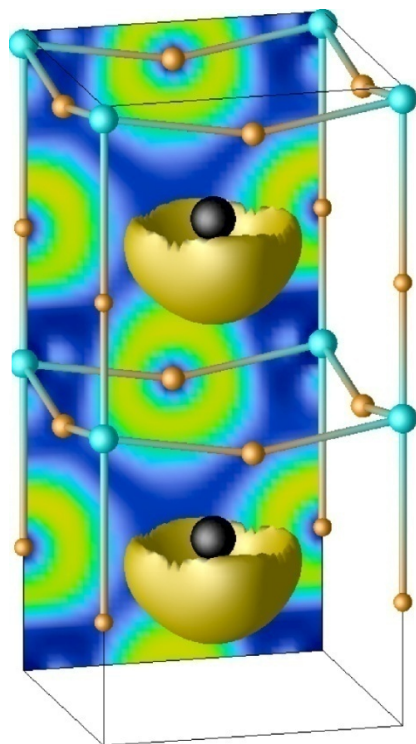


# Lone pairs in the solid state: Cooperative effects/coherence

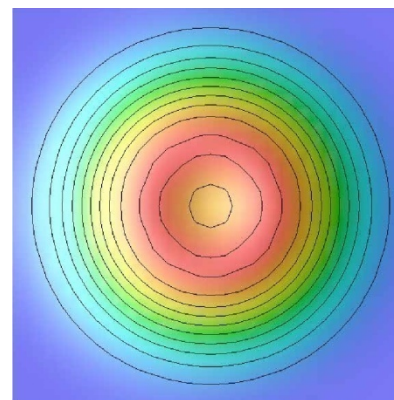
The expression of cooperative stereochemical activity of the lone pair plays an important role in the development of polar behavior.



PbTiO<sub>3</sub> above  
766 K  
Pm-3m



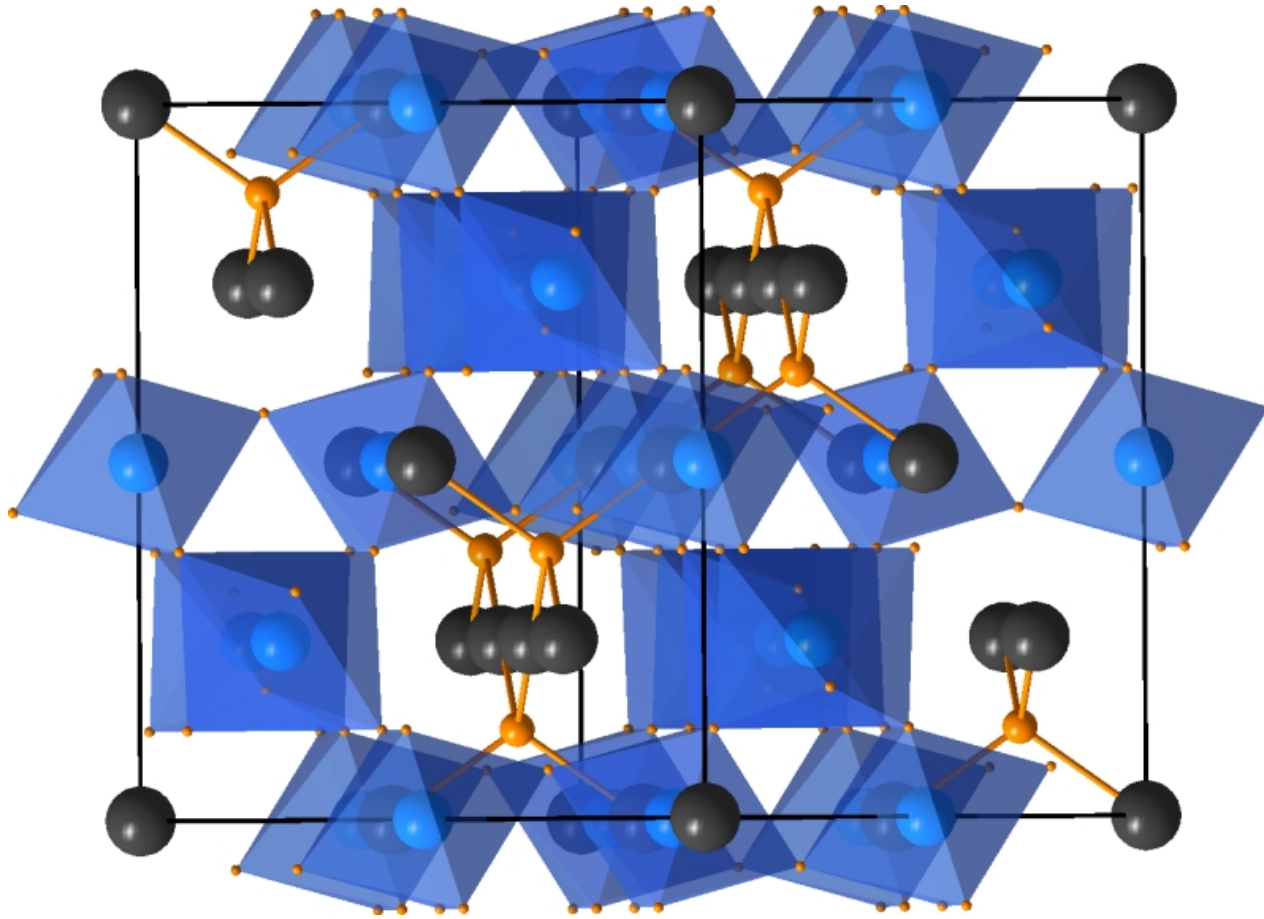
PbTiO<sub>3</sub> below  
766 K  
P4mm



Even above the phase transition, the Pb<sup>2+</sup> ion (here, in in Pb<sub>2</sub>NbYbO<sub>6</sub>) is not really where it is supposed to be.

Baldinozzi, Raulot, Seshadri, MRS Symp.  
Proc. 718 (2002) D12.7.1.

# Lone pairs in the solid state: Frustration

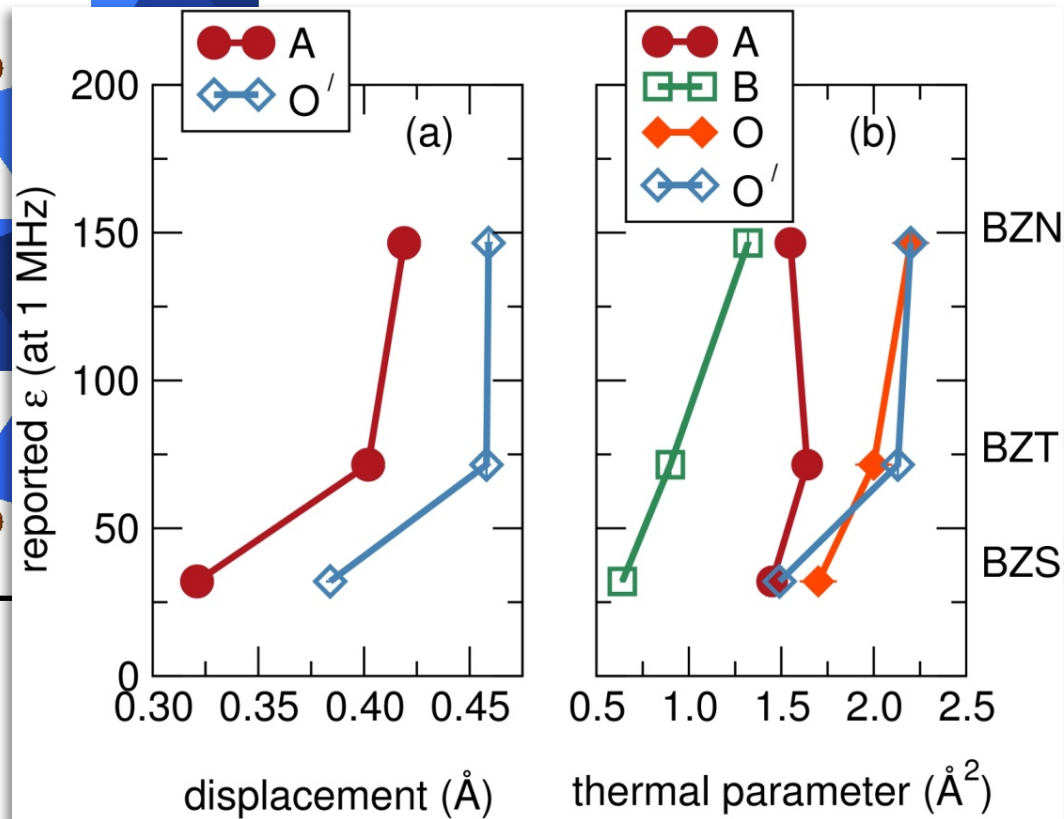
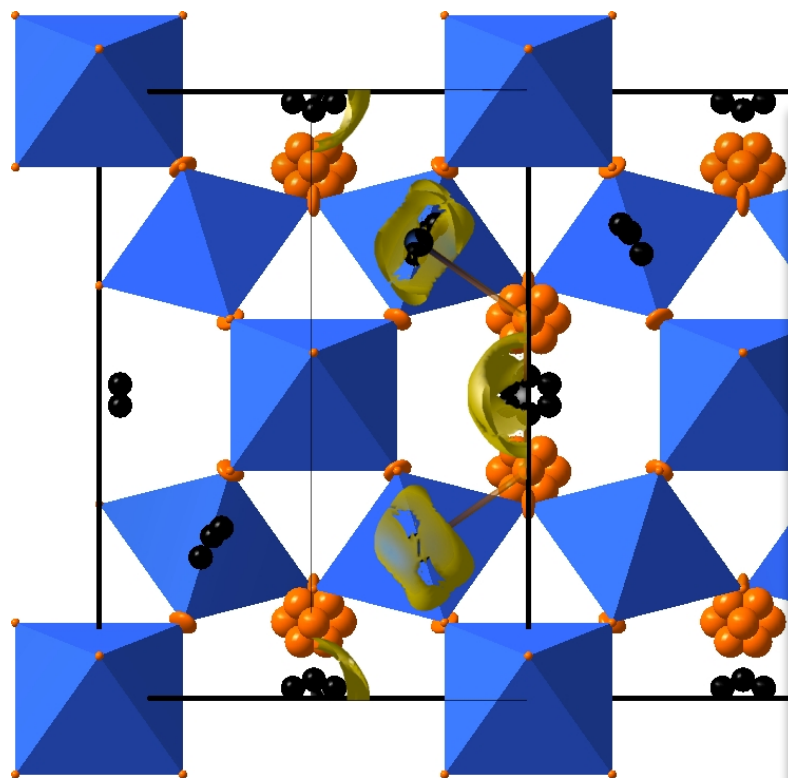


The cubic ( $Fd-3m$ ) structure of pyrochlore  $(CaNa)Nb_2O_6F$  [ $A_2B_2O_7$  or  $A_2B_2O_6O'$ ] The A site often has lone-pair cations ( $Pb^{2+}$  or  $Bi^{3+}$ ). Polar materials in this structure type are rare however.



