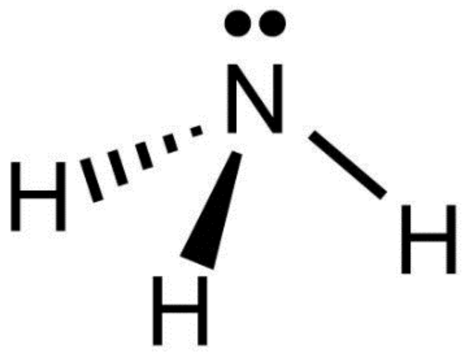
Lone Pairs, Hidden and Otherwise

seshadri@mrl.ucsb.edu UC SANTA BARBARA

N Lone Pair Electrons Cause Ammonia to be (Distorted) Tetrahedral, Rather than Planar

N: [He]$2s^2 2p^3$



we say the nitrogen lone pair is “stereochemically active”

Lone pairs: An introduction

Cation centered lone pairs – the important cations (note the valence is 2 below the group valence); the sub-valent state is particularly important in the last row:

	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 !

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

In many crystalline oxide and fluoride 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 is much shorter than typical cation-anion distances. The distances in (in Å) are indicated in **red**.

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Lone pairs: Visualization using the Electron Localization Function (ELF) shown for XeO_3

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.]

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

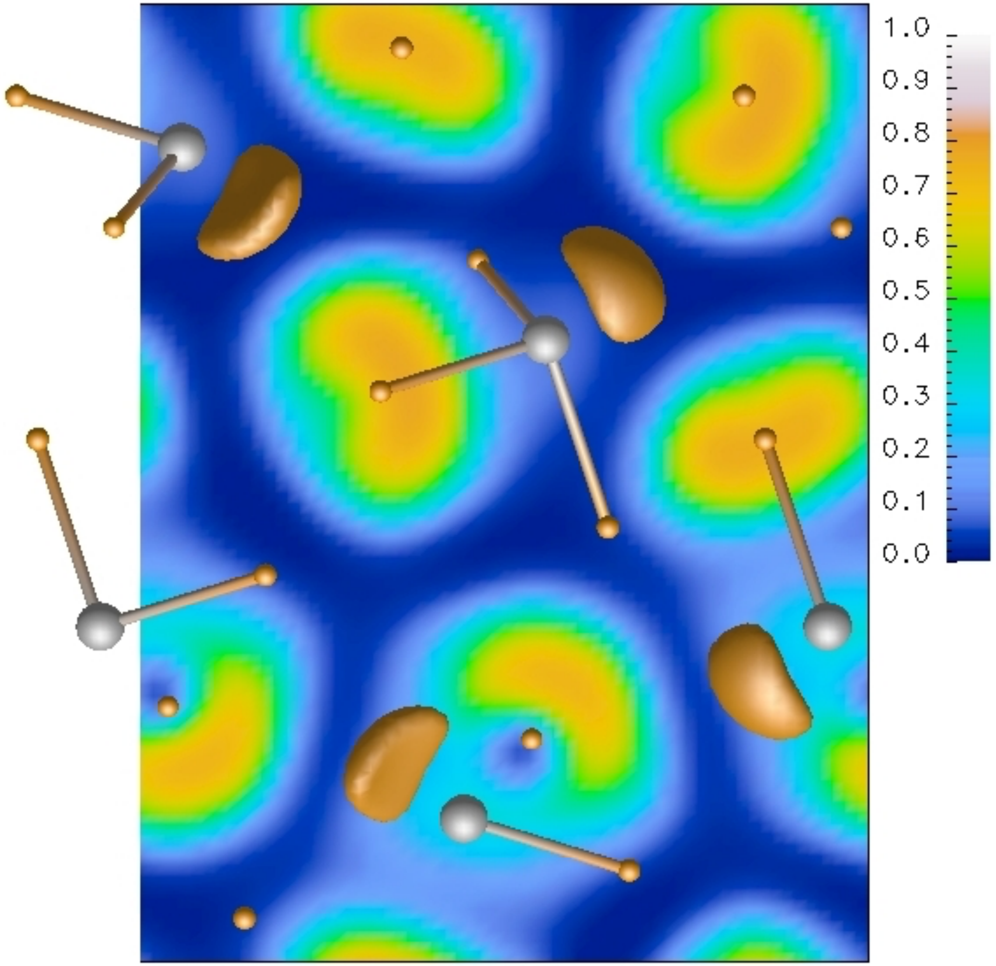
with

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

and

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

XeO_3



The electron density does not reveal lone pairs as readily.

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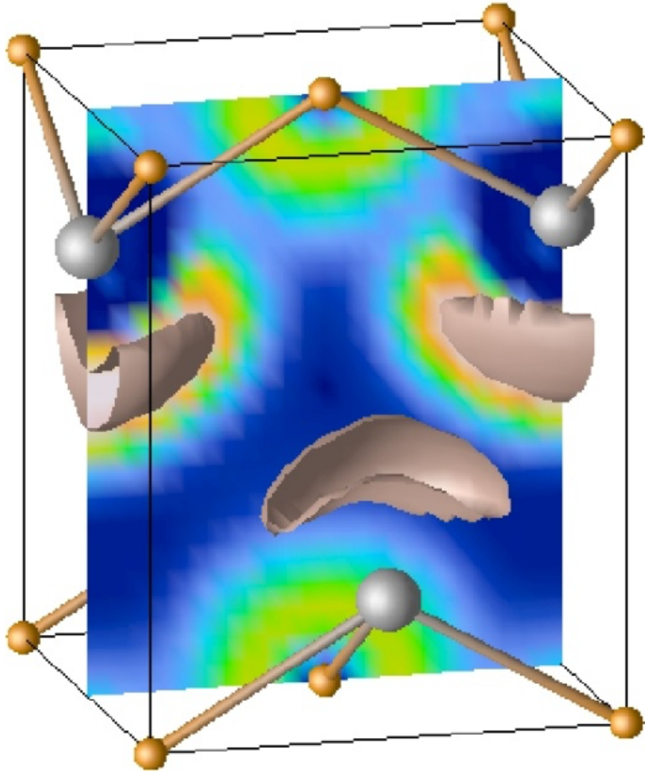
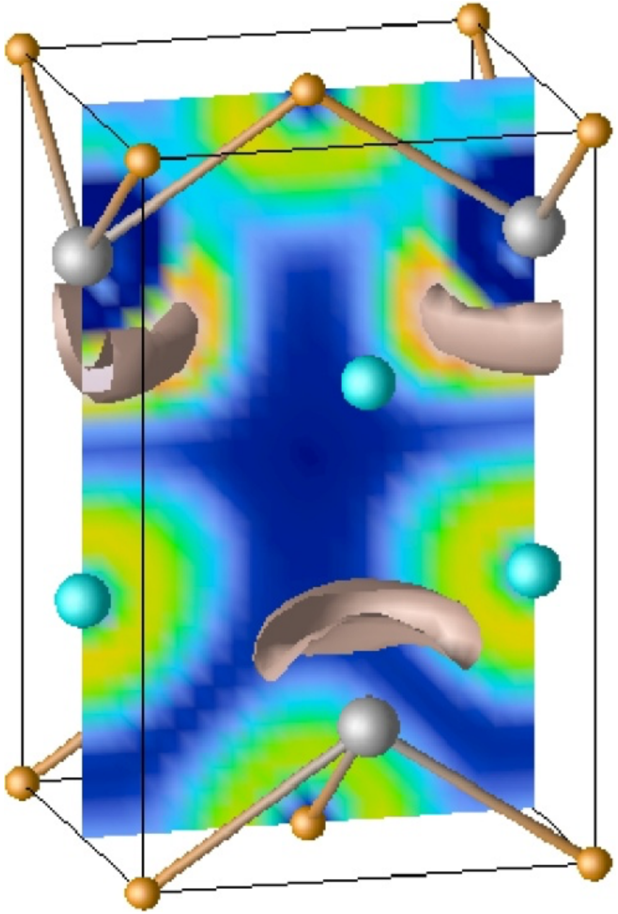
Lone pairs: Visualization using the Electron Localization Function (ELF) shown for α-PbO and BiOF

α-PbO



BiOF



Lone pairs typically visualized with ELF values (isosurfaces) between 0.65 and 0.90

Raulot, Baldinozzi, Seshadri, Cortona, *Solid State Sciences* **4** (2002) 467;
Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 487.

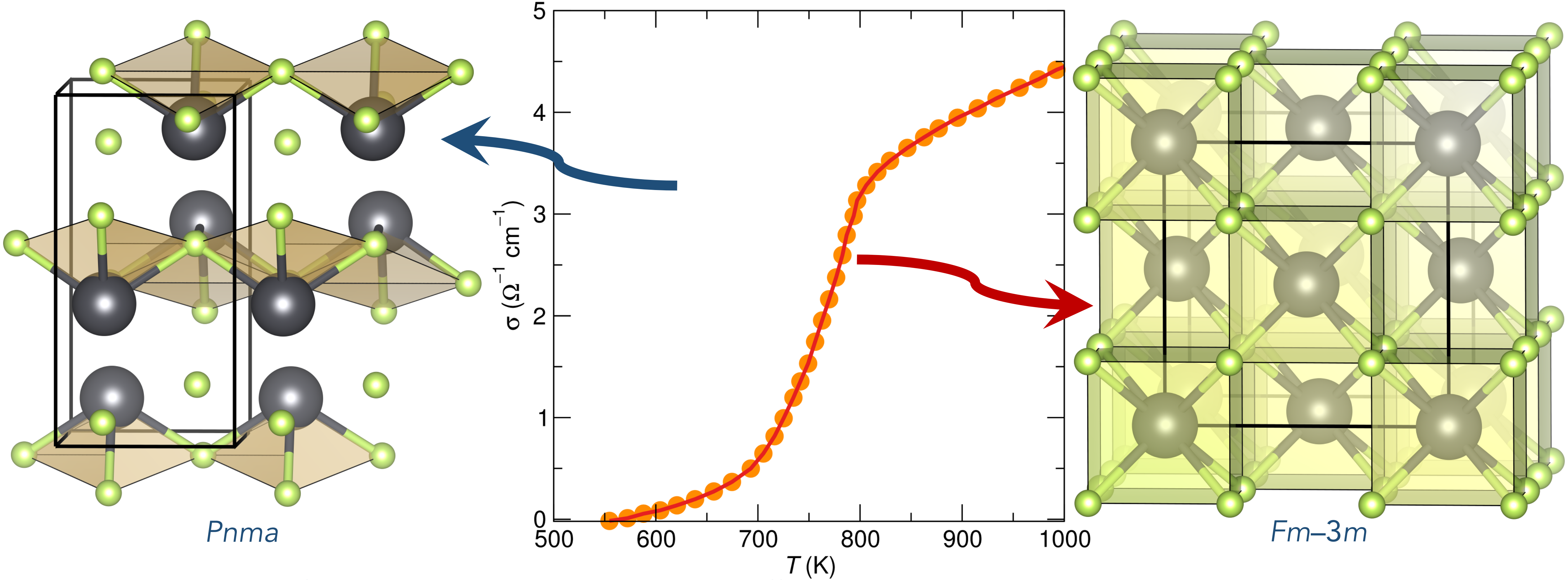
Lone pairs: Visualization using the Electron Localization Function (ELF) shown for XeO_3

Cation-centered lone pairs (often with Pb^{2+} as the central cation, but also Sn^{2+} and 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
- Thermoelectrics
- "Protected" photovoltaic materials?

