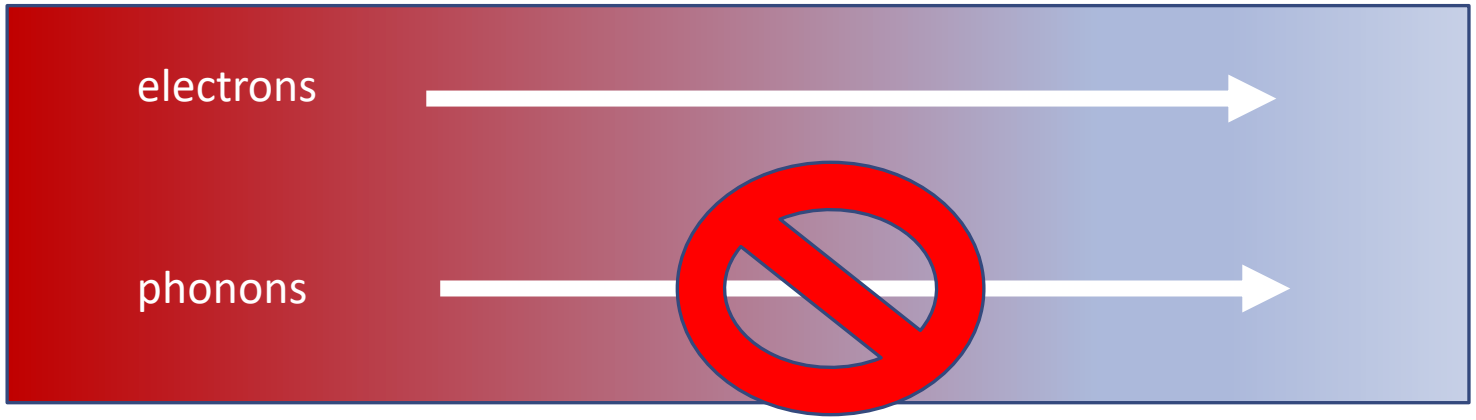
Lone Pairs and Thermoelectric Properties

OLIVIA LONG

What is a thermoelectric

1821 – Thomas Seebeck



High electron mobility and low phonon mobility

What makes a good thermoelectric?

Figure of merit:

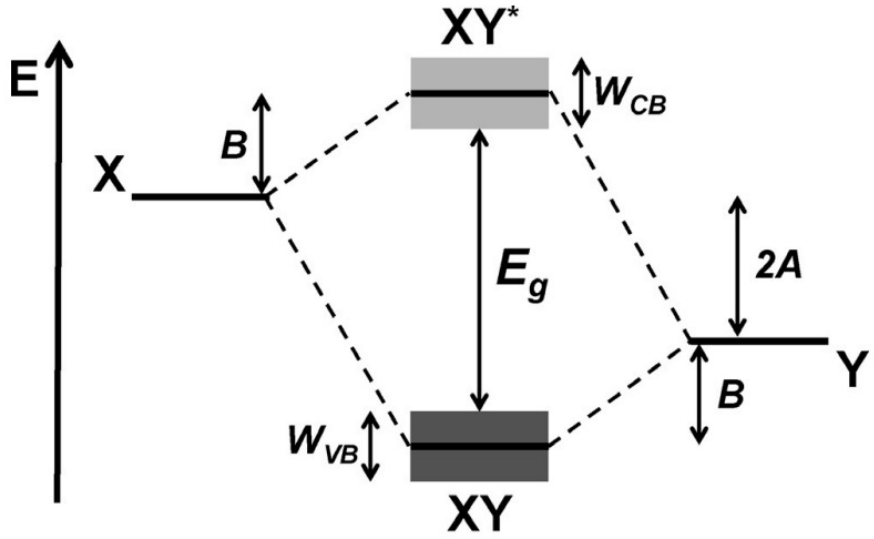
$$zT = \frac{\sigma \times \mathrm{S}^2}{\kappa_\mathrm{L} + \kappa_\mathrm{e}} T$$

Band gap engineering

Band gap arises from difference between HOMO and LUMO

Ways to alter:

