Electronically driven lattice instabilities: Covalent origins and property impacts

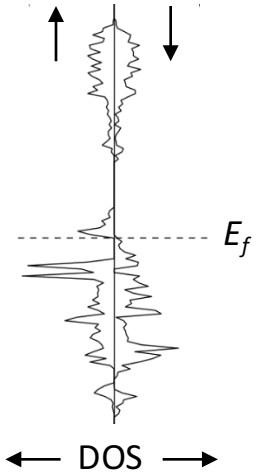
Doug Fabini

Materials 286G Final Presentation

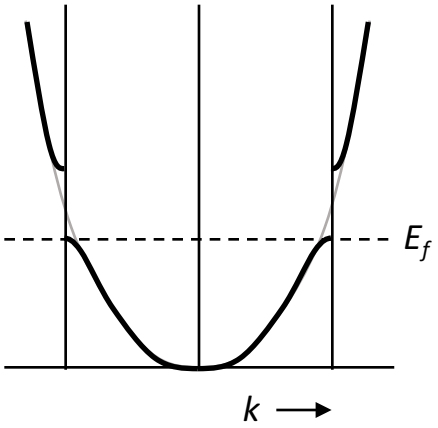
June 1, 2016

Degeneracy begets instability

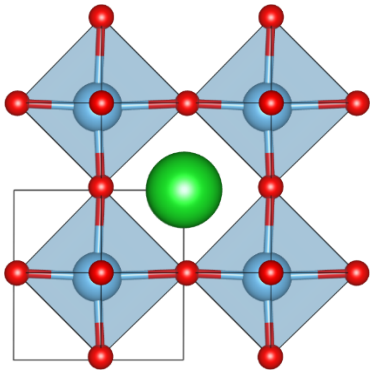
Stoner magnetism



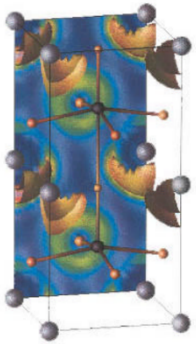
Peierls distortion



1st and 2nd order Jahn-Teller effects, back-bonding



Lone pair electrons in high symmetry environments



Schildkamp, Fischer. Rhomboedrisches $BaTiO_3$: Strukturuntersuchung bei 132 K und 196 K, *Z. Kristallogr.*, **1981**, *155*, 217 – 226.
Seshadri. Visualizing lone pairs in compounds containing heavier congeners of the carbon and nitrogen group elements, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **2001**, *113*, 487 – 496.

Thermodynamic competition: Many degeneracies that are lifted at low T are restored at high T

$F = U - TS$

$G = U - TS + pV$

...

energy minimized — entropy maximized

$T \longrightarrow$

ferroelectric → paraelectric

Peierls-distorted insulator → undistorted metal

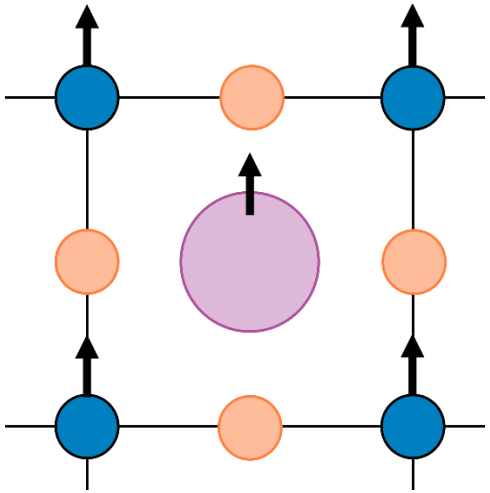
...

Thus, systems near instabilities exhibit strongly temperature dependent behavior.