# Lone pairs in the solid state: $(\text{Bi}, \text{Zn})_2(\text{M}^{5+}, \text{Zn})_2\text{O}_7$

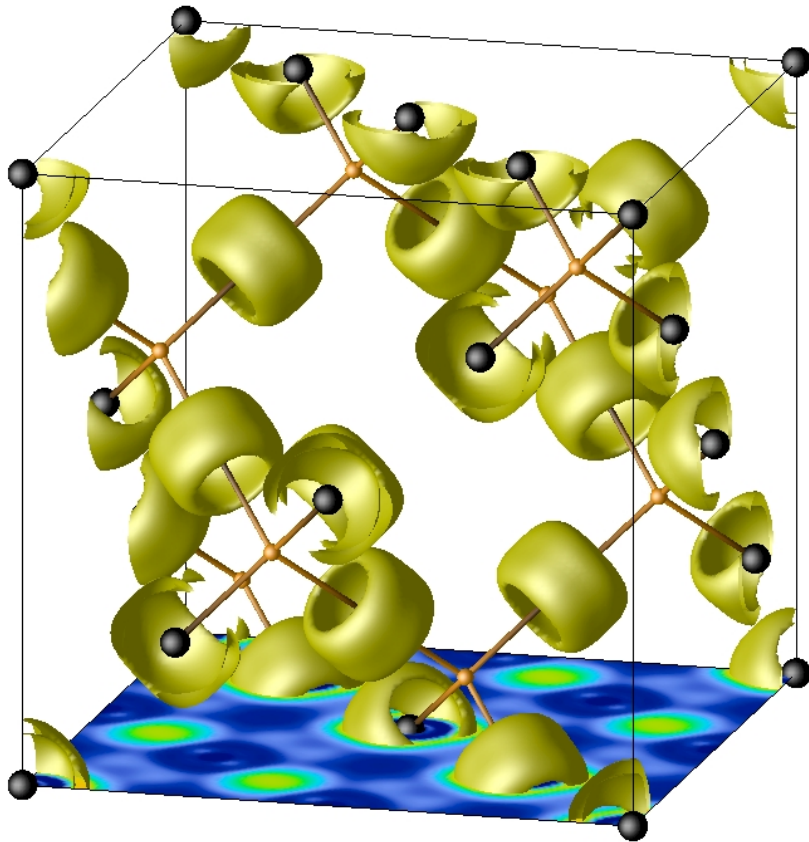
In  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  (BZN) and other related pyrochlores, the A-site is disordered.



# Lone pairs in the solid state: Frustration

$\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$ , the pyrochlore analogue of perovskite  $\text{PbTiO}_3$ , is cubic down to 2 K.  
[Hector, Wiggin, J. Solid State Chem. 177 (2004) 139]

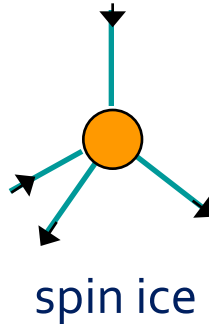
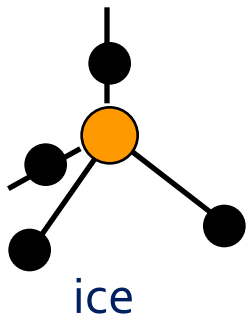
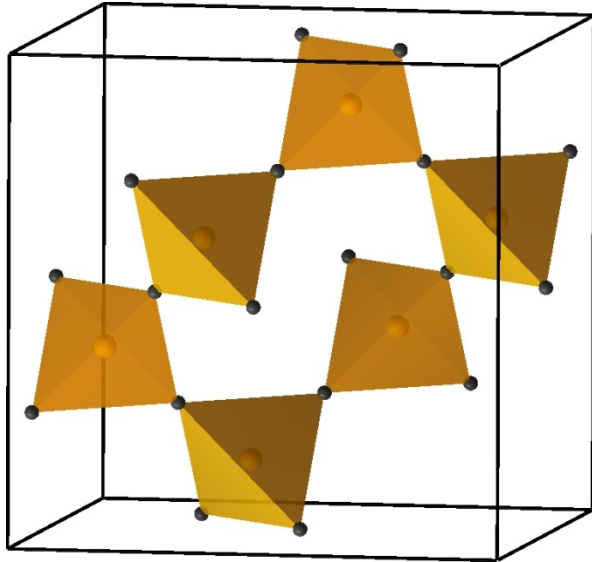
Question: Is the absence of a phase transition related to the frustrated topology of the pyrochlore lattice? **Is BTO a manifestation of charge ice?**



The  $\text{Bi}_2\text{O}'$  network in  $\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$ , and the associated lone pair ELFs:

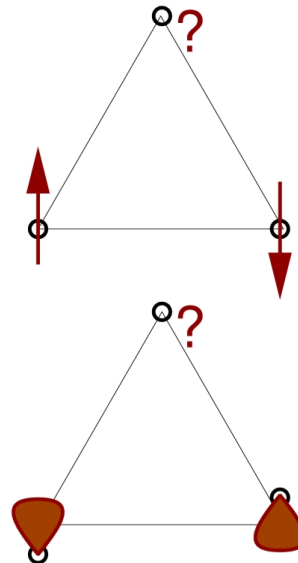
# Lone pairs in the solid state: Frustration

The more familiar spin ice



The A atom network of connected  $A_4$  tetrahedra in  $A_2B_2O_7$  is frustrated with respect to certain kinds of magnetic ordering.

Similarities with the crystal structure of ice  $I_h$ : the notion of spin ice.

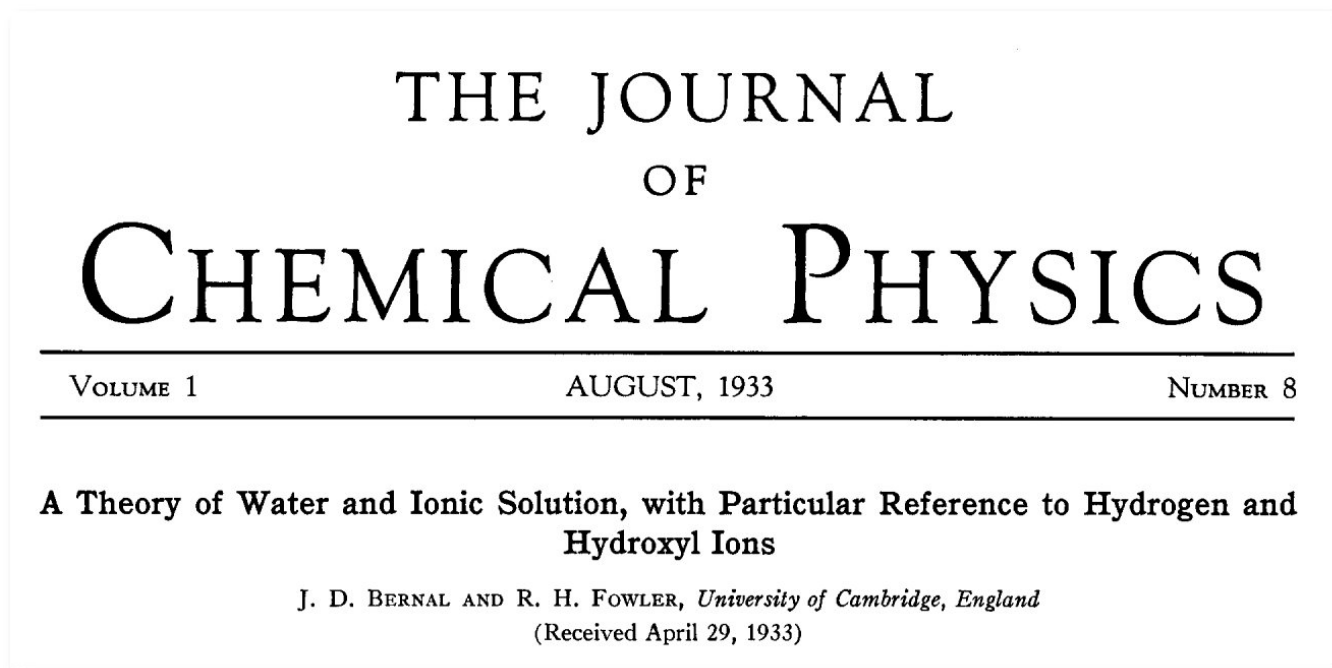


Well-known frustration of spins on corners of triangles.



# Lone pairs in the solid state: All about ice

The precise analogy with ice: Bernal-Fowler (1933) Ice rules



- Oxygens in ice- $I_h$  form a wurtzite (tetrahedral) lattice, with an O-O distance of  $2.76 \text{ \AA}$
- The  $0.95 \text{ \AA}$  OH bond of  $H_2O$  is retained in ice- $I_h$
- Each oxygen must have two H at  $0.95 \text{ \AA}$  and two at  $1.81 \text{ \AA}$ , but which two?



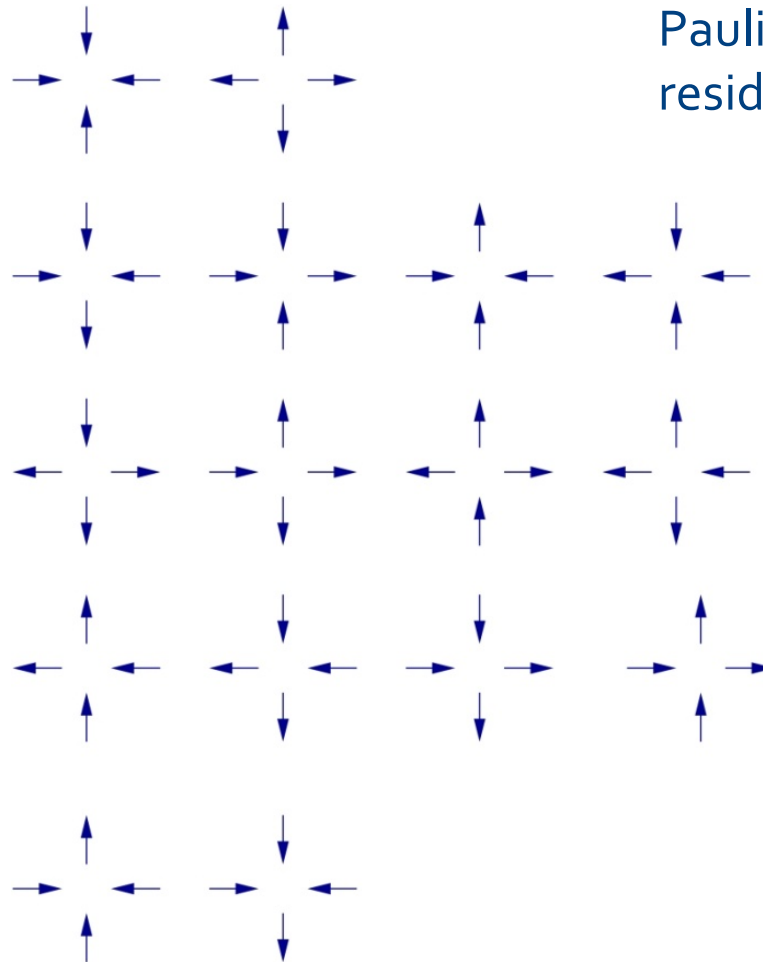
# Lone pairs in the solid state: All about ice

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 506]

## The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

16 ways of arranging  
H around O.