- Electronegativities
- Bond strength
- Doping



Phonon scattering

Boundary scattering

Doping

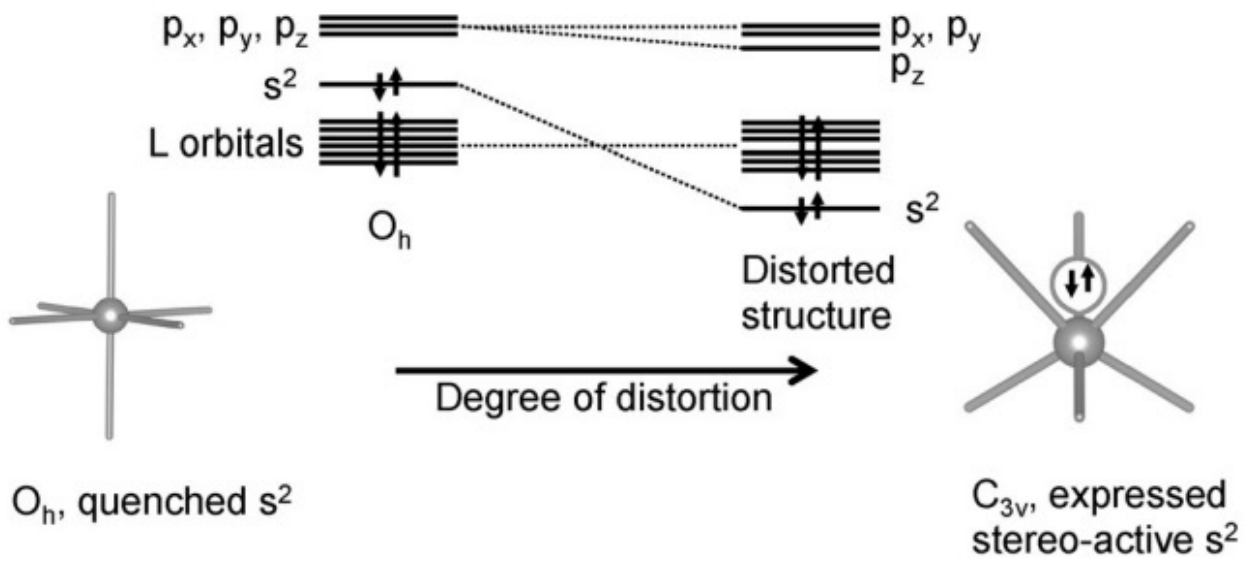
Large molecular weight

Complex crystal structure

Charge density wave distortions

Lone pair effects

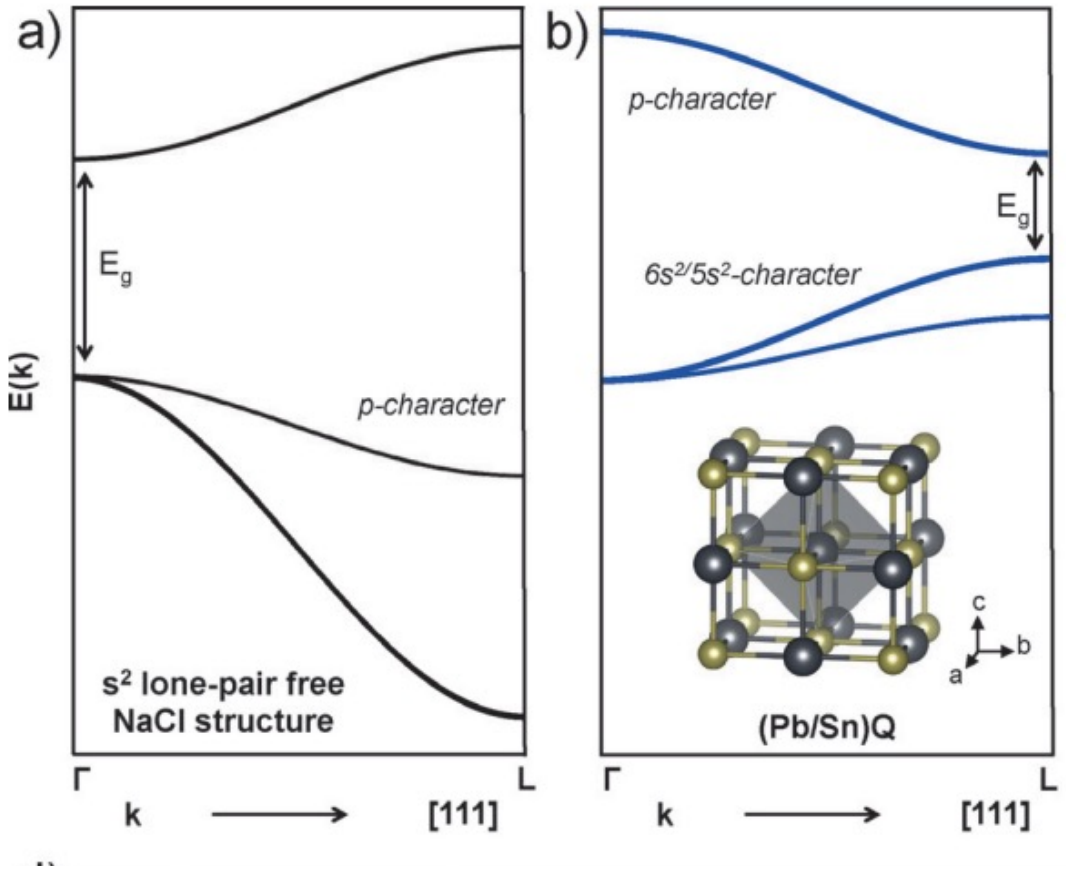
Typically comes from Group 13-15 cations