Now consider a high temperature phase, with a mechanically unstable lattice…

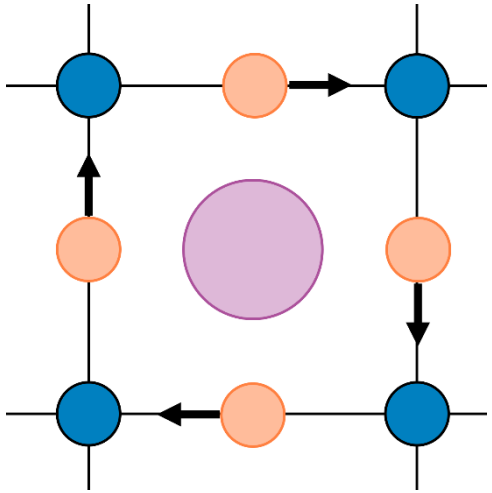
Polar versus non-polar lattice instabilities

Polar mode



- e.g. ferroelectric mode in cubic $PbTiO_3$ at Γ
- Covalently-driven
- Contributes directly to dielectric response

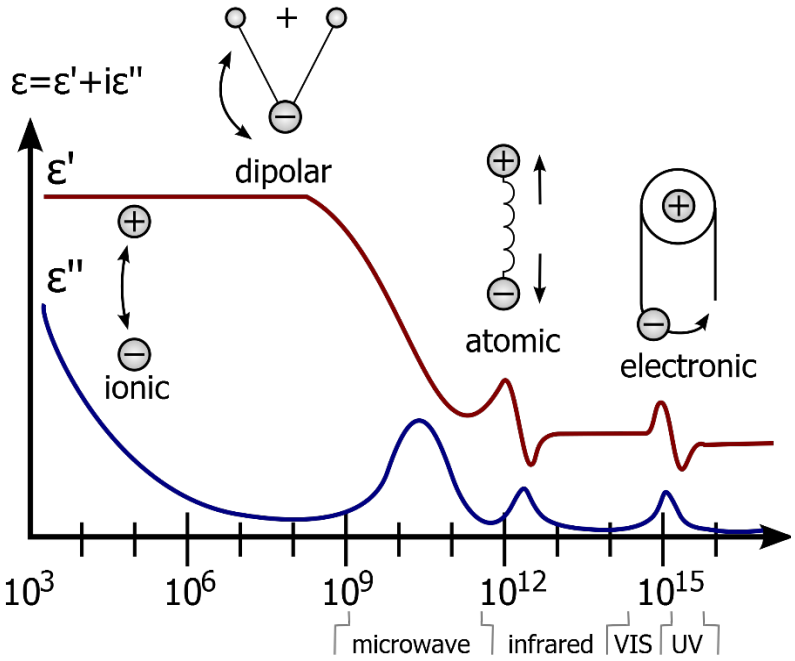
Non-polar mode



- e.g. octahedral rotations in cubic $SrTiO_3$ at M, R
- Electrostatically-driven

(Simplistic) picture of electrical transport:

Orbital overlap and **electronegativities** (band theory, carrier effective masses) set upper bound on mobility. Scattering of carriers by **defects**, **impurities**, and **phonons** reduces mobility from this limit to its practical value.