Pauling (1935): Ice- $I_h$  has  
residual entropy

# Lone pairs in the solid state: All about ice

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 506]

## The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

16 ways of arranging  
H around O. Only 6  
obey the ice rules:

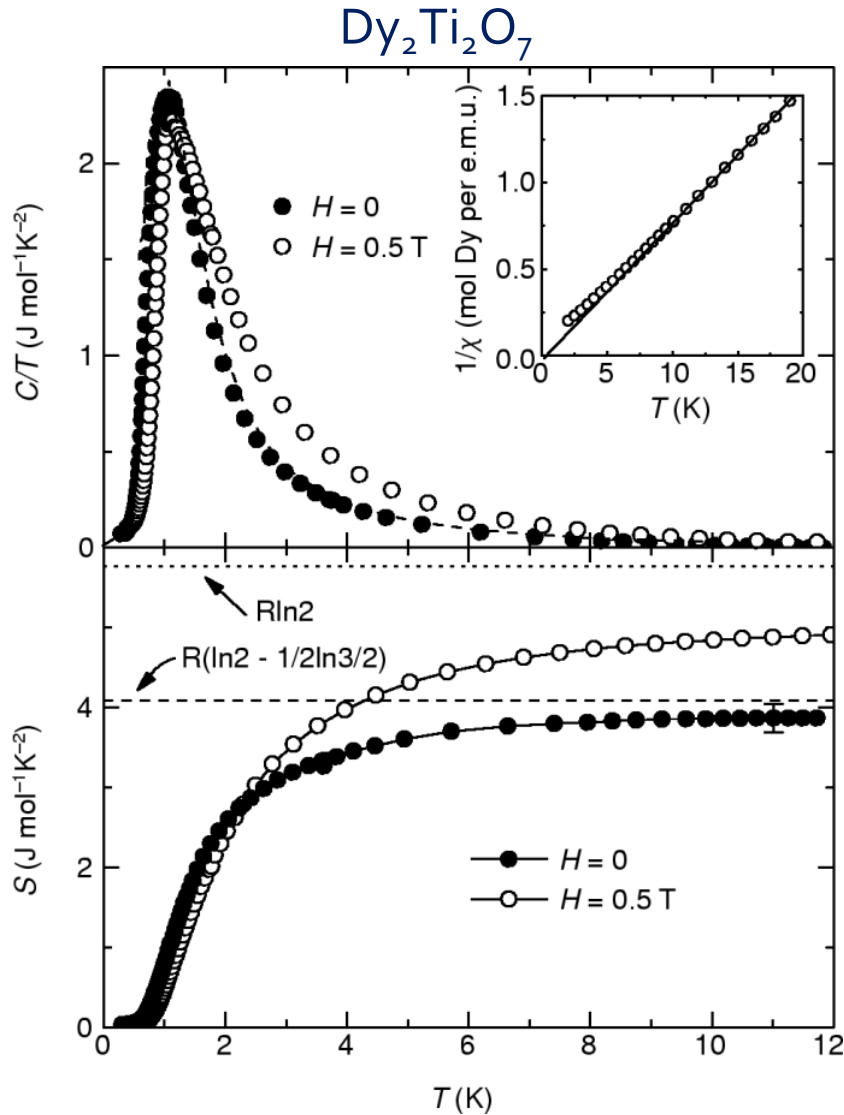
$$S = k_B \ln W \text{ and}$$
$$W = 6(1/2)(1/2) = 3/2$$



Pauling (1935): Ice- $I_h$  has  
residual entropy

Calculated by Pauling: 0.80 cal/K/mol  
Measured by Giauque: 0.82 cal/K/mol

# Lone pairs in the solid state: Heat capacity signatures



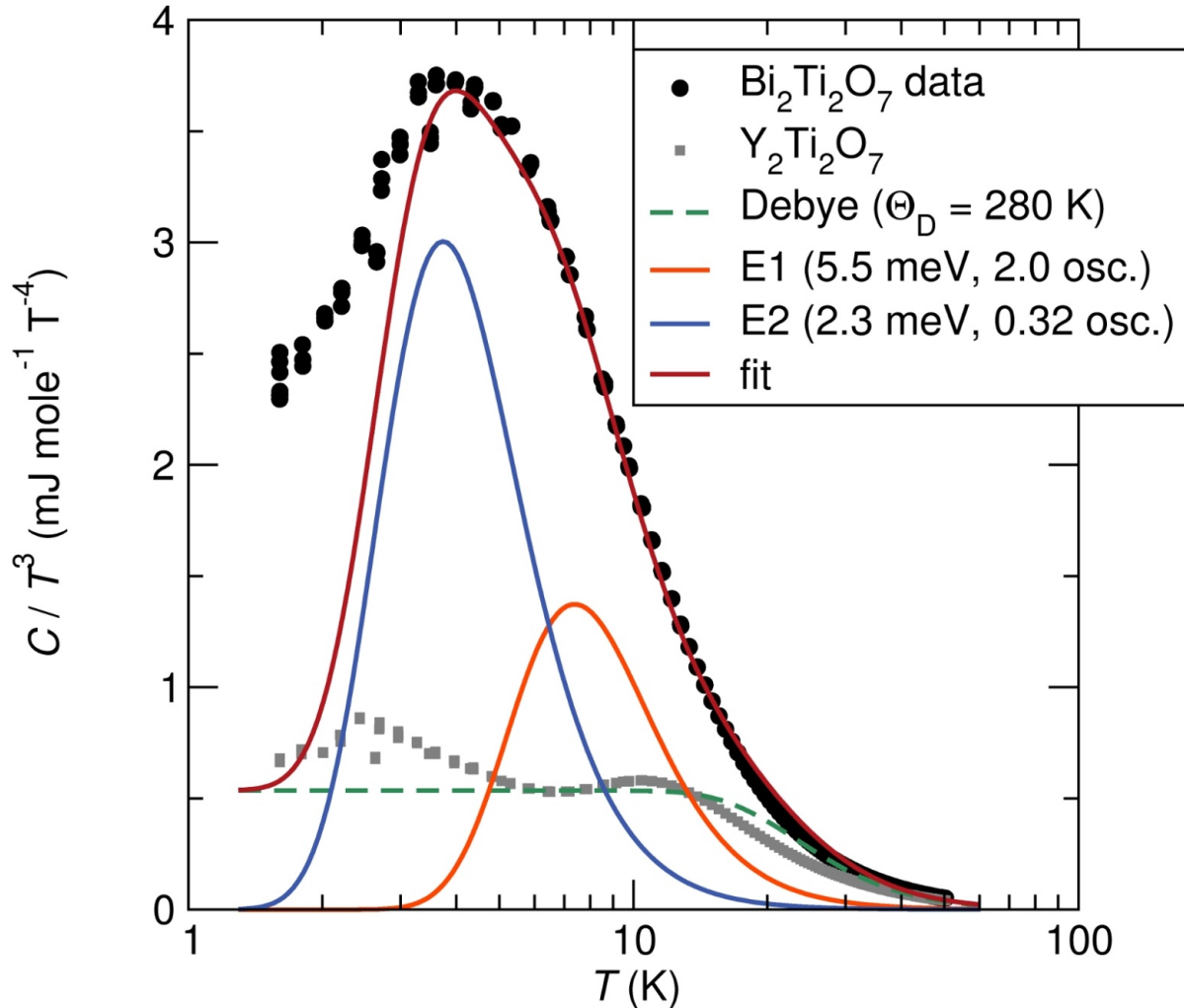
The incomplete ordering of spins at low temperatures in spin-ice results in characteristic heat capacity signatures.



# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ heat capacity

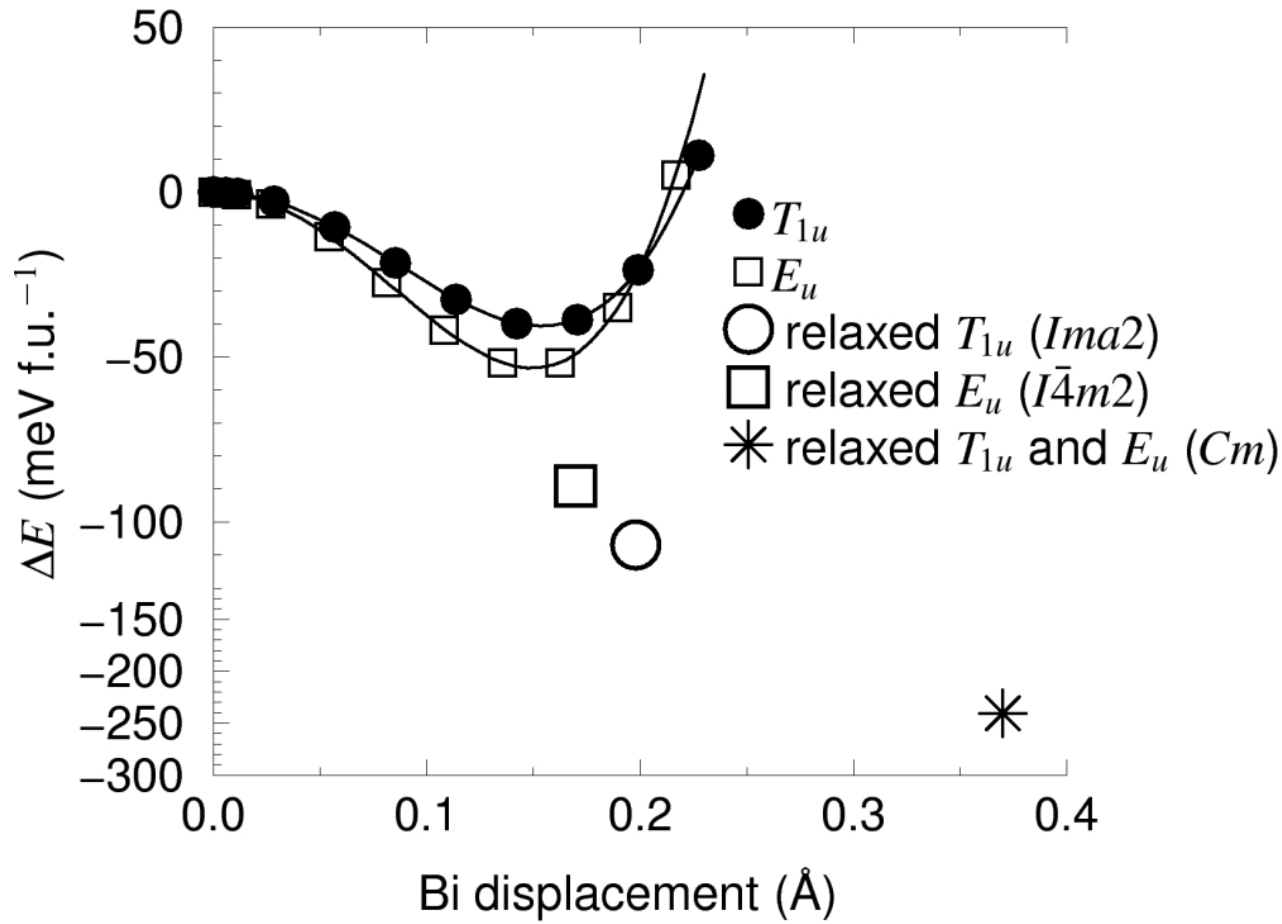
Does charge ice have residual entropy ?