Lone pairs in ionic conductors: PbF_2

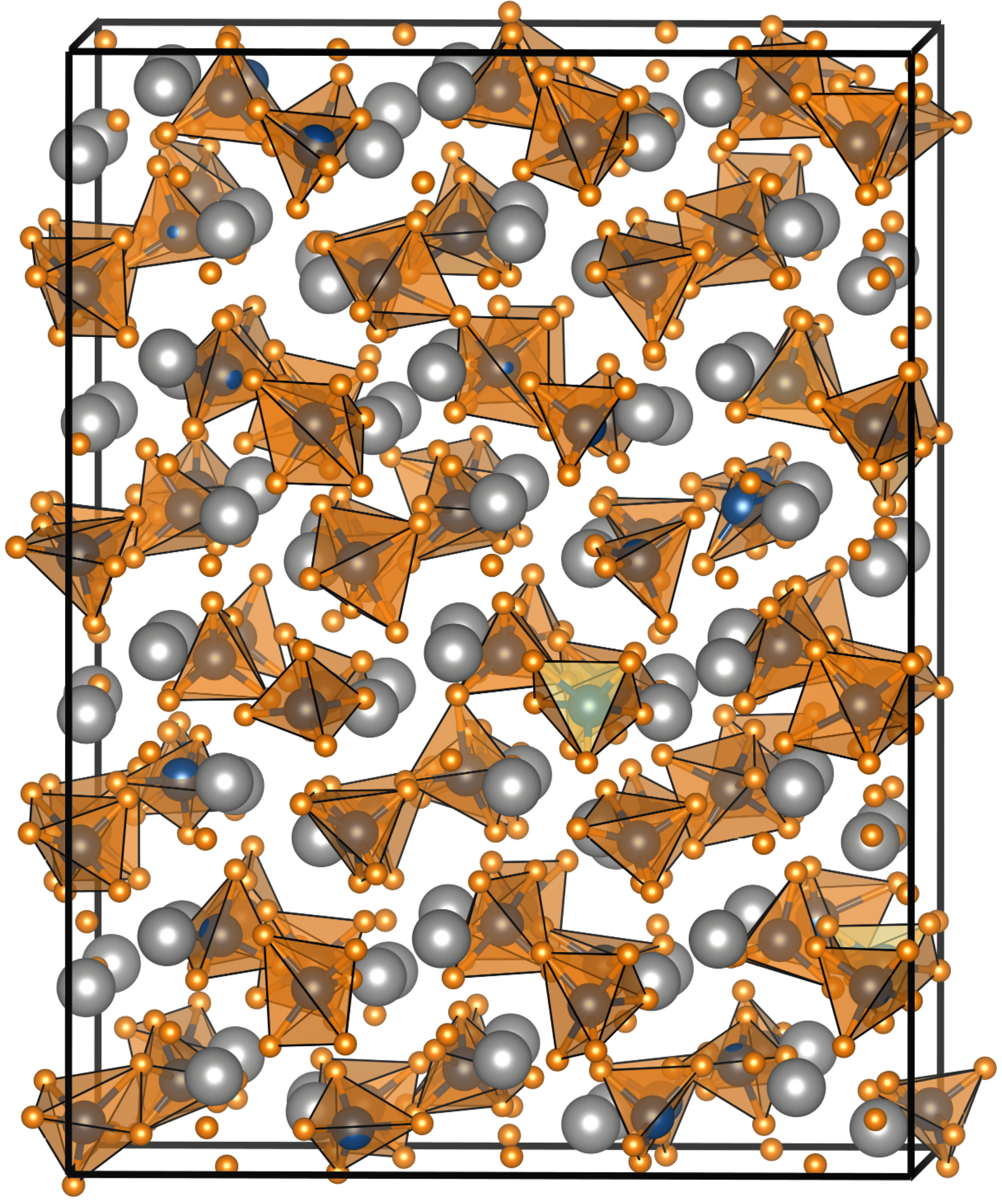
Funke , Sci. Technol. *Adv. Mater.* **14** (2013) 043502, quoting Michael Faraday from 1839: "*… fluoride of lead. When a piece of that substance, which had been fused and cooled, was introduced into the circuit of a voltaic battery, it stopped the current. Being heated, it acquired conducting powers before it was visibly red hot in daylight; and even sparks could be taken against it whilst still solid.*"



Conductivity redrawn from Derrington, Navrotsky, O'Keeffe, *Solid State Commun.* **18** (1976) 47–49.

Lone pairs inspired ionic conductors: $La_2Mo_2O_9$

Inspired by the structure of β-$SnWO_4$, $La_2Mo_2O_9$ was proposed as an oxide-ion conductor. Ordered crystal structure displayed here.

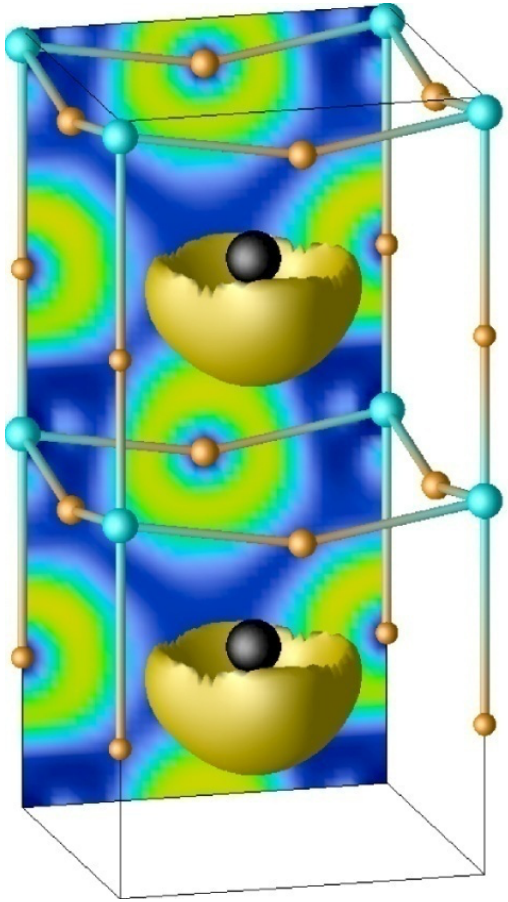


First report of high oxide-ion conductivity: Lacorre, Goutenoire, Bohnke, Retoux, Laligant, *Nature* **404** (2000) 856–858.

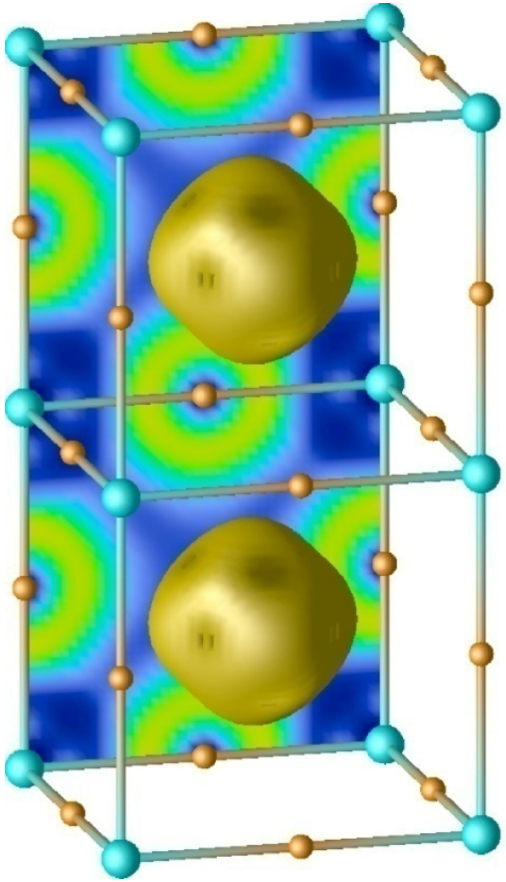
Structure at room temperature: Radosavljevic Evans, Howard Evans, *Chem. Mater.* **17** (2005) 4074–4077.

Temperature-effects in ferroics: $PbTiO_3$

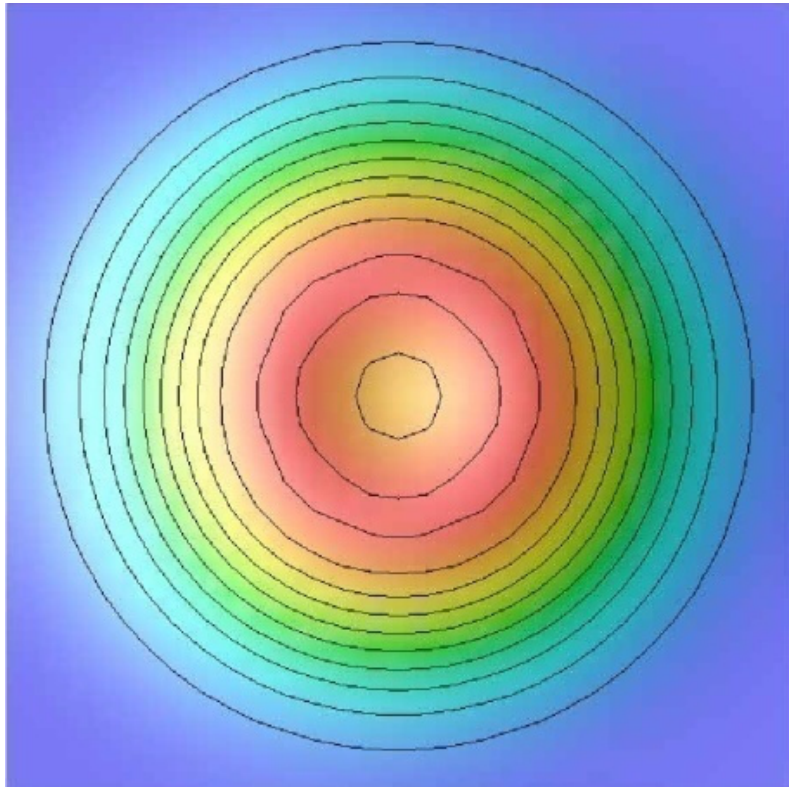
The expression of cooperative stereochemical activity of the lone pair plays an important role in the development of polar behavior.



$PbTiO_3$ above 766 K
Pm–3m



$PbTiO_3$ below 766 K
P4mm

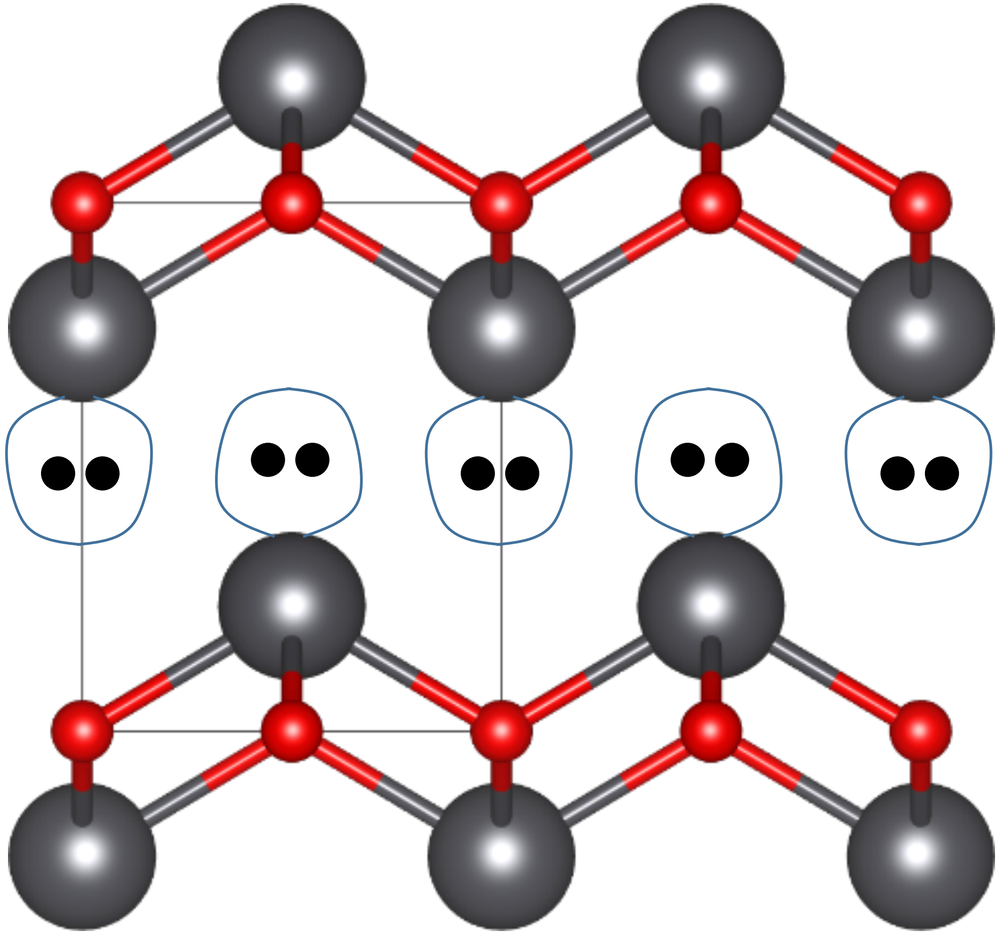


Even above the phase transition, the Pb^{2+} ion (here in Pb_2NbYbO_6) is not really where it is supposed to be [Baldinozzi, Raulot, Seshadri, *MRS Symp. Proc.* **718** (2002) D12.7.1.]