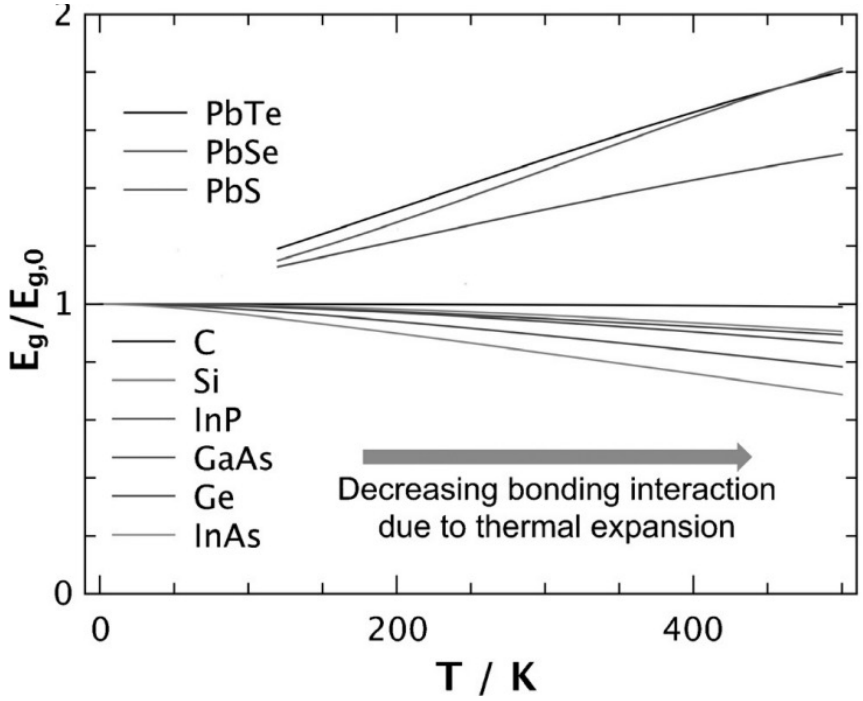
13 IIIA	14 IVA	15 VA
5 $^2P^\circ_{1/2}$ **B** Boron 10.81 $1s^2 2s^2 2p$ 8.2980	6 $^3P_0$ **C** Carbon 12.011 $1s^2 2s^2 2p^2$ 11.2603	7 $^4S^\circ_{3/2}$ **N** Nitrogen 14.007 $1s^2 2s^2 2p^3$ 14.5341
13 $^2P^\circ_{1/2}$ **Al** Aluminum 26.982 $[Ne]3s^2 3p$ 5.9858	14 $^3P_0$ **Si** Silicon 28.085 $[Ne]3s^2 3p^2$ 8.1517	15 $^4S^\circ_{3/2}$ **P** Phosphorus 30.974 $[Ne]3s^2 3p^3$ 10.4867
31 $^2P^\circ_{1/2}$ **Ga** Gallium 69.723 $[Ar]3d^{10} 4s^2 4p$ 5.9993	32 $^3P_0$ **Ge** Germanium 72.630 $[Ar]3d^{10} 4s^2 4p^2$ 7.8994	33 $^4S^\circ_{3/2}$ **As** Arsenic 74.922 $[Ar]3d^{10} 4s^2 4p^3$ 9.7886
49 $^2P^\circ_{1/2}$ **In** Indium 114.82 $[Kr]4d^{10} 5s^2 5p$ 5.7864	50 $^3P_0$ **Sn** Tin 118.71 $[Kr]4d^{10} 5s^2 5p^2$ 7.3439	51 $^4S^\circ_{3/2}$ **Sb** Antimony 121.76 $[Kr]4d^{10} 5s^2 5p^3$ 8.6084
81 $^2P^\circ_{1/2}$ **Tl** Thallium 204.38 $[Hg]6p$ 6.1083	82 $^3P_0$ **Pb** Lead 207.2 $[Hg]6p^2$ 7.4167	83 $^4S^\circ_{3/2}$ **Bi** Bismuth 208.98 $[Hg]6p^3$ 7.2855
113 **Nh** Nihonium (286)	114 **Fl** Flerovium (289)	115 **Mc** Moscovium (289)