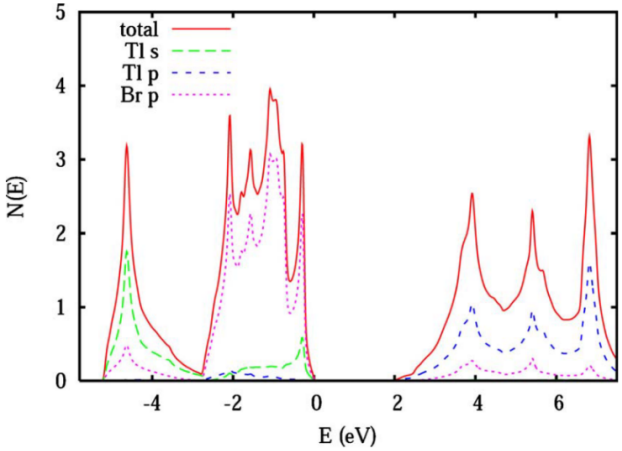


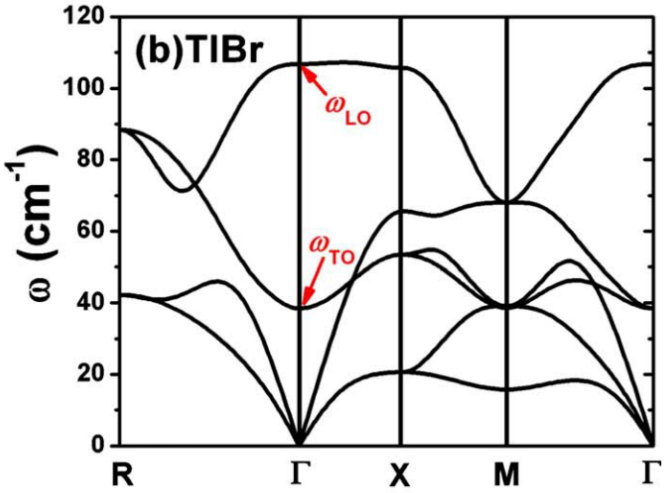
If scattering from charged defects or impurities is dominant, effective dielectric screening can enhance mobilities!

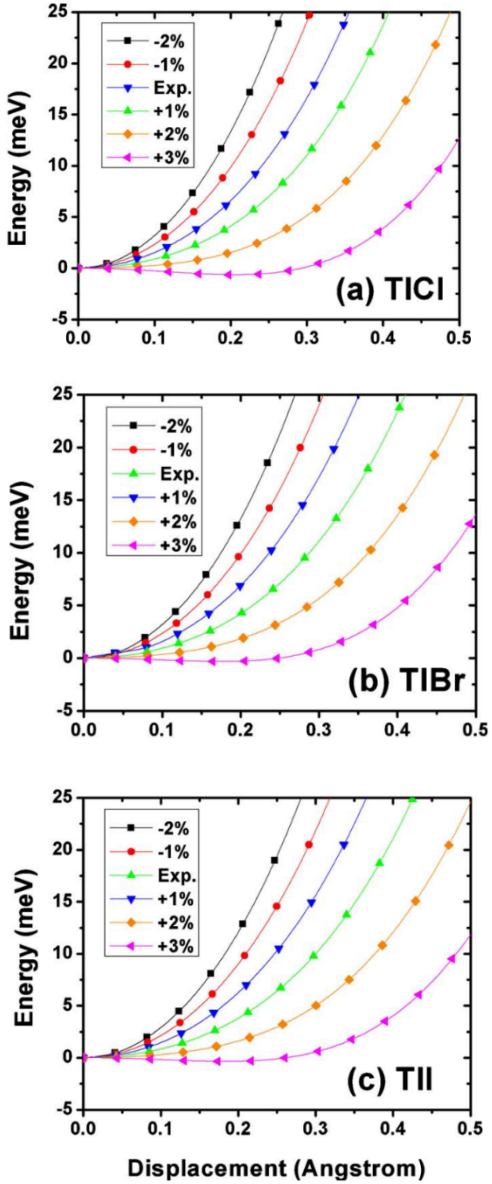
Figure from Beau Lambert, psrc.usm.edu/mauritz/dilect.html

Case study: Lone pair-driven proximal instability in Tl*X* (*X* = Cl, Br, I)

- Lattice expansion, electrostatic penalty to displacement
- Elevated Born charges & LO/TO splitting
- Relation to dielectric properties (Lydanne—Sachs—Teller)







Du, Singh. Enhanced Born charge and proximity to ferroelectricity in thallium halides, *Phys. Rev. B*, **2010**, *81*, 144114.