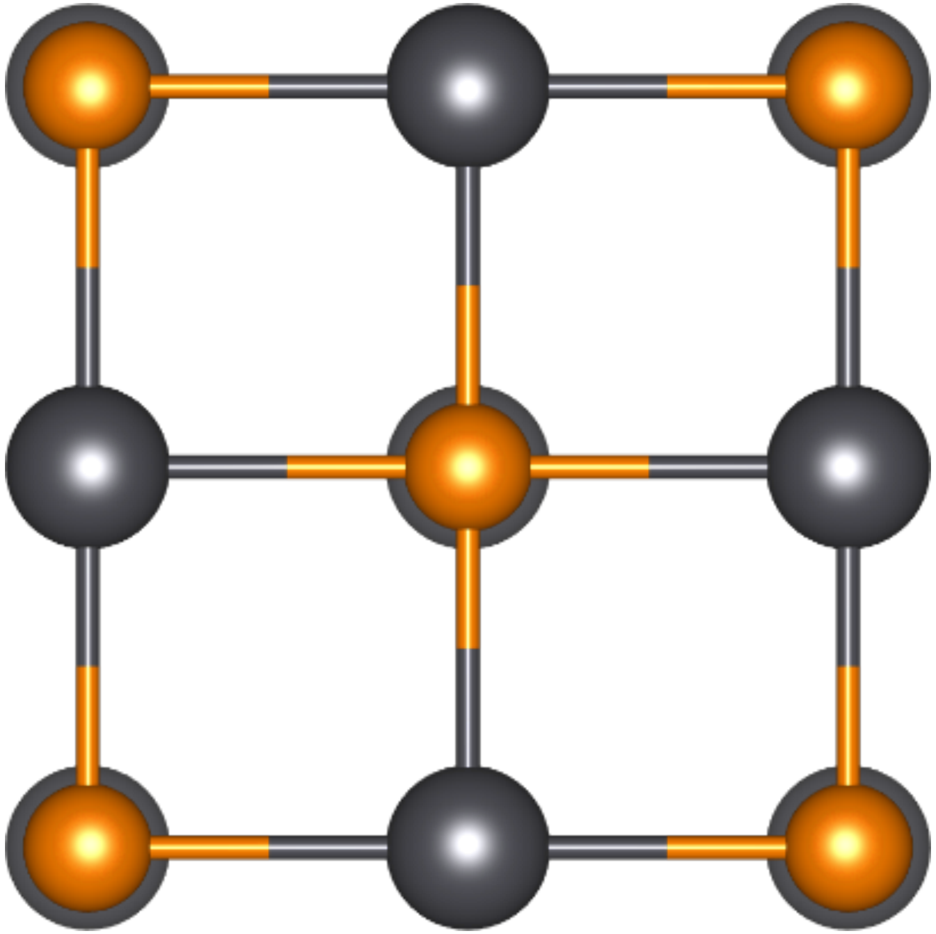
Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 487.

Chemistry counts: The role of the anion in Pb^{2+}: $[Xe]5d^{10}6s^2$

Stereochemically “active” lone pair: PbO



Stereochemically “inactive” or “silent” lone pair: PbS



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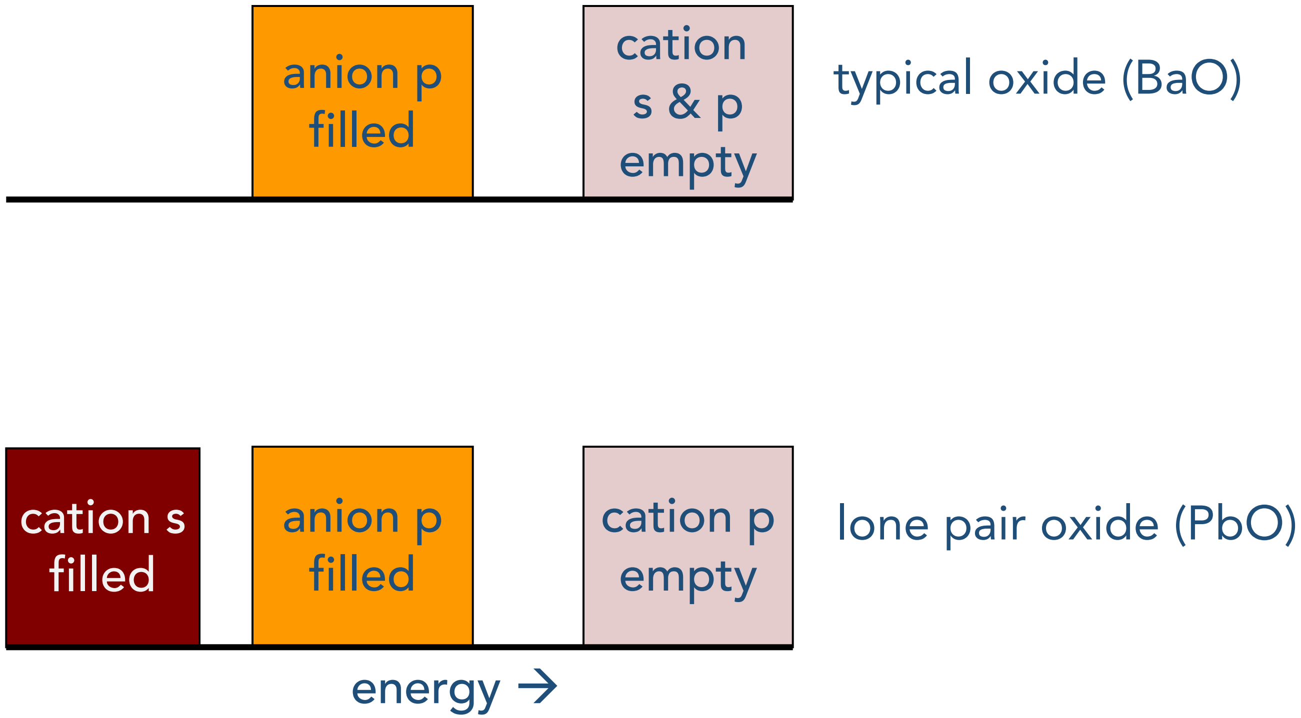
Chemistry counts: The role of the anion

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.



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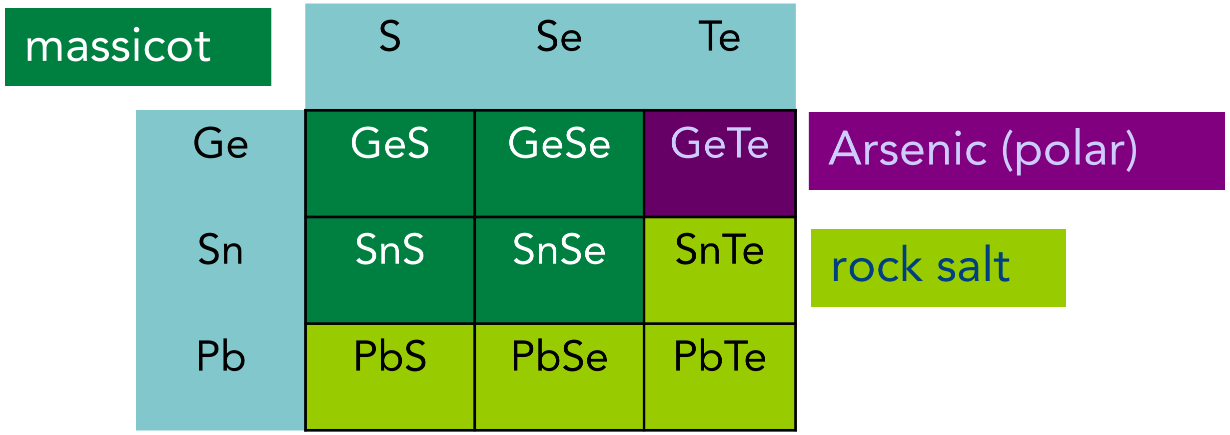
Chemistry counts: The role of the anion

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

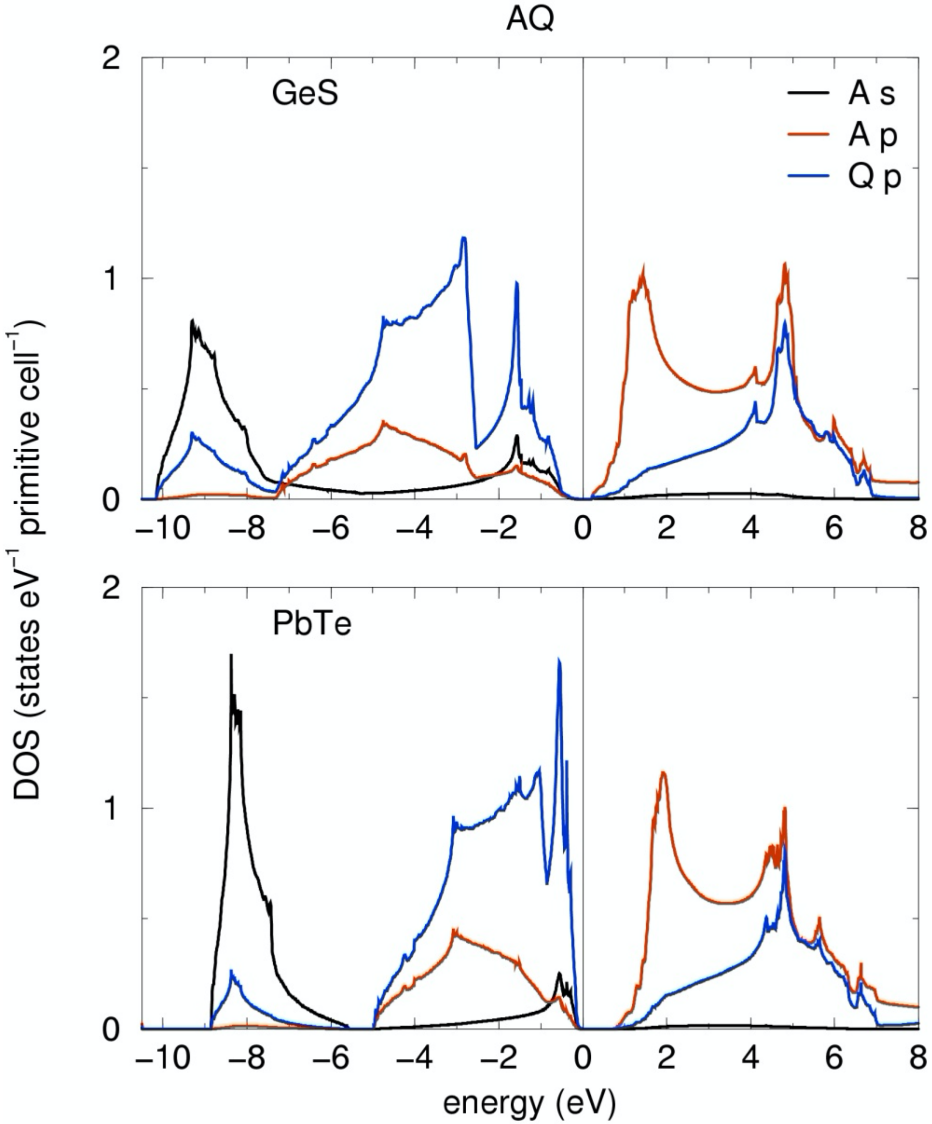


massicot

Arsenic (polar)

rock salt

	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 could be intermediated by empty cation p.