Comparing  $\text{Bi}_2\text{Ti}_2\text{O}_7$  with  $\text{Y}_2\text{Ti}_2\text{O}_7$  (the latter has no lone pairs, and displays simple Debye behavior)



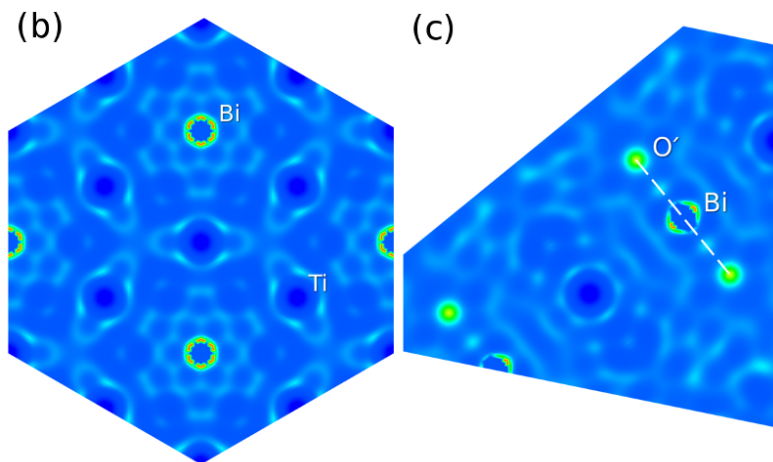
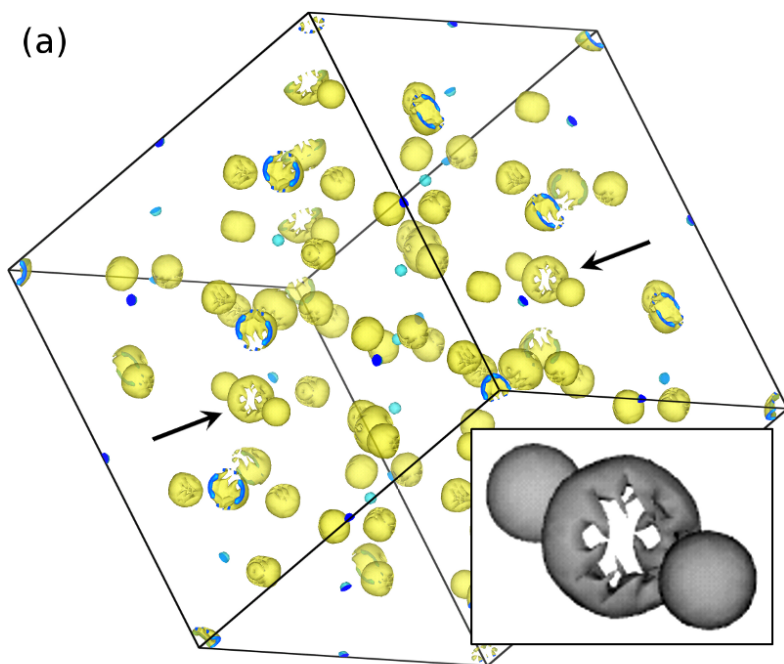
# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ heat capacity

Computed instabilities – calculations by Craig Fennie (Cornell) and Karin Rabe (Rutgers) suggest that  $\text{Bi}_2\text{Ti}_2\text{O}_7$  is potentially a ferroelectric with  $P \sim 40 \mu\text{C}/\text{cm}^2$ .



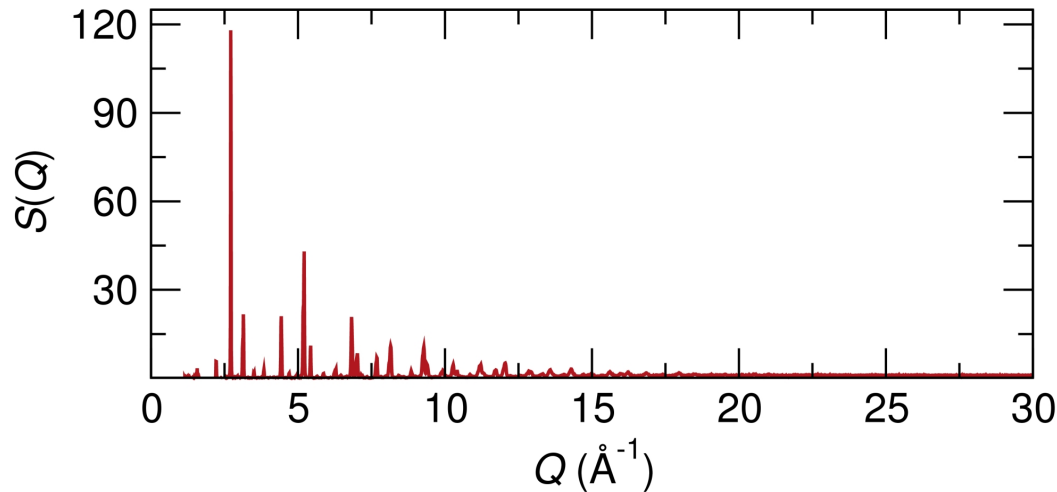
# Lone pairs in the solid state: (in)coherent lone pairs

Maximum Entropy Method (MEM/Rietveld) reconstruction of the nuclear density suggests (without bias), the displacements of Bi and O'.



# Studying local structure: The pair distribution function

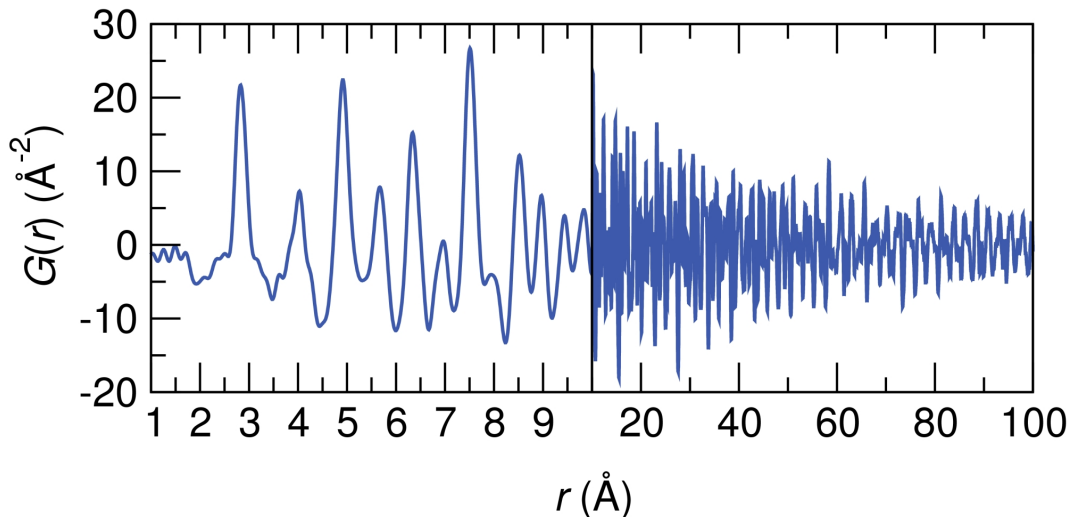
$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ$$



The total scattering structure factor:  $S(Q)$

Sine Fourier transform

The Pair Distribution Function (PDF):  $G(r)$





# Acquiring and analyzing the pair distribution function

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ$$

The Lujan Neutron Science Center at Los Alamos: "a powerful linear accelerator that accelerates protons to 84% the speed of light. When these protons strike a target of tungsten metal, neutrons are produced"

Data shown in this talk: NPDF (Thomas Proffen).

Analysis using RMCProfile



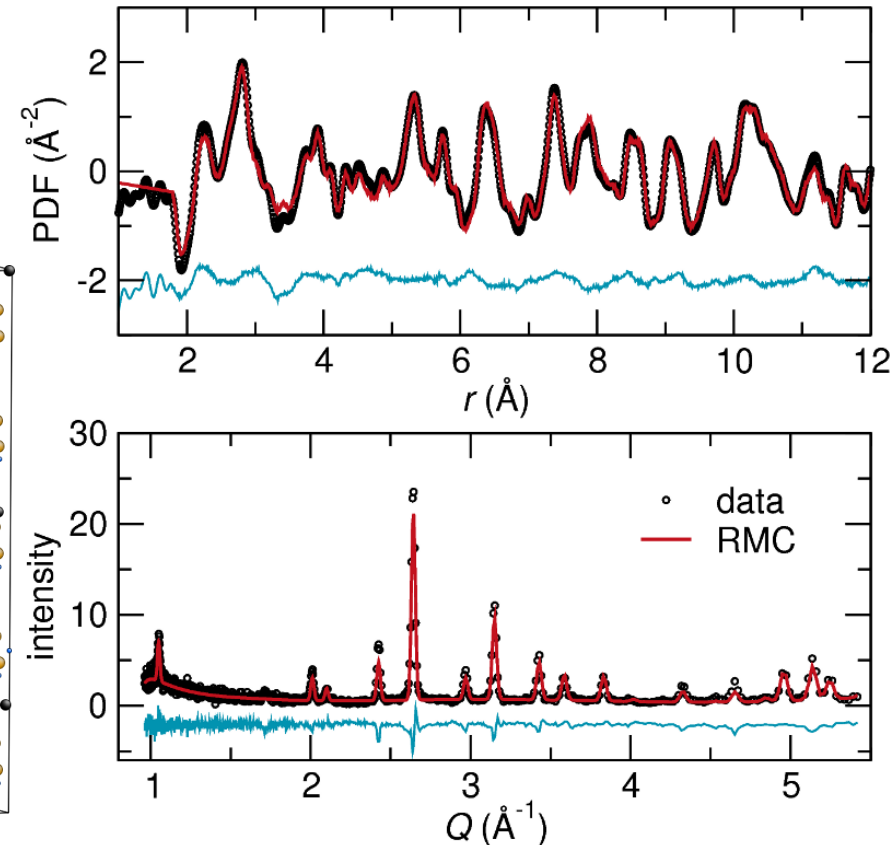
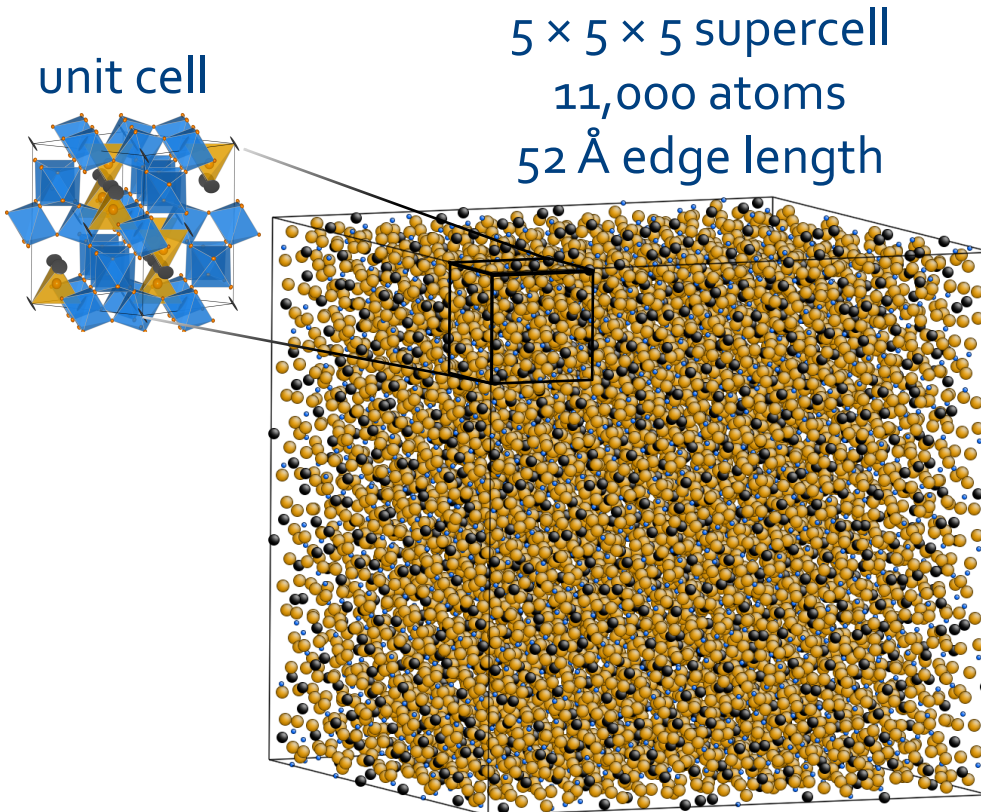
# The reverse Monte Carlo (RMC) method:

Metropolis Monte Carlo: Randomly move atoms to minimize energy

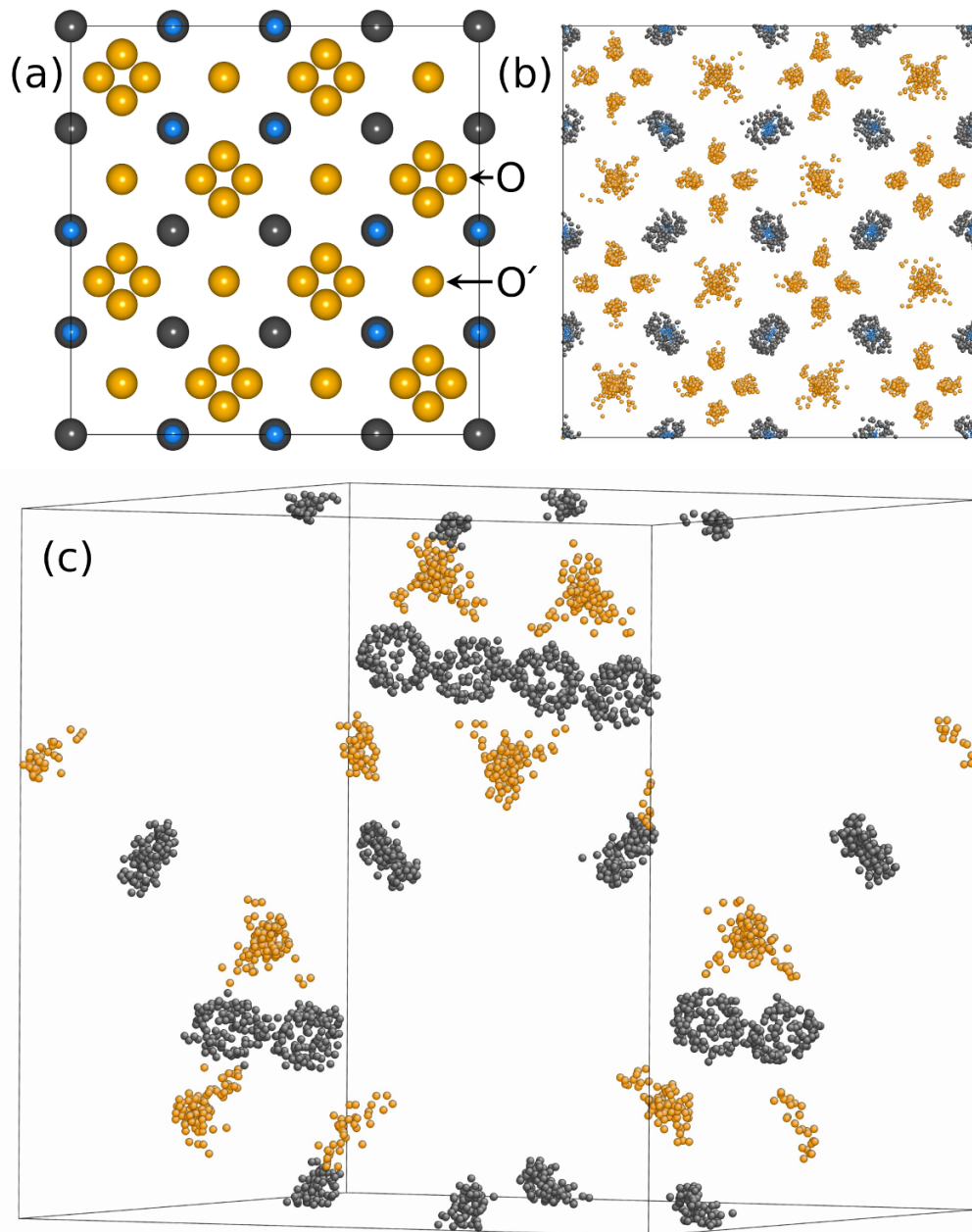
acceptance criterion:  $\exp(-\Delta U/kT)$

Reverse Monte Carlo: Randomly move atoms to achieve a fit to data

acceptance criterion:  $\exp(-\Delta\chi^2/\sigma)$



# Lone pairs in the solid state: (in)coherent lone pairs

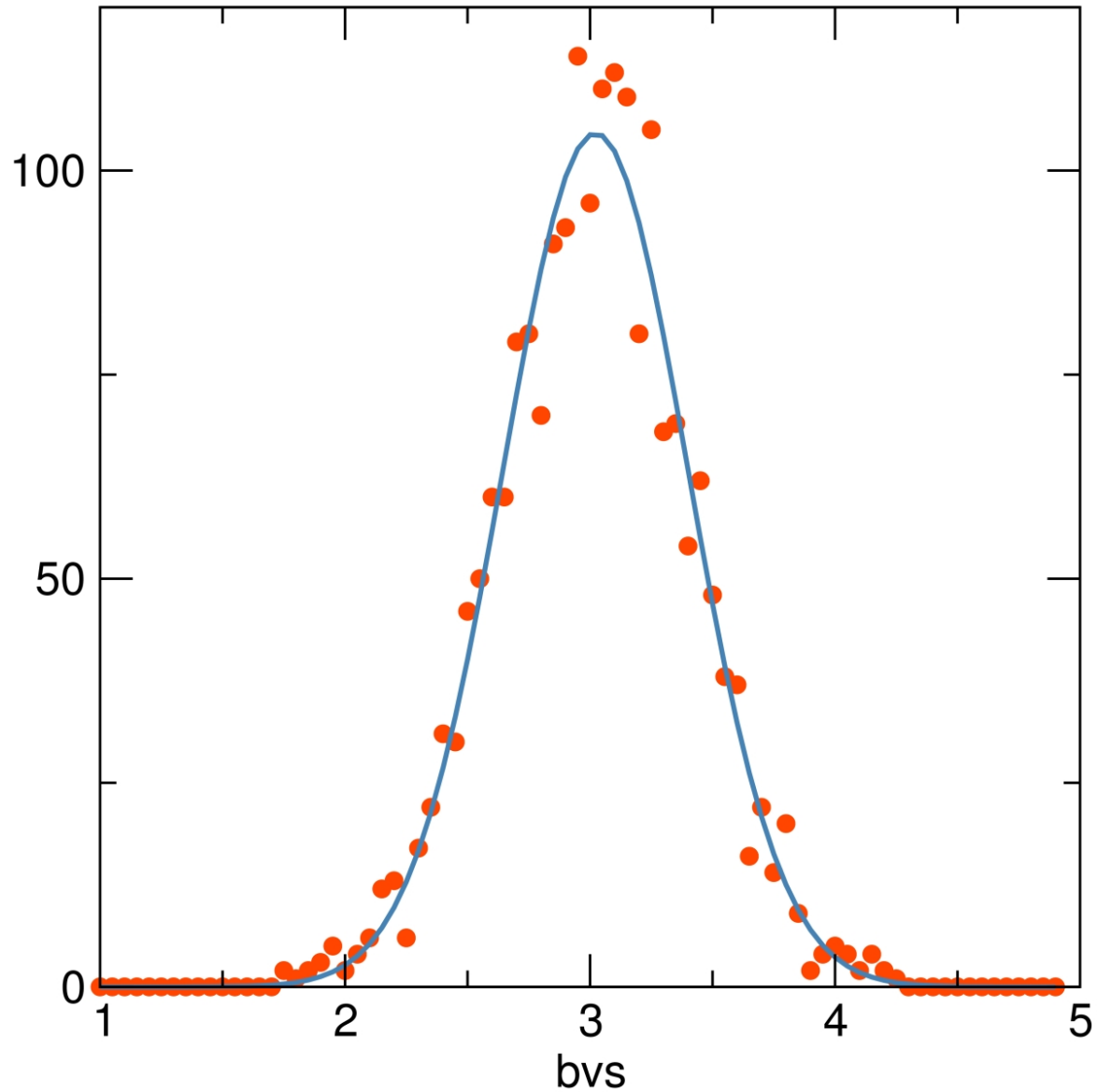


What does the local structure of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  look like? NPDF/RMC:

Ti and O are well-behaved, Bi and O' are not.

Bi form rings weighted by hexagons; O' form tetrapods.

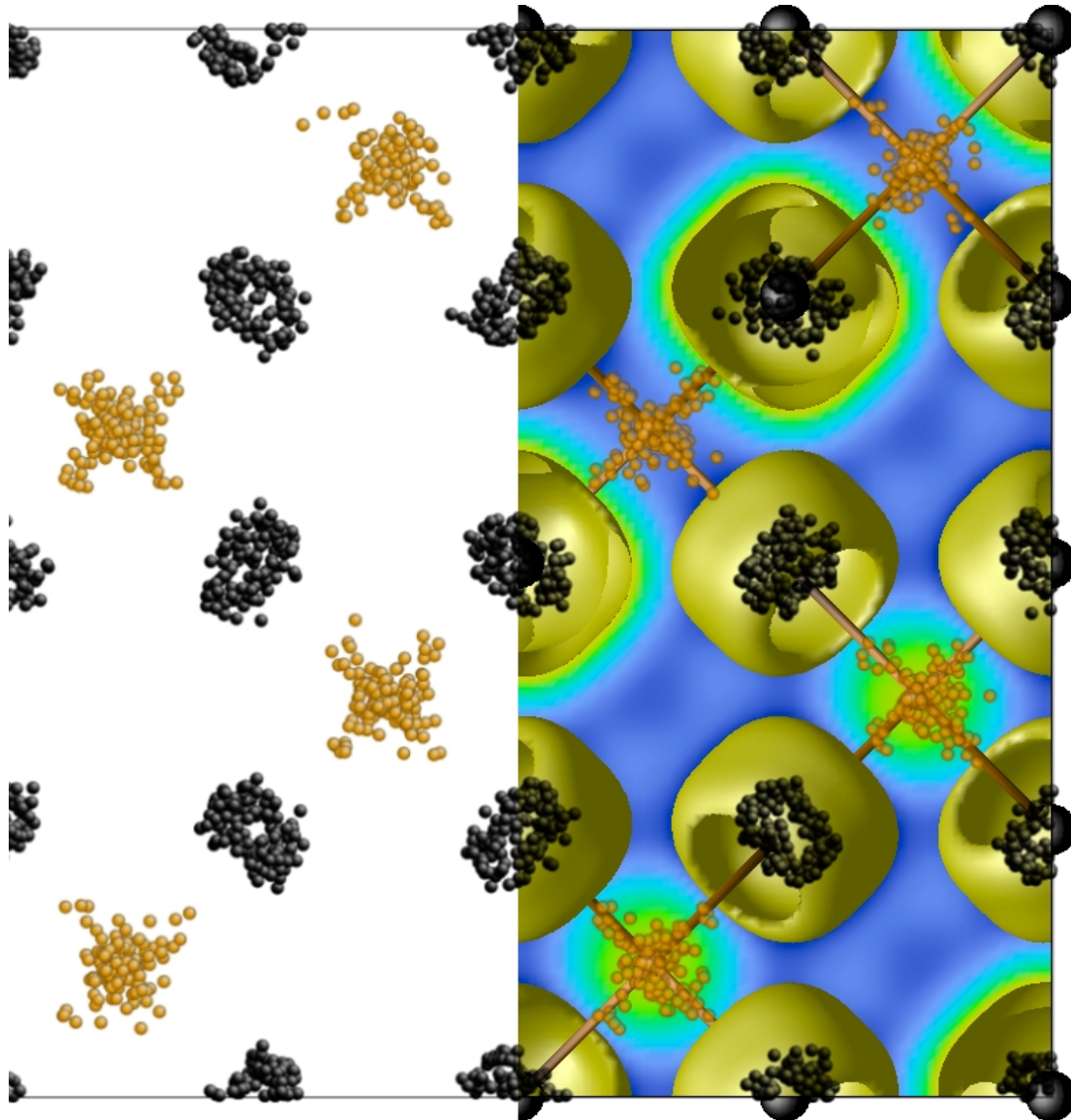
# Lone pairs in the solid state: (in)coherent lone pairs



BVS of Bi = Bi<sup>3+</sup>, as a sanity check !