Case study: Chemical tuning of the ferroelectric transition in $KTa_{1-x}Nb_xO_3$:Ca

Cubic

↓ T_c

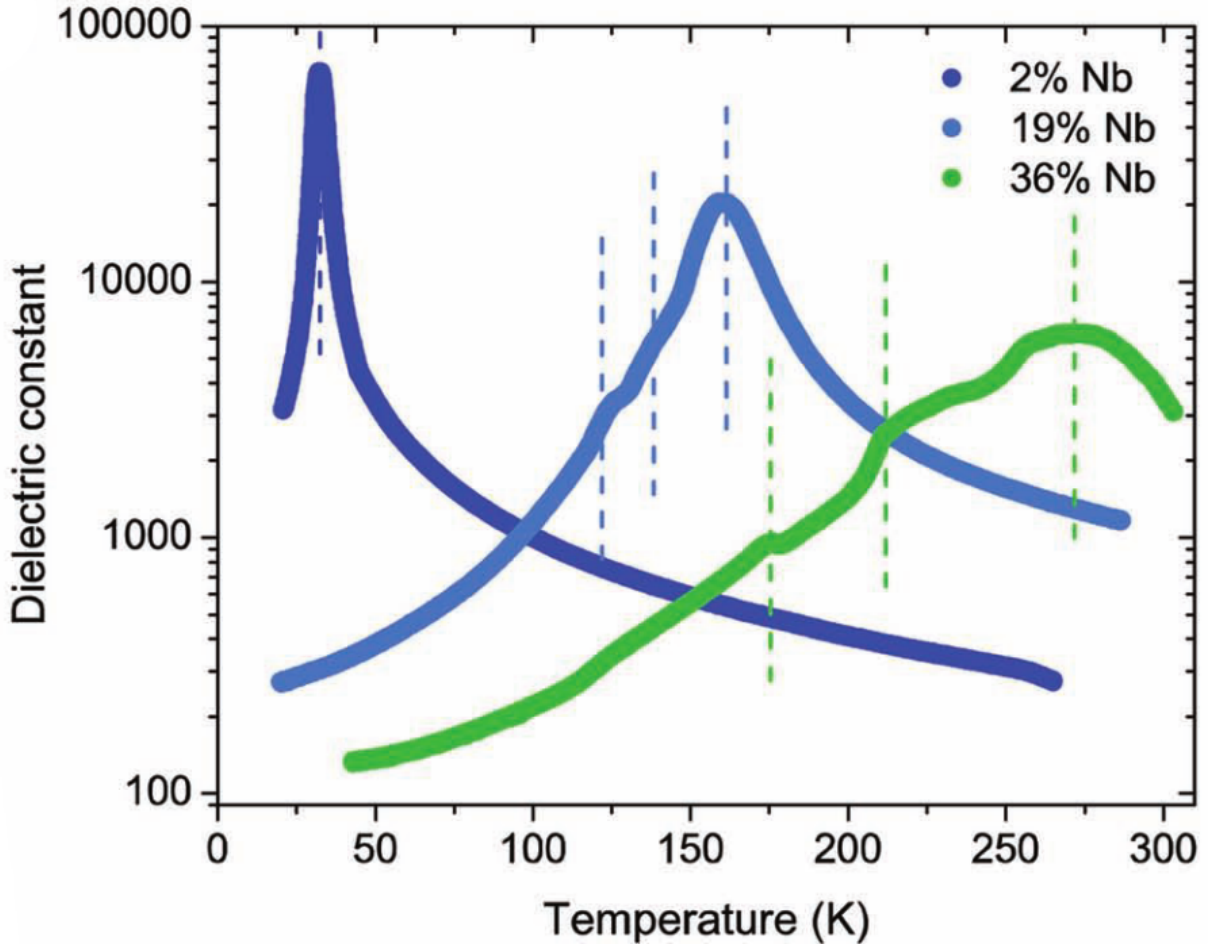
Tetragonal [100]