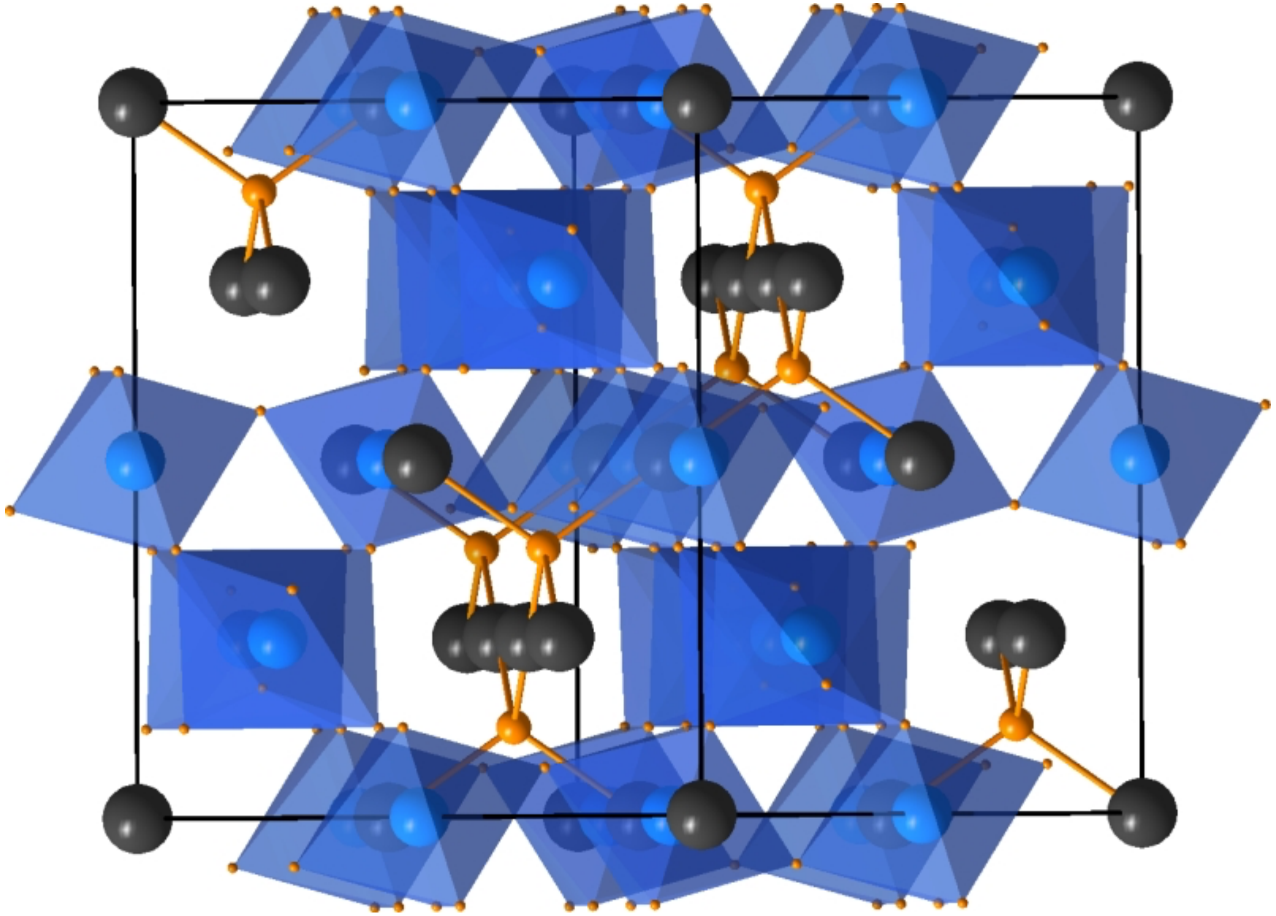
Born effective charges and LO–TO splitting indicative.

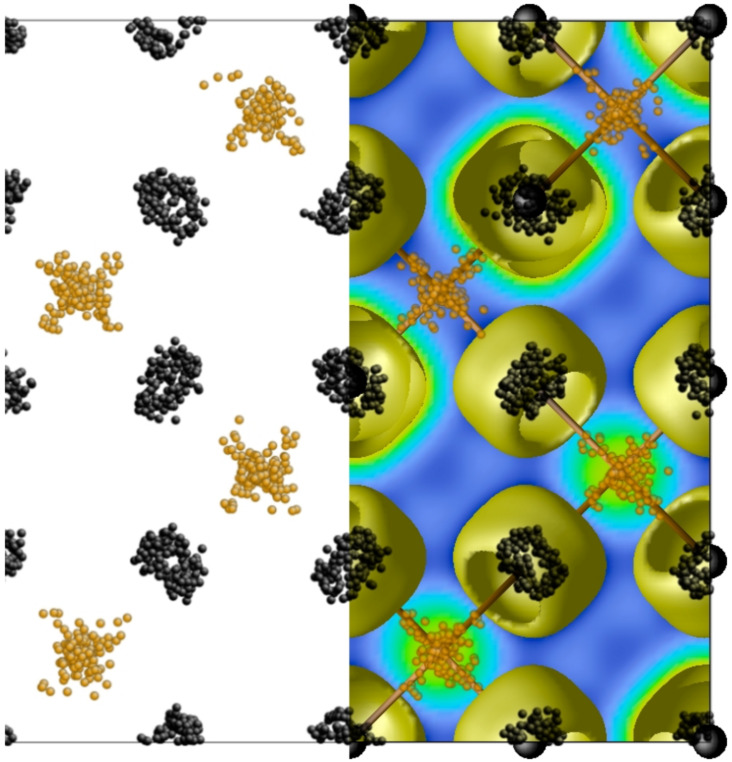
Cation s states are narrow and largely unmixed with anion p in cases when the lone pair is not stereochemically active (cf. the inert pair effect). Scalar relativistic effects are important !

Waghmare, Spaldin, Kandpal, Seshadri, *Phys. Rev. B.* **67** (2003) 125111.

Dynamically disordered lone pairs in pyrochlore oxides: $Bi_2Ti_2O_7$

Frustration on the pyrochlore lattice disallows ordering of lone-pair off-centering, unlike in perovskite $PbTiO_3$





$Bi_2Ti_2O_7$: synthesis and cubic average structure at 2 K: Hector, Wiggin, *J. Solid State Chem.* **177** (2004) 139]; Lone pair ELF visualization: Seshadri, *Solid State Sci.* **8** (2006) 259; RMC neutron scattering analysis of $Bi_2Ti_2O_7$: Shoemaker, Seshadri, Hector, Llobet, Proffen, Fennie, *Phys. Rev. B* **81** (2010) 144113(1–9).

seshadri@mrl.ucsb.edu

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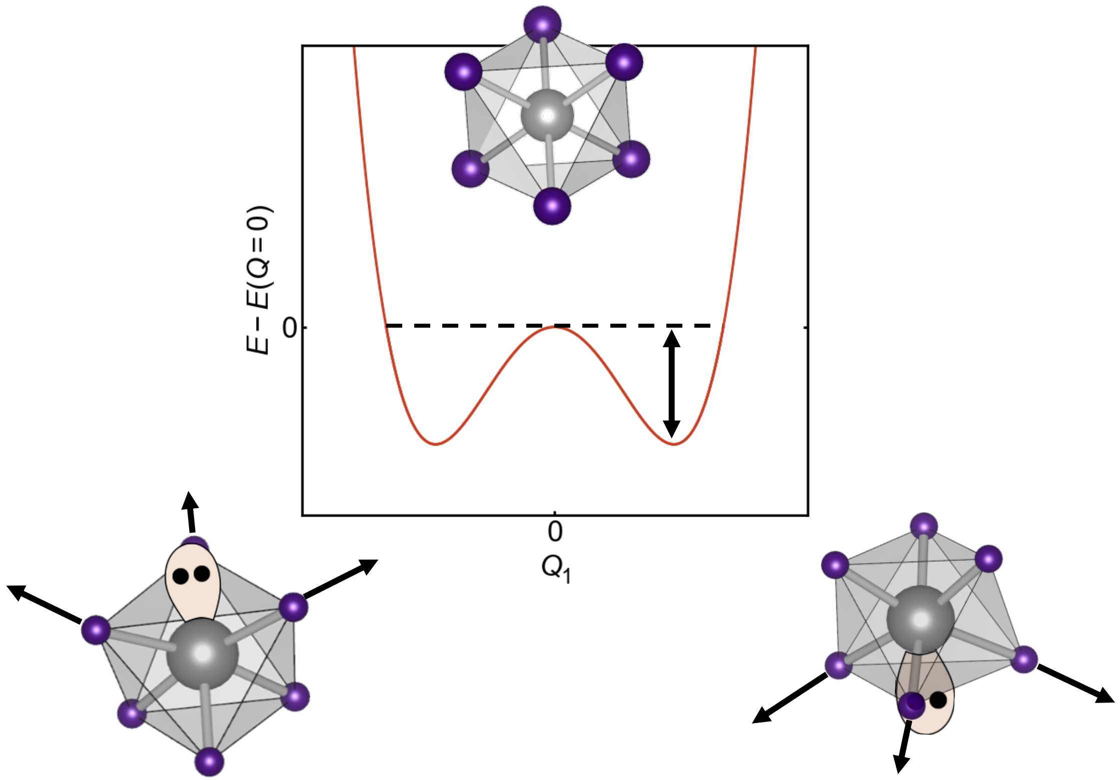
Enter the halide perovskites of the divalent, heavier carbon group elements

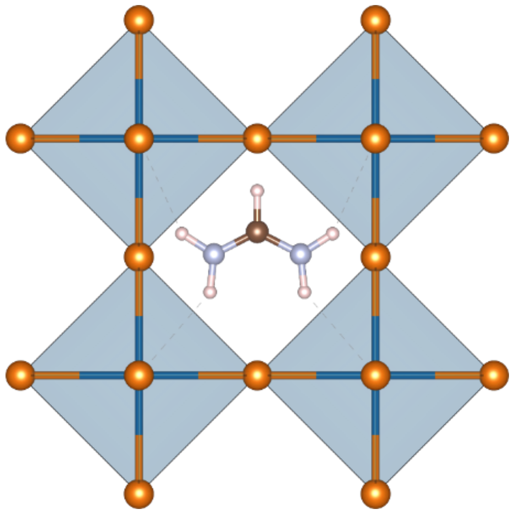
Double Well Potentials of Varying Breadth and Barrier Height

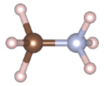
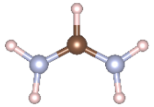


…but whether this matters for properties (and whether it manifests crystallographically) is a question of energy scales.