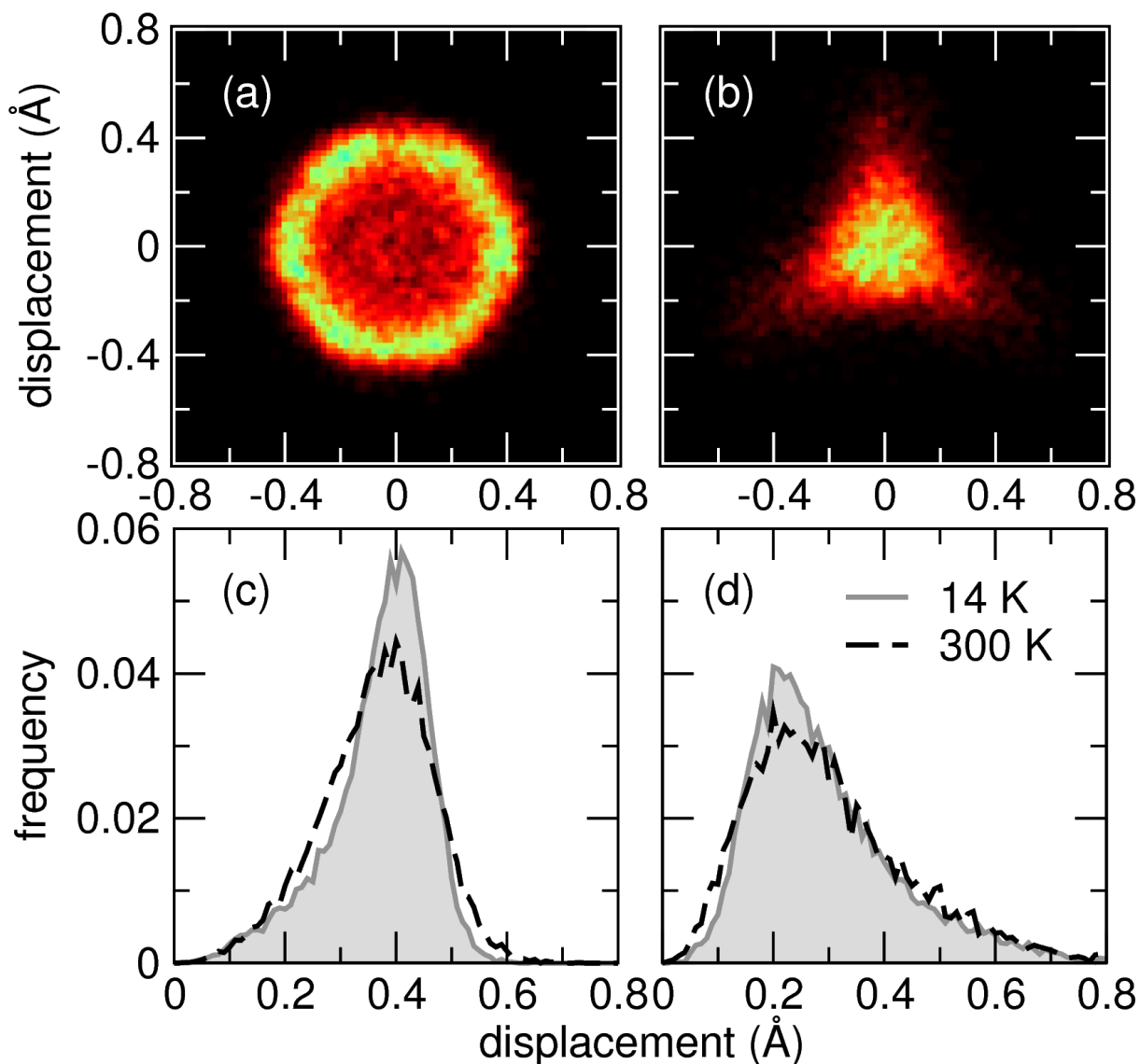
# Lone pairs in the solid state: (in)coherent lone pairs



The ELF of the ideal structure predict the nature of incoherent Bi displacements.

Note: The lone-pair to nucleus distance should be close to 1 Å

# Lone pairs in the solid state: (in)coherent lone pairs

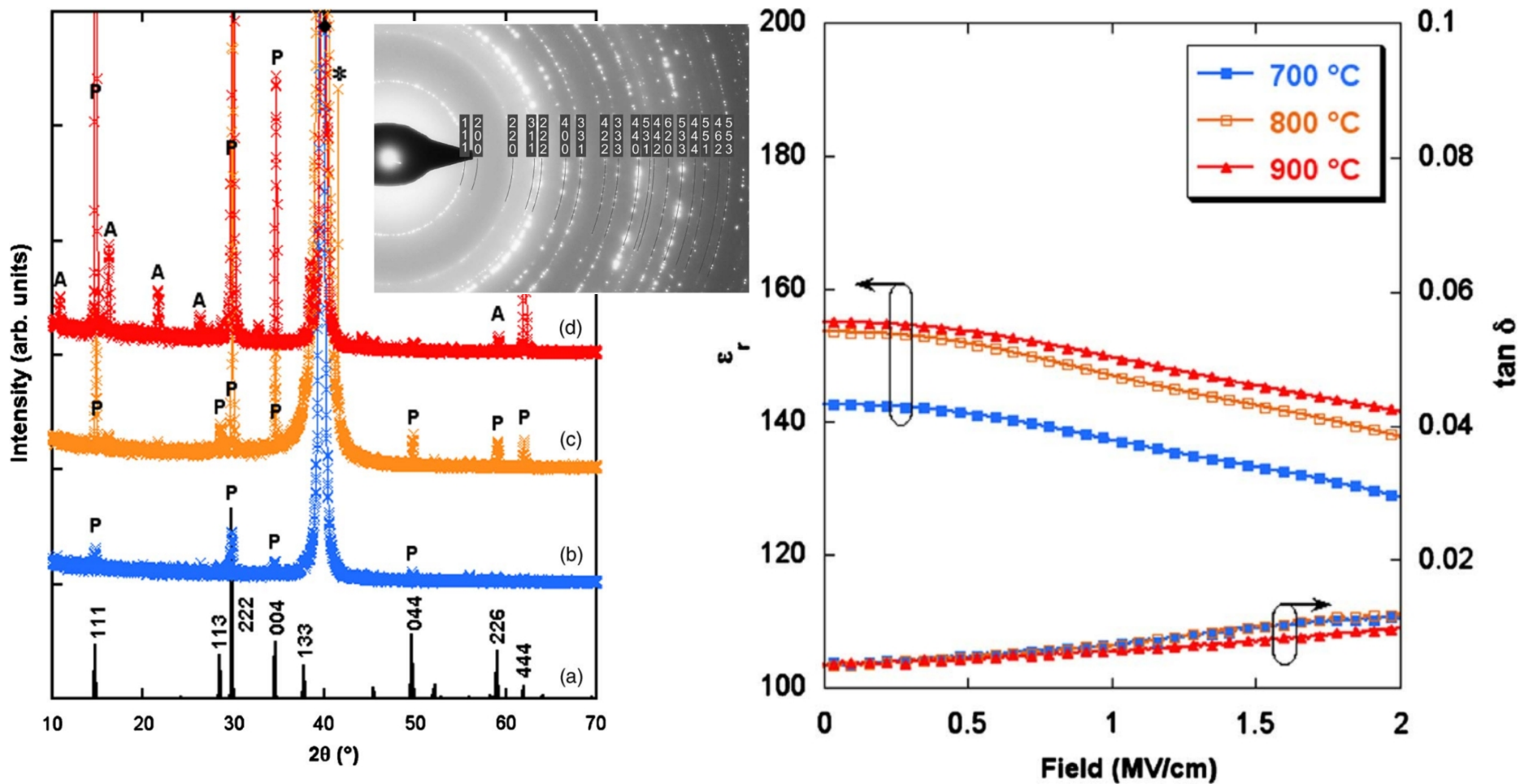


Projection of (a) Bi and (b) O' positions. (c) and (d) are histograms of the atomic displacements from the ideal positions at 14 K and 300 K.

Applying the Lindemann criterion, the Bi<sub>2</sub>O' lattice has melted!

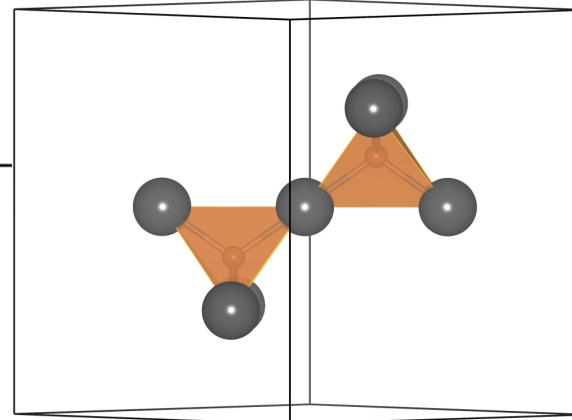
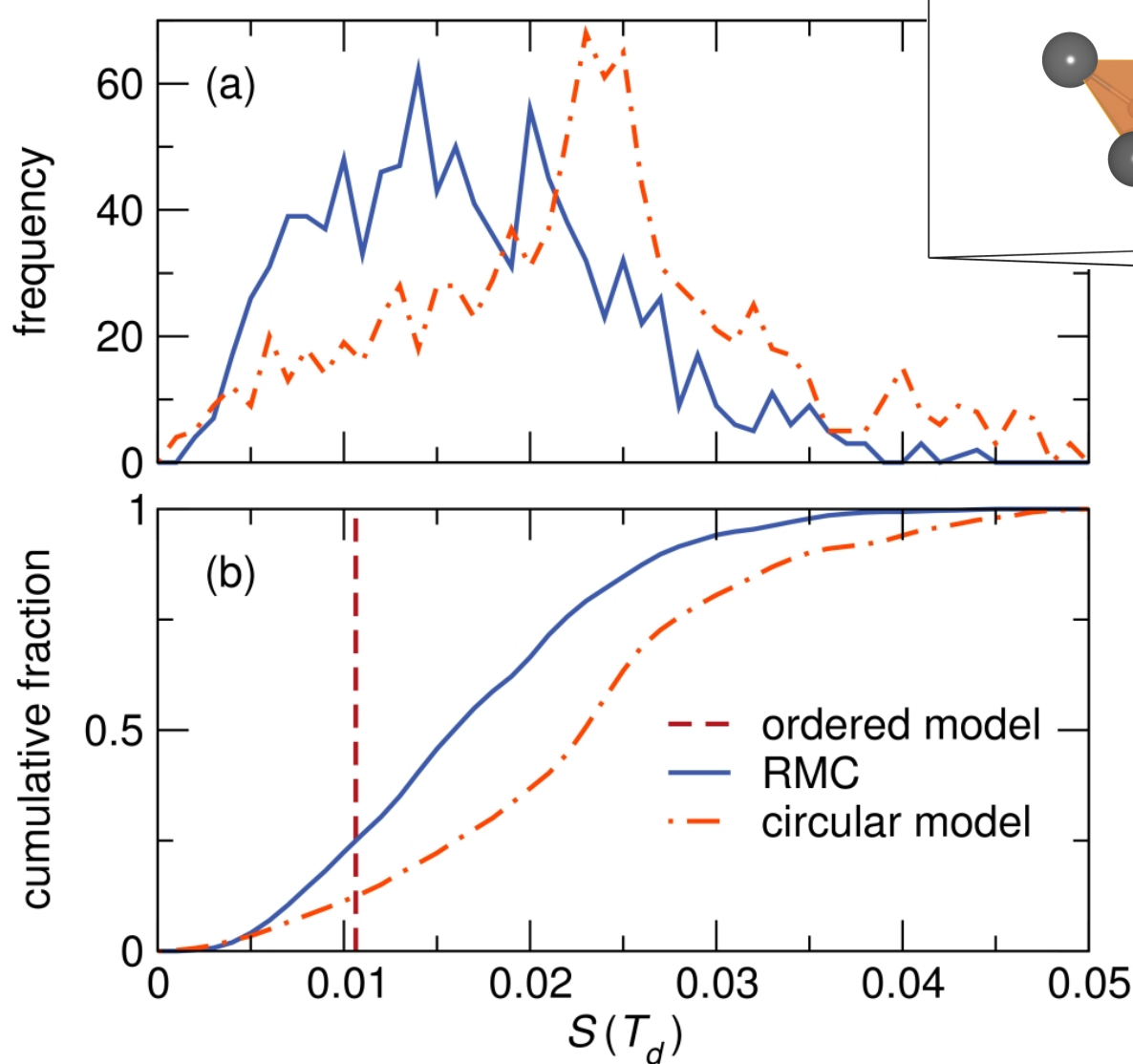
Not much change with T: displacements are static