↓

Orthorhombic [110]

↓

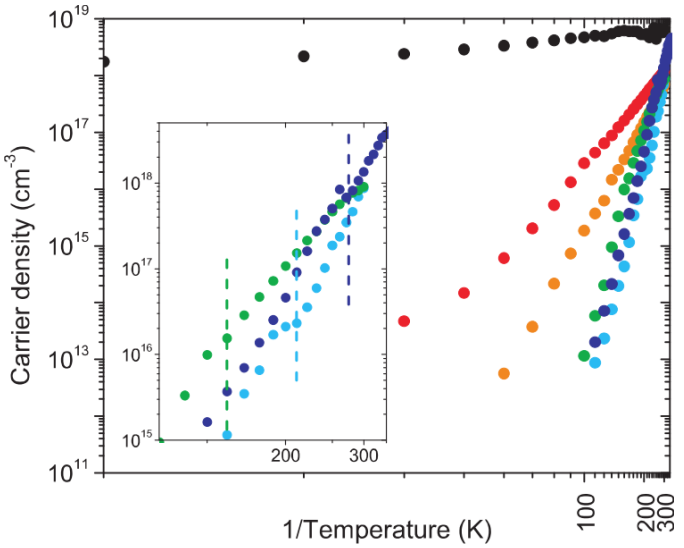
Rhombohedral [111]

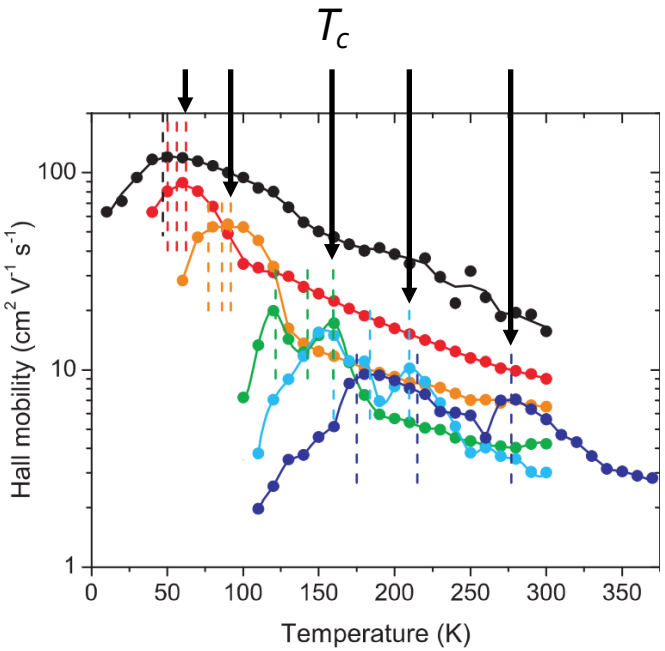


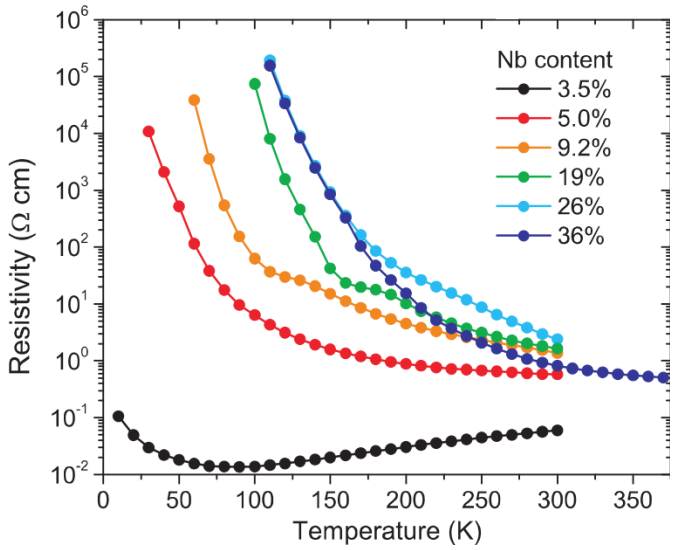
Siemons, McGuire, Cooper, Biegalski, Ivanov, Jellison, Boatner, Sales, Christen. Dielectric-constant-enhanced hall mobility in complex oxides, *Adv. Mater.* **2012**, *24*, 3965 – 3969.