Halide Perovskites: Cations on the Octahedral Site have Lone Pairs

AMX_3



A	M	X
Cs^+	Ge^{2+}	Cl^-
 $(CH_3NH_3)^+$	Sn^{2+}	Br^-
 $[CH(NH_2)_2]^+$	Pb^{2+}	I^-

Ge^{2+}:	$3d^{10}\ 4s^2$
Sn^{2+}:	$4d^{10}\ 5s^2$
Pb^{2+}:	$5d^{10}\ 6s^2$

Note that the cations in almost all "familiar" semiconductors and solar cells (Si/Ge, III–V, II–VI, I–III–VI) do not have this configuration.

Exception: The IV–VI family described previously

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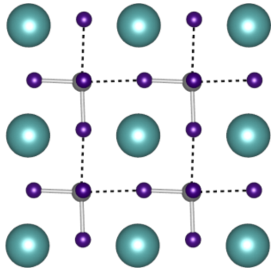
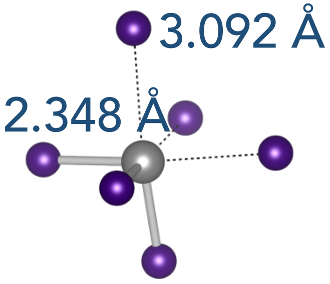
Halide Perovskites: Lone Pairs Result can Induce in Long-Range Distorted Structures in Some

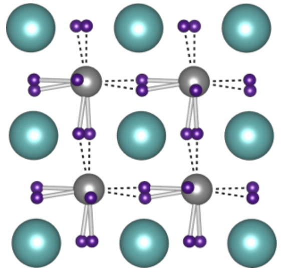
BiFeO$_3$-type
*R*3*m* (#160 polar)



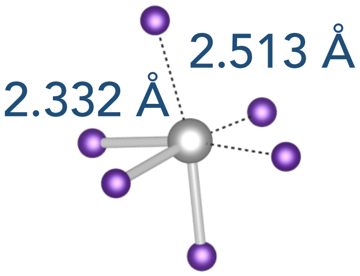
e.g. CsGeCl$_3$



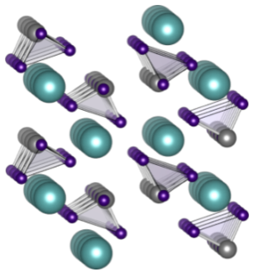
LiNbO$_3$-type
*R*3*c* (#16, polar)



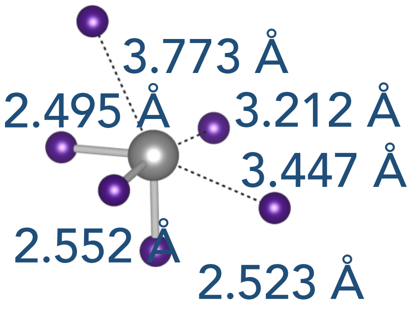
e.g. CsPbF$_3$



*P*2$_1$/*n* (#14, centrosymmetric)



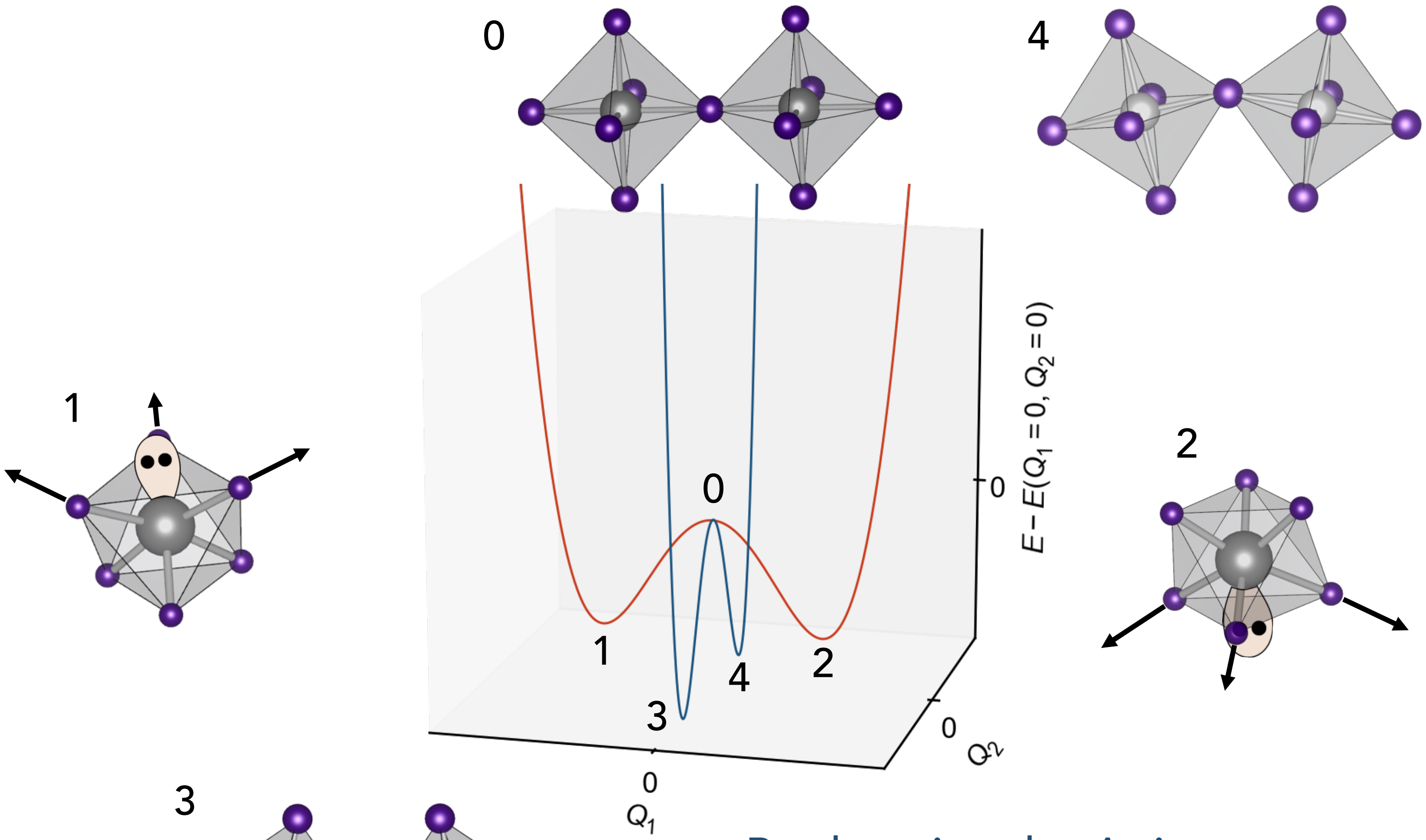
e.g. CsSnCl$_3$

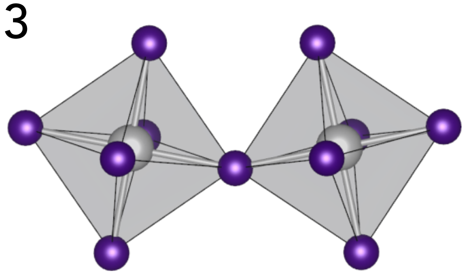


Structures from:

- Thiele, Rotter, Schmidt, *ZAAC* 1950
- Berastegui, Hull, Eriksson, *J. Phys. Condens. Matter* 2001
- Poulsen, Rasmussen, *Acta Chem. Scand.* 1970

But Frequently Not: Connectivity in Perovskite Results in Octahedral Tilting Modes, that Compete

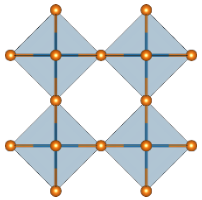




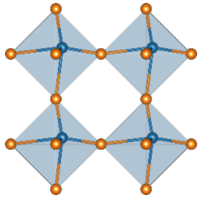
By changing the *A*-site countercation, dication *M*, and halide, we are tuning the energy scales of these two intabilities, relative to one another and to *kT*

The importance of the *A*-site size: Examples of Perovskite Titanium Oxides

$BaTiO_3$
Ferroelectric

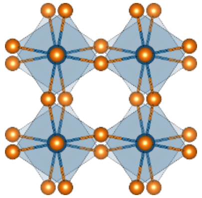


$SrTiO_3$
Quantum paraelectric



Ground state is fully ordered [111] Ti^{4+} displacements

A-site Ba^{2+} right sized:
pseudo-Jahn–Teller instability of Ti^{4+} is favored



Non-polar, tilted ground state ($a^+b^-b^-$ in Glazer notation)

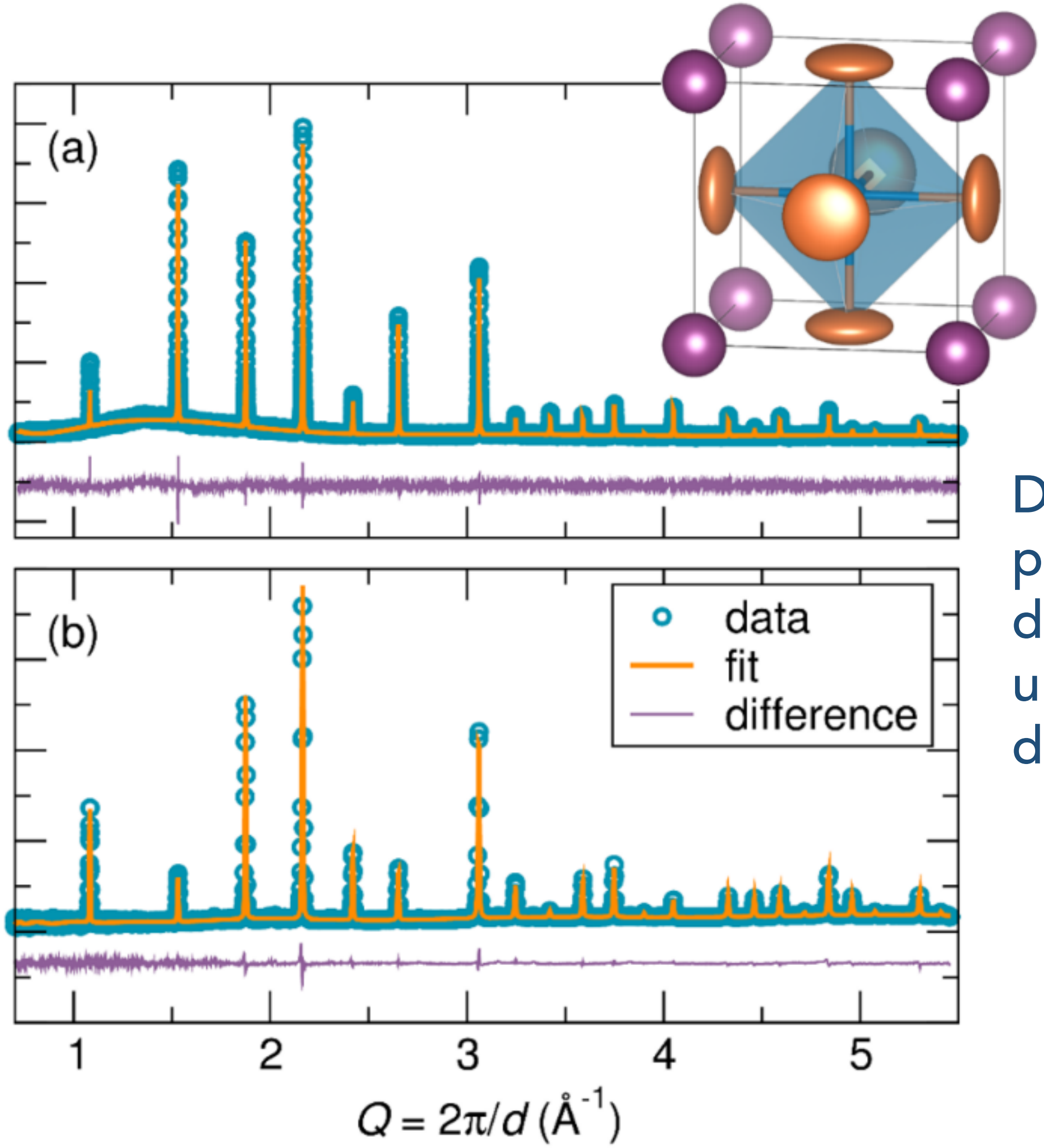
A-site Sr^{2+} too small:
tilting instability is favored

seshadri@mrl.ucsb.edu UC SANTA BARBARA

X-ray and Neutron Diffraction Indicate a Cubic “Average” Structure in $CsSnBr_3$ above 300 K