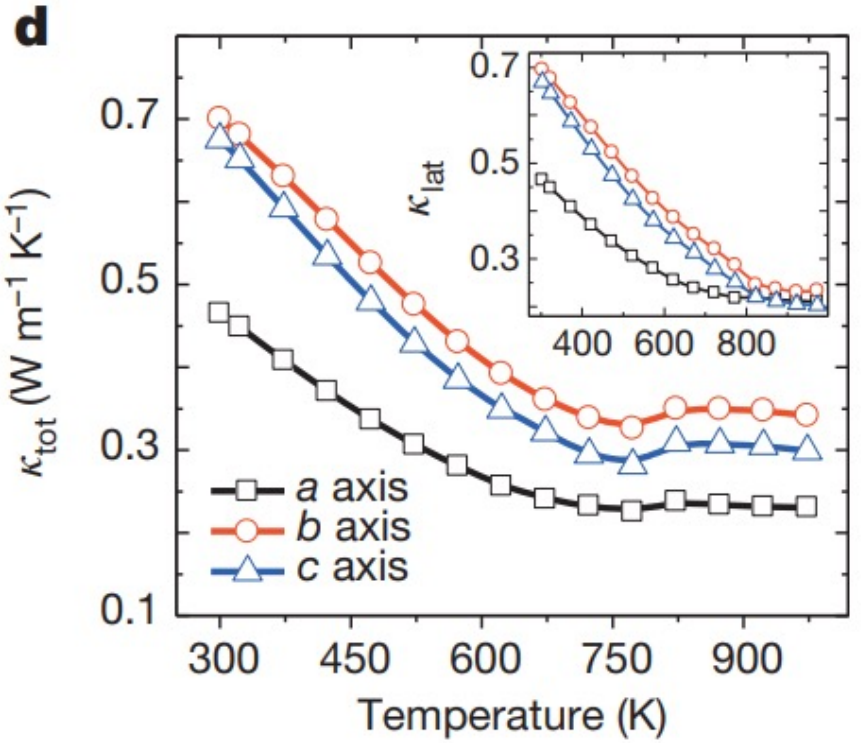
Wolfgang G. Zeier, Alex Zevalkink, Zachary M. Gibbs, Geoffroy Hautier, Mercouri G. Kanatzidis, and G. Jeffrey Snyder. *Angew. Chem. Int. Ed.* **2016**, *55*, 6826 – 6841