Hall mobility tracks the dielectric response

- Ancillary experiments show mobility enhancement not due to other effects
- Additional features from lower *T* phase transitions in Nb-rich alloys







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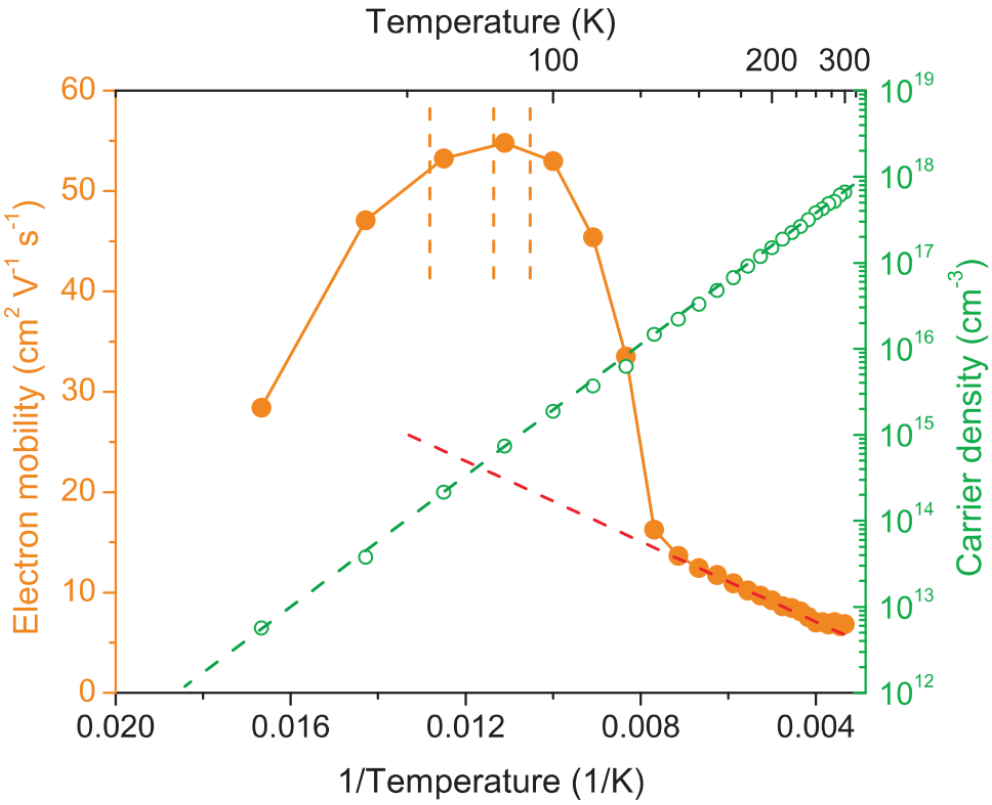
Mobility is greatly enhanced in the vicinity of T_c

$KTa_{0.919}Nb_{0.092}O_3$:Ca



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Outlook

Exploiting electronic—lattice instabilities through chemical tuning presents a novel pathway to enhanced transport in functional materials.

Alloying s^0d^0 transition metal ions (SOJT) or s^2d^{10} main-group ions (lone pair stereochemistry) should enable property tunability over a wide temperature range.

Recently, systems with lone pair-bearing ions have been observed to exhibit unusual temperature dependence of structure and dynamics: These are ideal experimental platforms to further explore the relationship between proximal instability and functional properties.