X-ray
11-BM @ APS

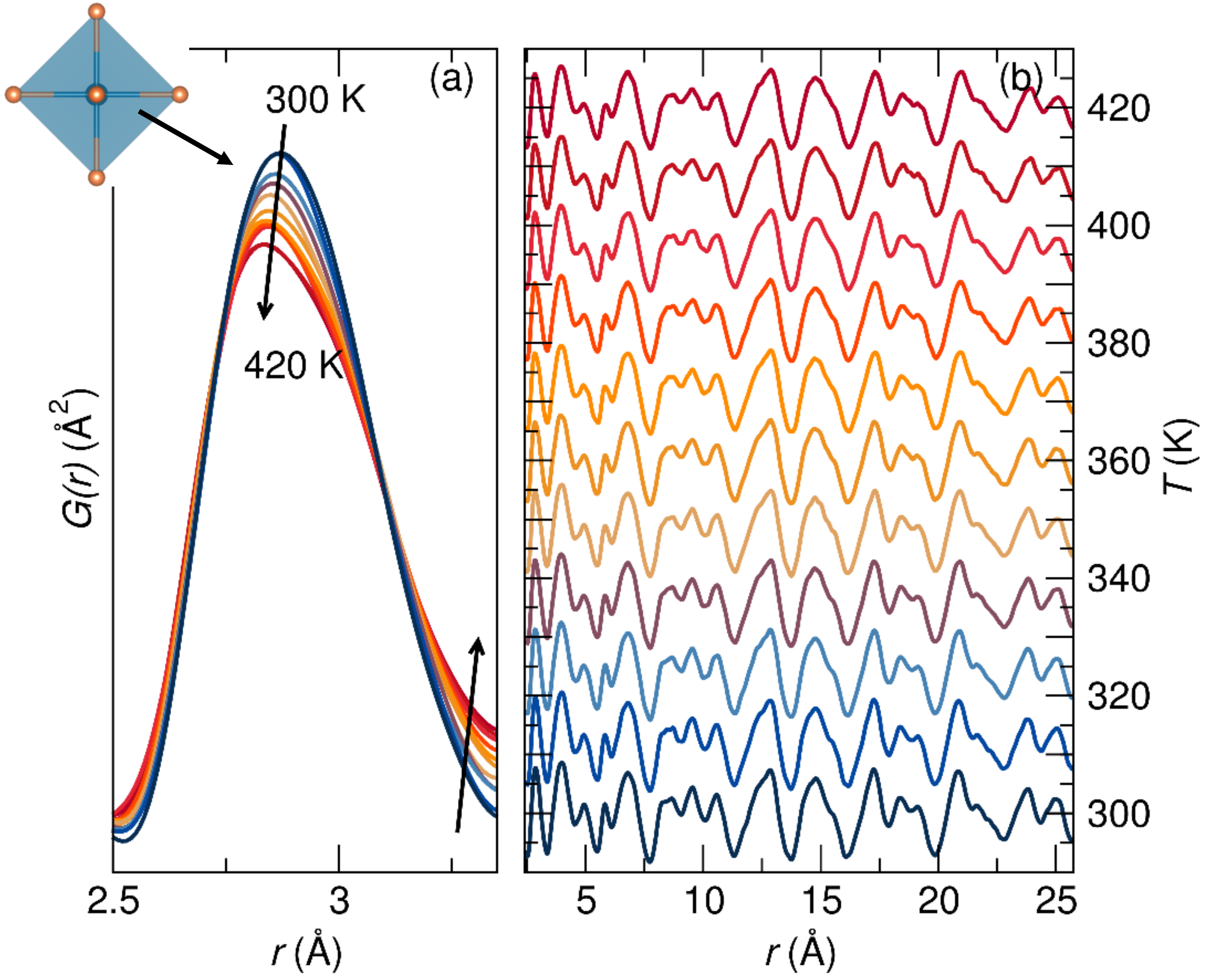
neutron
POWGEN @ SNS



Dynamic phenomena and non-periodic disorder are hidden in such a description, beyond seemingly uncorrelated, harmonic thermal displacements.

Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven, Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

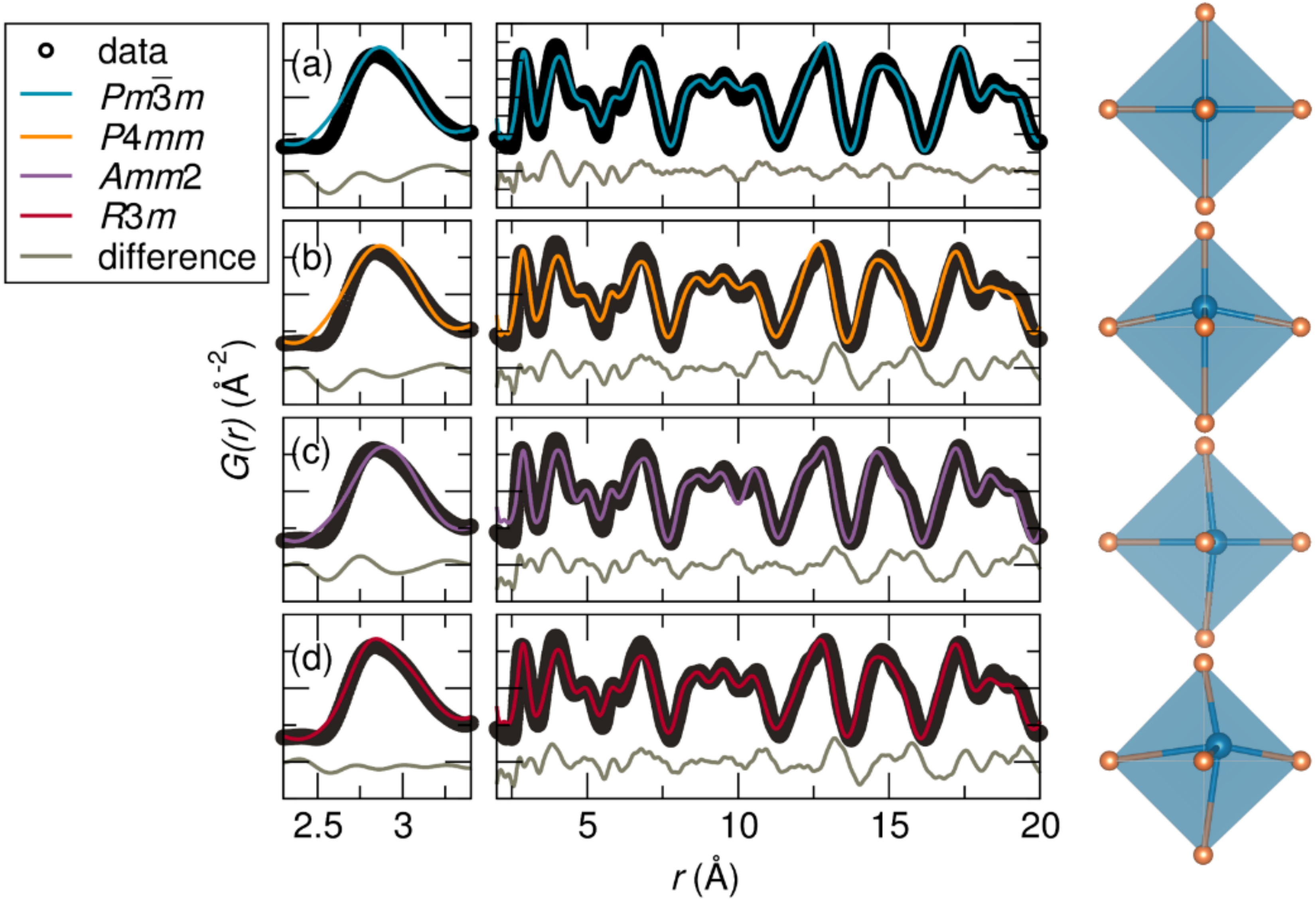
Total Scattering Reveals Hidden Dynamic Distortions in $CsSnBr_3$



11-ID-B @ APS

Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven, Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

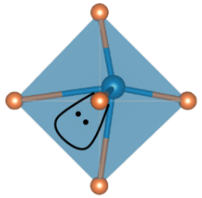
These Octahedral Distortions are *Locally* Well Described By 3+3 Coordinated Sn^{2+}



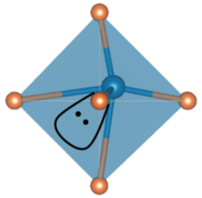
Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven, Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

Ab initio Calculations Clearly Implicate Lone Pairs as the Cause of these Distortions