# Lone pairs in the solid state: (in)coherent lone pairs



Thin films of  $\text{Bi}_2\text{Ti}_2\text{O}_7$  (Stemmer group, UCSB). High dielectric constant that is not field tunable: Suggest displacements are frozen at RT.

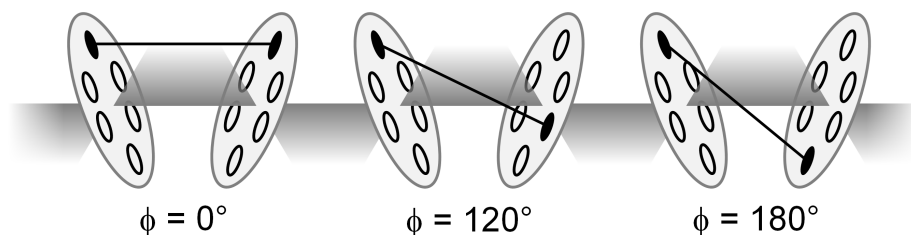
# Lone pairs in the solid state: (in)coherent lone pairs



Continuous Symmetry Measure (Avnir et al.) allow "distances" from ideal polyhedra to be quantified.

Here,  $\text{OBi}_4$  tetrahedra are more ideal than circular rings suggest, but less ideal than  $\beta$ -cristobalite-type distortions.

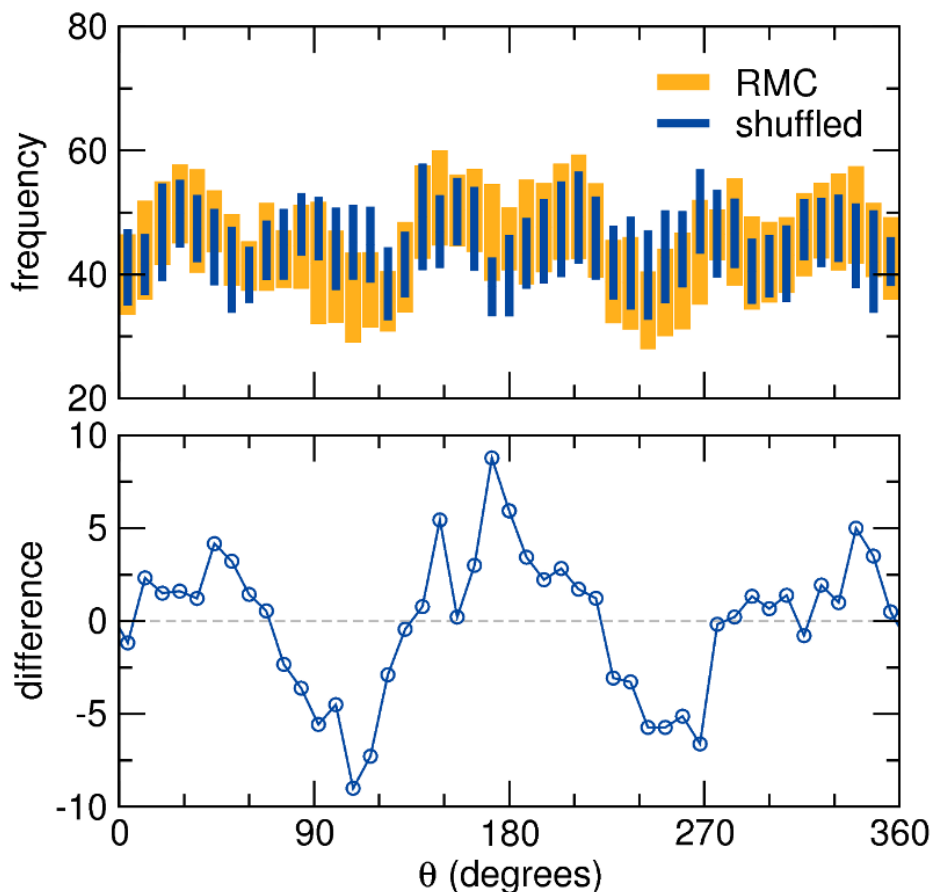
# Lone pairs in the solid state: (in)coherent lone pairs



Are there correlations at the local level between atomic displacements ?

RMC suggests a slightly antiferrodistortive propensity with which neighboring Bi displace.

$\text{Bi}_2\text{Ti}_2\text{O}_7$  is a frustrated antiferroelectric?

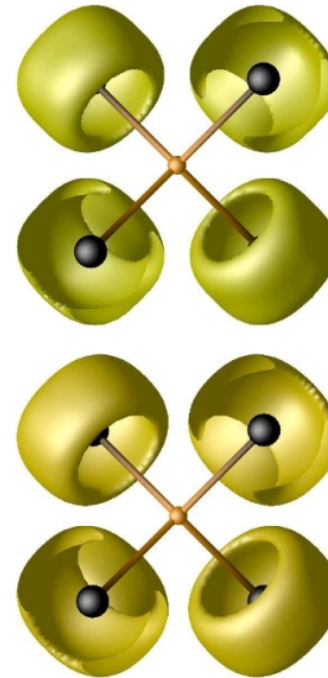
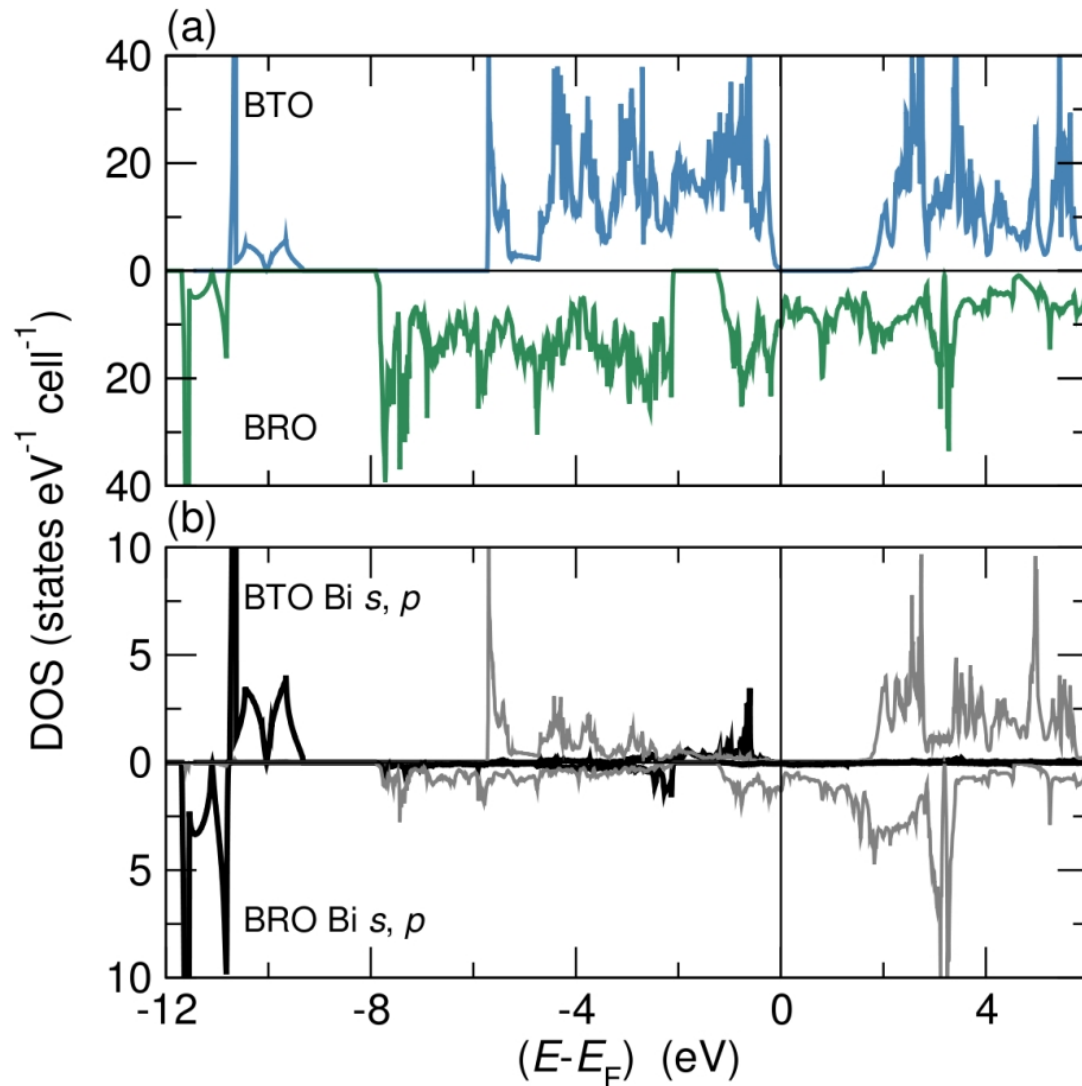


Shoemaker, Seshadri, Hector, Llobet, Proffen, Fennie, Phys. Rev. B 81 (2010) 144113(1-9).