Band diagrams



Temperature dependence





Increasing band gap with increasing temperature

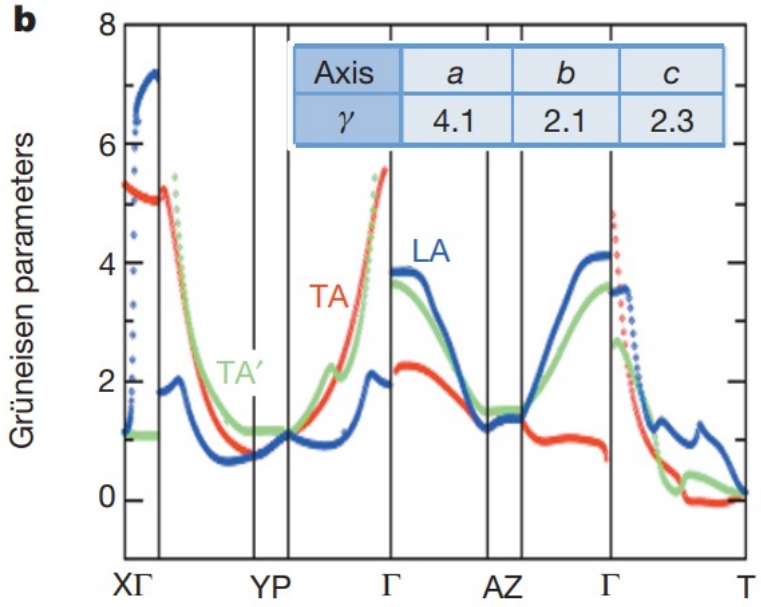
Wolfgang G. Zeier, Alex Zevalkink, Zachary M. Gibbs, Geoffroy Hautier, Mercouri G. Kanatzidis, and G. Jeffrey Snyder. *Angew. Chem. Int. Ed.* **2016**, *55*, 6826 – 6841

Li-Dong Zhao, Shih-Han Lo, Yongsheng Zhang, Hui Sun, Gangjian Tan, Ctirad Uher, C. Wolverton, Vinayak P. Dravid & Mercouri G. Kanatzidis. *Nature*. **2014**, *508*, 373-377