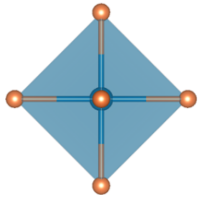
Sn^{2+}
lone pair

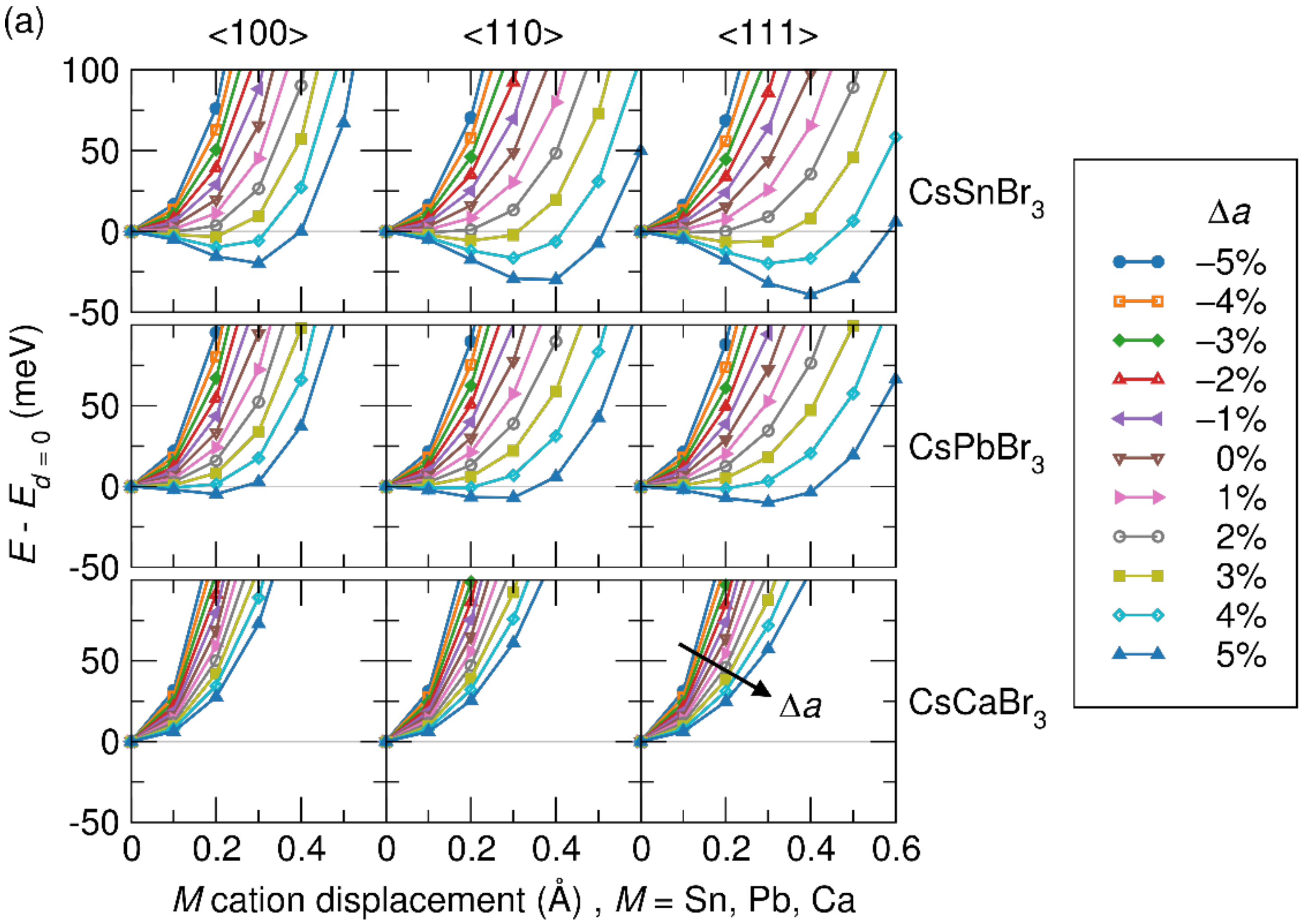


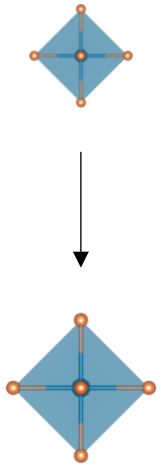
Pb^{2+}
lone pair



Ca^{2+}
no LP







The energy scale indicates competition with vibrational entropy and octahedral tilting

Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven,
Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

seshadri@mrl.ucsb.edu

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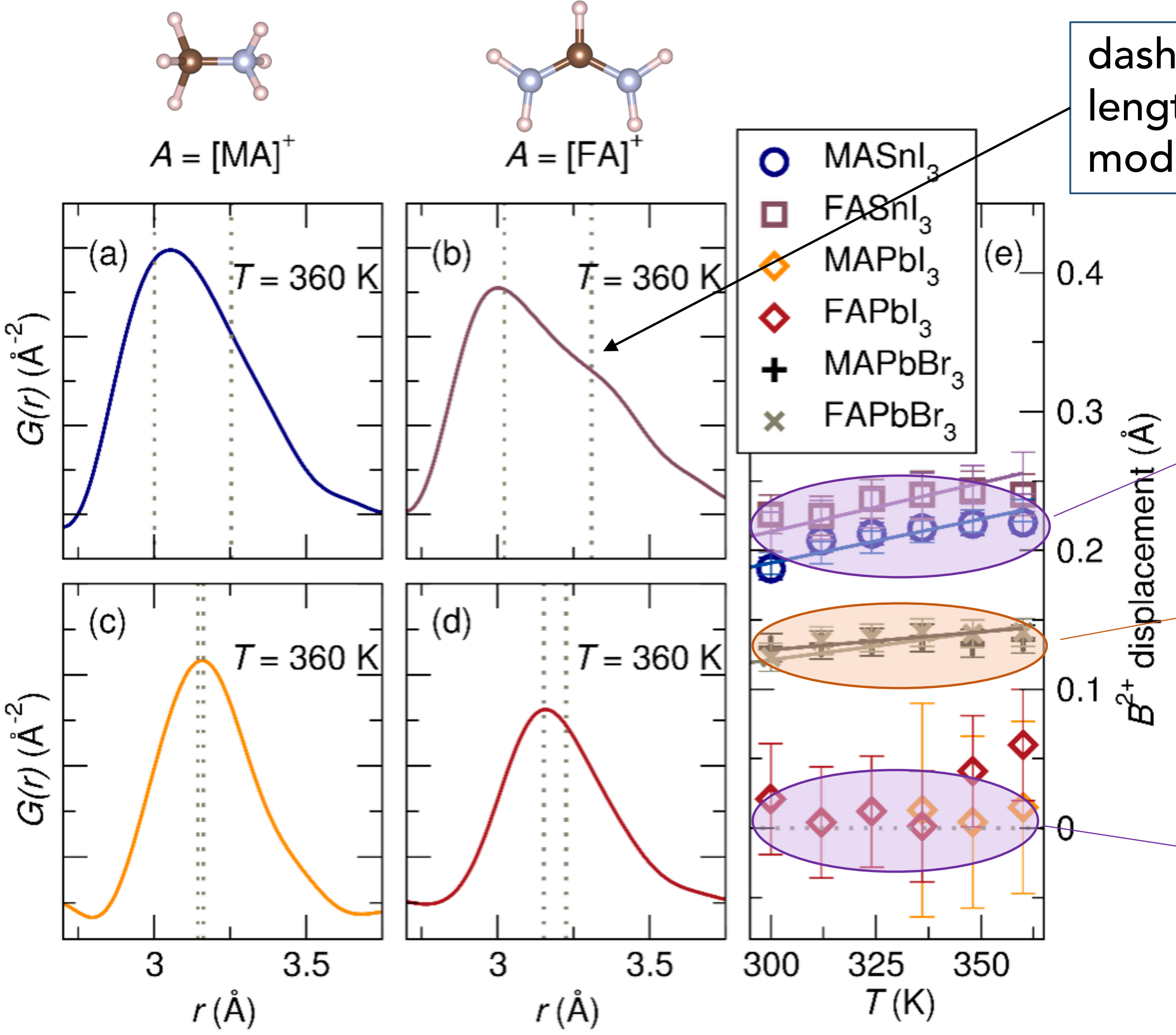
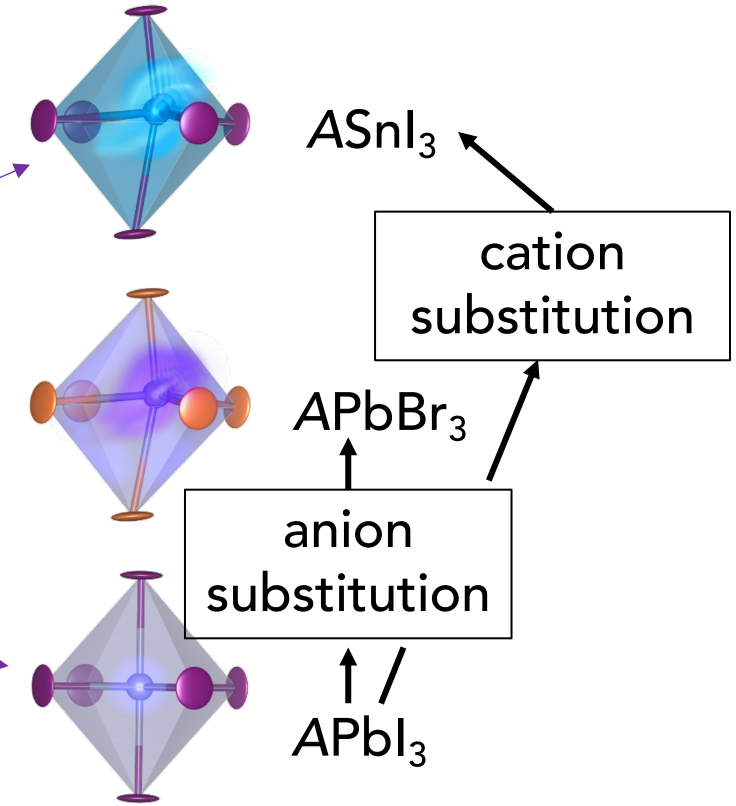
This Instability is Tunable Across the High-performing Hybrid Perovskites

$ASnI_3$

$APbI_3$



dashed lines are the different bond lengths of this 3+3 coordination model



$ASnI_3$

cation substitution

$APbBr_3$

anion substitution

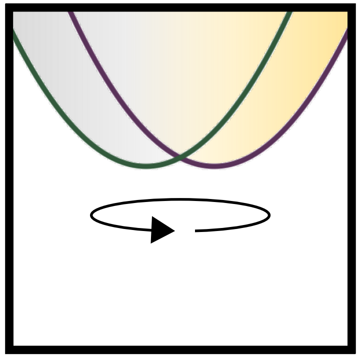
$APbI_3$

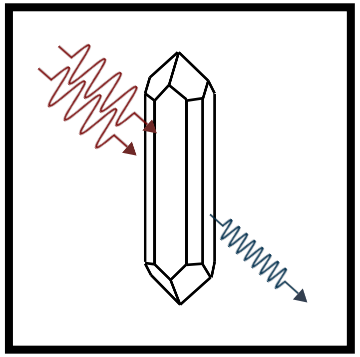
Laurita, Fabini, Stoumpos, Kanatzidis, Seshadri, *Chem. Sci.* **8** (2017) 5628 – 5635.

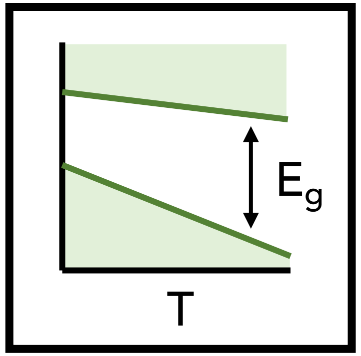
Consequences:

There are many definite (and possible) property impacts as a consequence of soft, anharmonic bonding, acentric metal coordination, and broken symmetries

- ☐ Local or macroscopic non-centrosymmetry
  - ☐ Non-linear optical response, piezoelectricity
  - ☐ (When also polar) pyroelectricity
    - ☐ (When also switchable) ferroelectricity
  - ☐ Relativistic spin polarization
  - ☐ (When also polar) bulk photovoltaic effect
- ☐ Large (ionic) dielectric response
- ☐ Large thermal expansion [1, 2]
- ☐ $\mathrm{d}E_g/\mathrm{d}T > 0$ (vide infra)
- ☐ Low thermal conductivity
- ☐ Large compressibility?