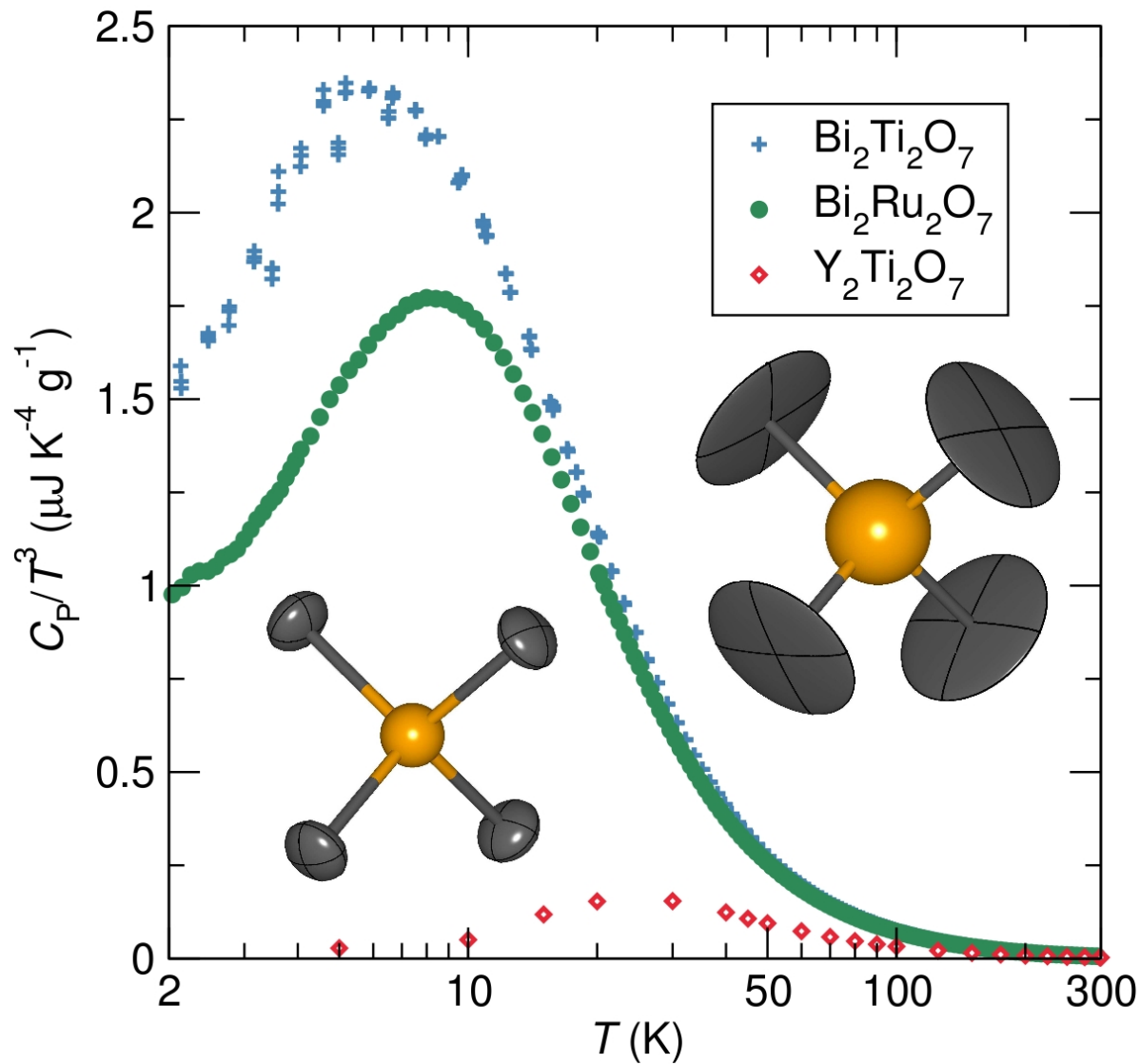


# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ vs. $\text{Bi}_2\text{Ru}_2\text{O}_7$

$\text{Bi}_2\text{Ti}_2\text{O}_7$  is an insulator and  $\text{Bi}_2\text{Ru}_2\text{O}_7$  is metallic. ELF networks in the cubic compounds are similar.

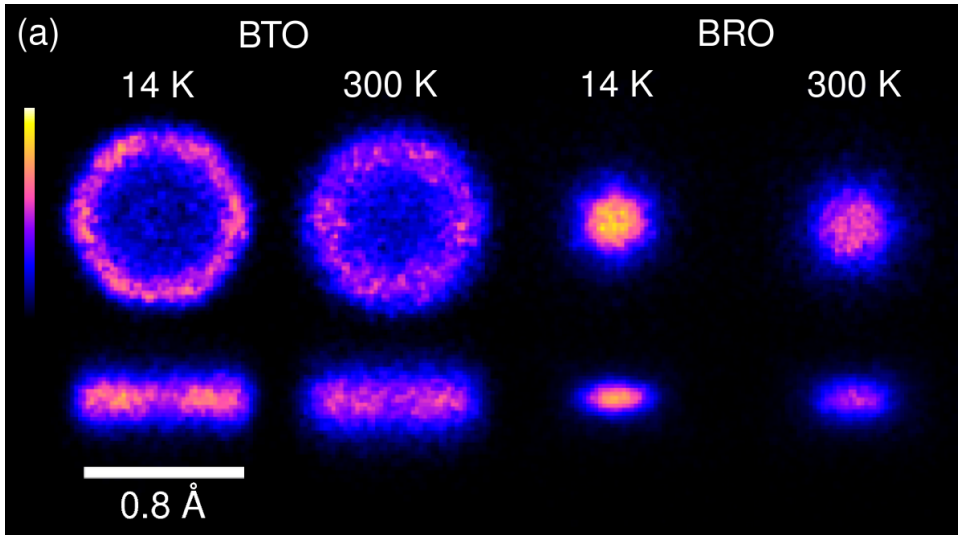


# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ vs. $\text{Bi}_2\text{Ru}_2\text{O}_7$



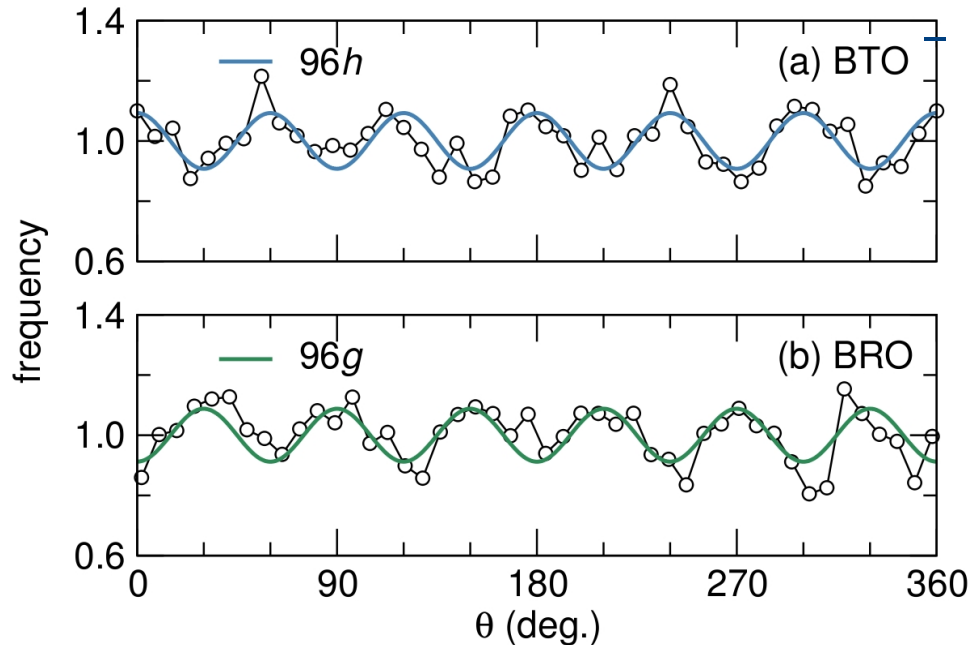
Both heat capacity (lattice-only) and Bragg-Rietveld structures suggest BRO has Bi atoms displaced to a smaller extent.

# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ vs. $\text{Bi}_2\text{Ru}_2\text{O}_7$

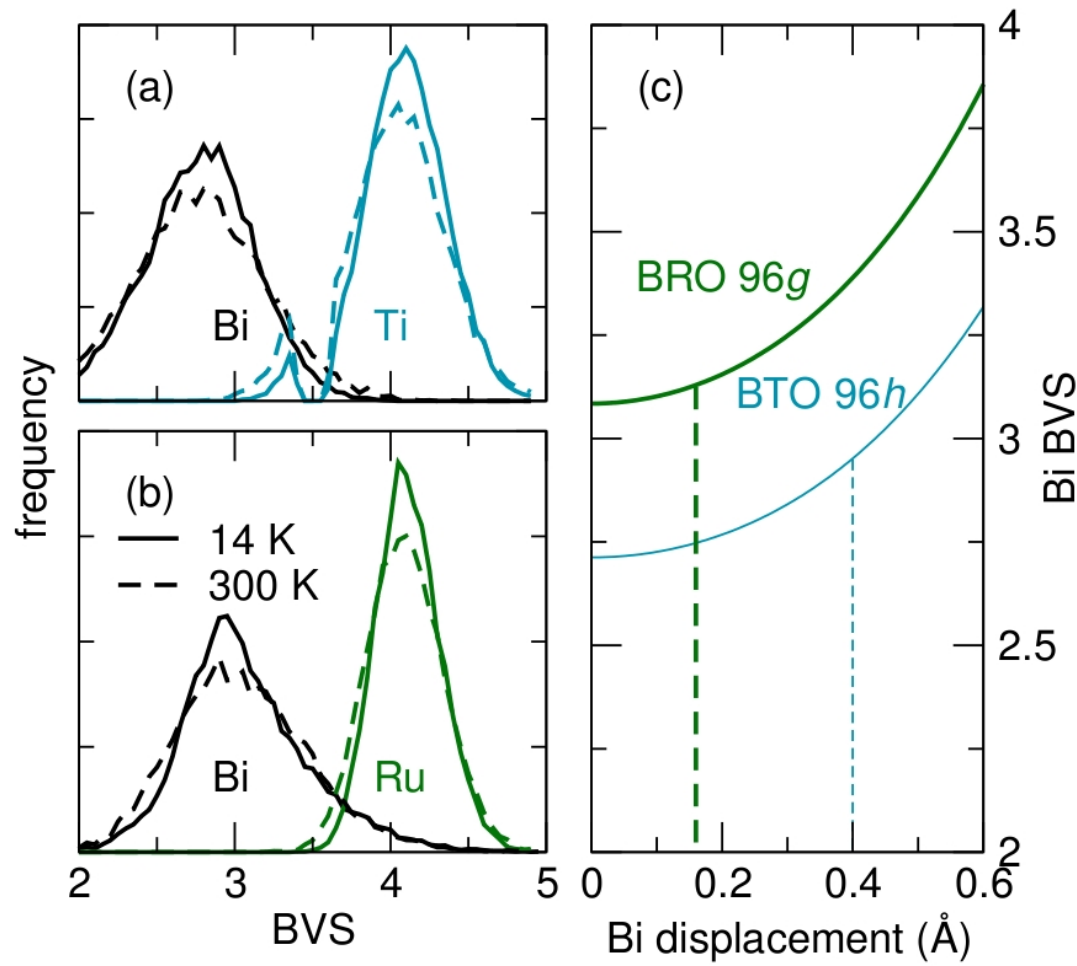


RMC supports the view the Bi are much less displaced in BRO.

Curiously, the precise propensity of displacement around the O-Bi-O' axes are distinctly different in the two compounds.



# Lone pairs in the solid state: $\text{Bi}_2\text{Ti}_2\text{O}_7$ vs. $\text{Bi}_2\text{Ru}_2\text{O}_7$



Bond valence sum analysis:

Bi in BTO and BRO are  $\text{Bi}^{3+}$

Bi displacements in BTO are due to bond valence reasons, in addition to the lone pair.

Bi displacements in BRO are solely due to the lone pair, but are significantly smaller in magnitude. Screening plays a role in BRO.

# Findings:

1. The utility of the ELF in locating lone pairs.
2. Evidence that pyrochlores with lone pairs may be prevented from achieving a distorted ground state because of lattice topology.
3. Evidence for glassy disorder in an otherwise crystalline lattice, reminiscent of ice  $I_c$  or  $I_h$
4. Insights into polar behavior
5. Demonstrated exquisitely detailed information achievable using high quality total scattering and RMC, with appropriate analysis: BVS of multiple ions on a single site, distributions of continuous symmetry measures...







thank you