Anharmonicity

Large Grüneisen parameter (γ) = high phonon scattering

Arises from distortions, loss of inversion symmetry

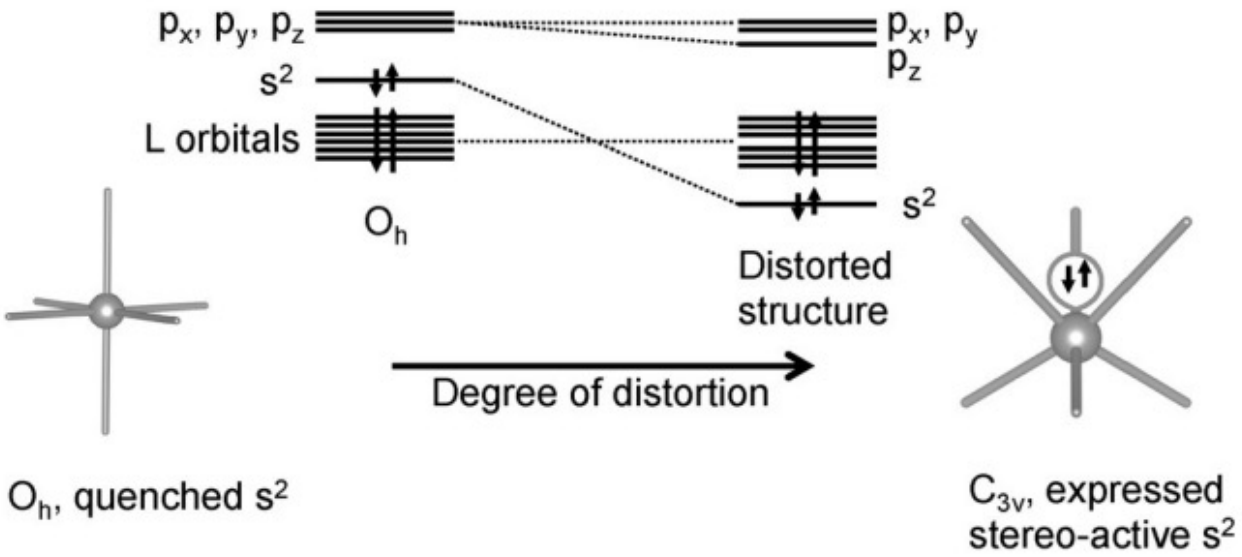


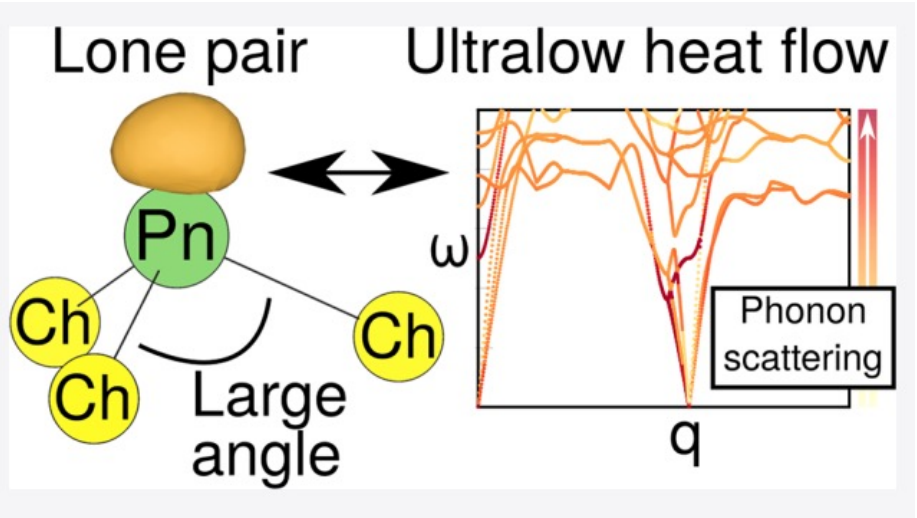
Wolfgang G. Zeier, Alex Zevalkink, Zachary M. Gibbs, Geoffroy Hautier, Mercouri G. Kanatzidis, and G. Jeffrey Snyder. *Angew. Chem. Int. Ed.* **2016**, *55*, 6826 – 6841

Coordination geometry

Coordination geometry of metal center

Ligand dependent



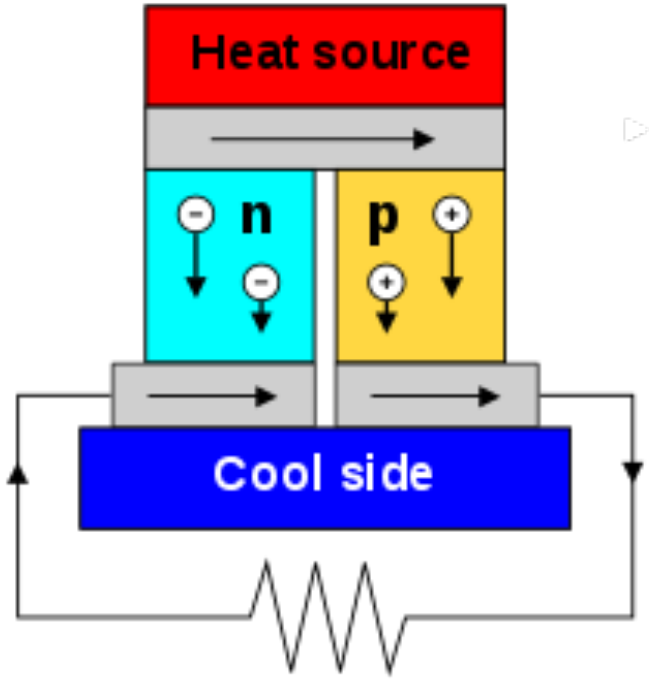


Wolfgang G. Zeier, Alex Zevalkink, Zachary M. Gibbs, Geoffroy Hautier, Mercouri G. Kanatzidis, and G. Jeffrey Snyder. *Angew. Chem. Int. Ed.* **2016**, *55*, 6826 – 6841

Eric B. Isaacs, Grace M. Lu, and Christopher Wolverton. *J. Phys. Chem. Lett*. **2020**, *11*, 5577−5583

Why do we want thermoelectrics?

Harness waste heat and recycle into energy



Ken Brazier. https://en.wikipedia.org/wiki/Thermoelectric_generator#/media/File:Thermoelectric_Generator_Diagram.svg

Summary

Many ways to alter band gap and optimize zT

Lone pairs distort lattice and disrupt high symmetry

Able to decouple electrical and thermal conductivity

Questions?