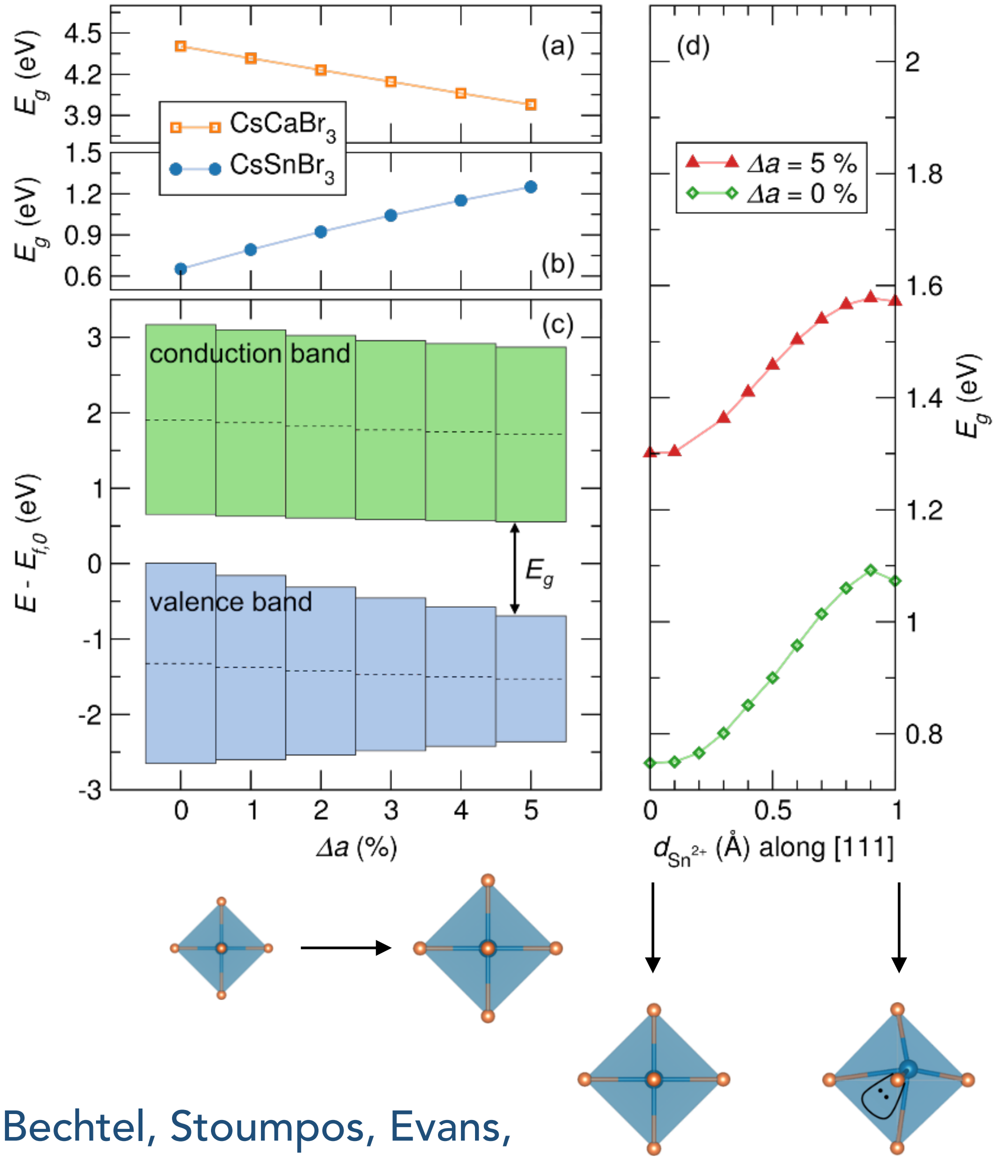


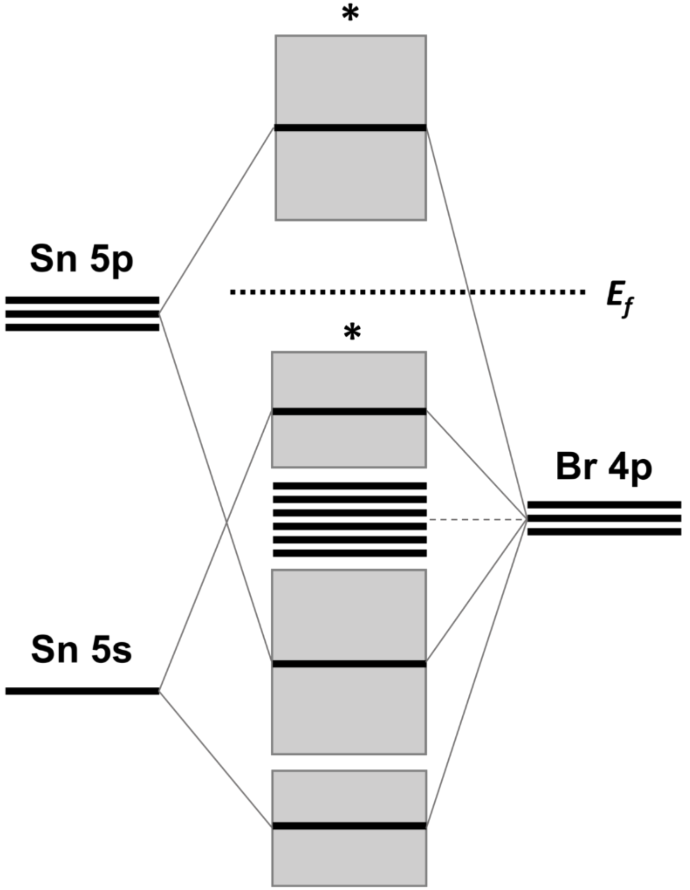


[1] Fabini, Stoumpos, Laurita, Kaltzoglou, Kontos, Falaras, Kanatzidis, Seshadri, *Angew. Chem. Int. Ed.* **55** (2016) 15392–15396.

[2] Schueller, Laurita, Fabini, Stoumpos, Kanatzidis, Seshadri, *Inorg. Chem.* 57 (2018) 695–701.

This Atypical Electronic Structure Due to the Lone Pair Causes Bandgap Widening With *T*

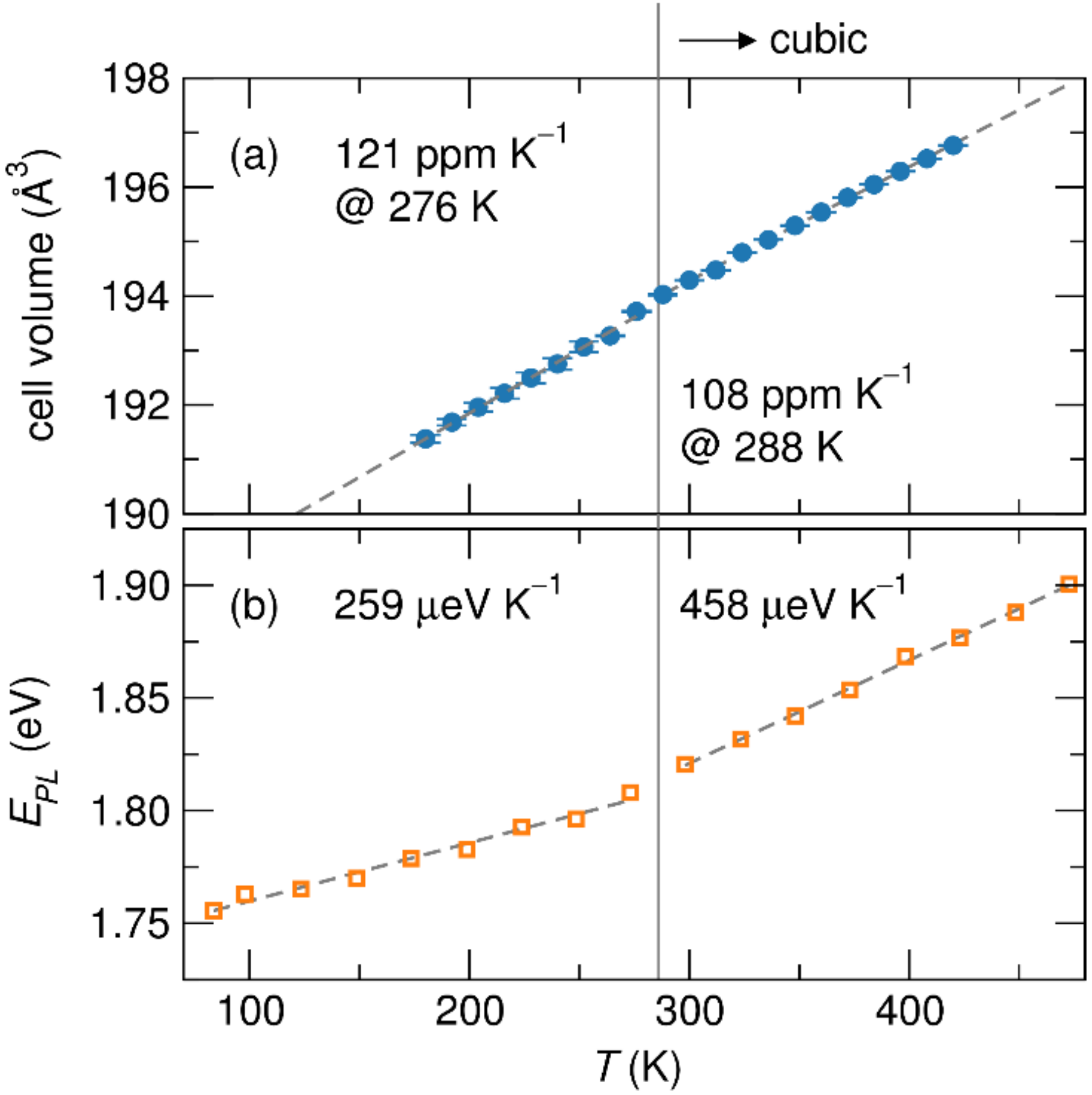




Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven, Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

seshadri@mrl.ucsb.edu UC SANTA BARBARA

This Atypical Electronic Structure Due to the Lone Pair Causes Bandgap Widening With *T*



Blue-shifting of PL peak (proxy for E_g) blue-shifts more with temperature in the cubic phase, despite a reduced thermal expansion coefficient

Dynamic deformations of the octahedra enhance the widening? Dynamic tilting surely also contributes…

Fabini(*), Laurita(*), Bechtel, Stoumpos, Evans, Kontos, Raptis, Falaras, Van der Ven, Kanatzidis, Seshadri, *J. Am. Chem. Soc.* **138** (2016) 11820–11832. (*) equal contribution

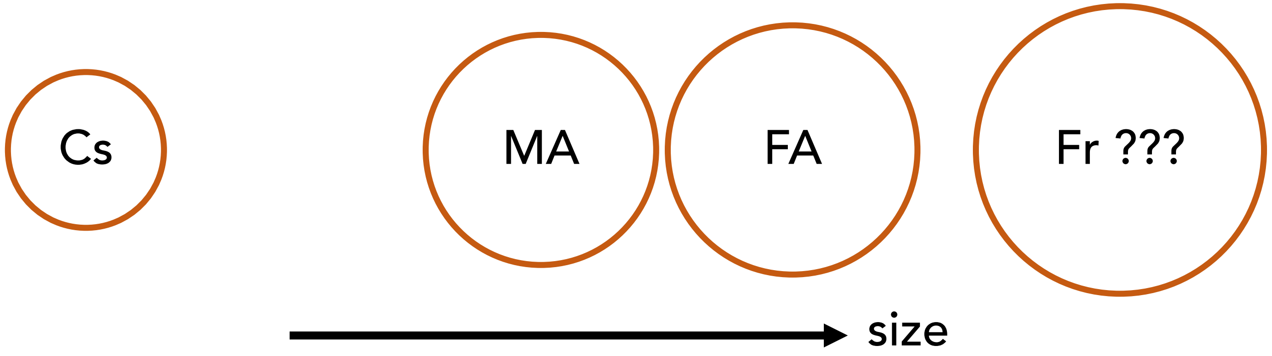
Implications

Even when it does not manifest crystallographically, dynamic polar deformations off the octahedral environment exist across the (Ge,Sn,Pb) halide perovskites.

This is in addition to dynamic octahedral tilting, and indeed competes with it.

The magnitude of this lone pair-induced distortion can be easily and predictably tuned.

- Lighter *M*, lighter *X* increase the strength. This will of course modulate other properties as well (bandgap, air-sensitivity, *etc.*)
- *A*-site cation size to tune strength of tilting instability (and to a lesser extent, bandgap)



This gives a direct, chemical handle for testing some of the hypotheses discussed at this workshop, as well as a strategy for the design of new materials with macroscopically-broken centrosymmetry, or proximity to this phase boundary.