The Search and Theoretical Guidance for Higher Tc Superconducting Materials: an update

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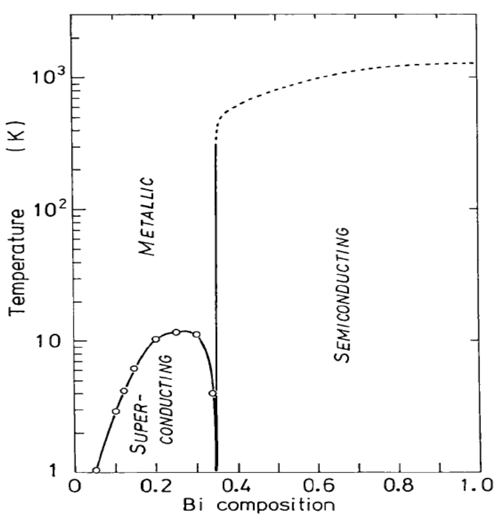
Project overview / history:

- Born out of earlier MURI; smaller subset of players
- Address a more focused set of questions about ***the connection between CDW formation/correlations and superconductivity***, and how we might use this information to design/discover new superconductors and/or improve existing ones
- Admixture of synthesis, experiment and theory
- Currently supports ½ postdoc (theory), ½ post-doc (experiment), and a staff scientist (MBE) + leverage one fellowship student (experiment)

Motivation

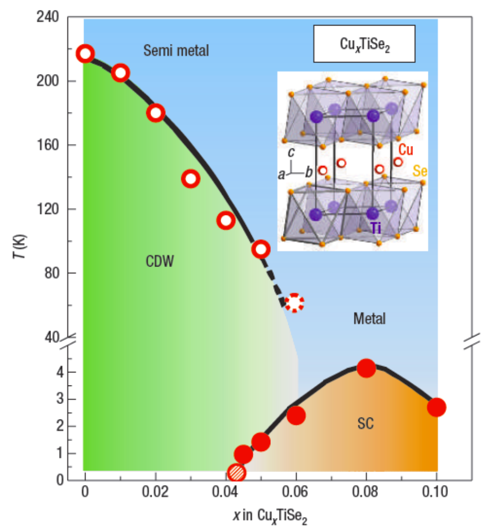
- CDW groundstate is often closely associated with superconductivity…

$BaPb_{1-x}Bi_xO_3$



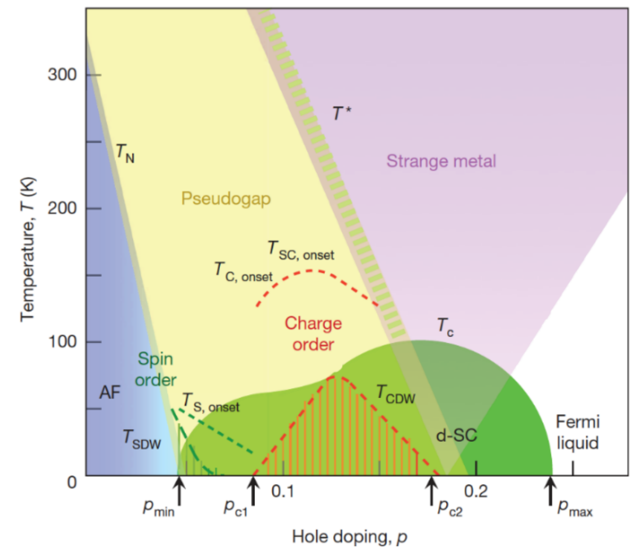
Uchida *et al.*,
Phase Trans. **8**, 95 (1987)

Cu_xTiSe_2



Morosan & co
Nat. Phys. **2**, 544 (2006)

$YBa_2Cu_3O_{6+x}$



Kivelson & co
Nature **518**, 179-186 (2015)

- Peierl’s type model inappropriate for nearly all materials of current interest
- Complex phase diagrams go beyond simple paradigm of competing phases
- Open questions about roles played by CDW fluctuations, short-range correlations, disorder, vestigial nematicity, intertwined order etc…

Our approach

- These materials are complicated, and the essential physics in each case might even be unrelated
- For an improved understanding, we seek (1) model systems; (2) new experimental approaches; and (3) new materials
- For all cases, we incorporate material-specific theory guidance

1. Model systems

- Role of valence skipping elements: Tl-doped PbTe (*expt & theory*)
- Role(s) played by disorder: (a) 2H $TaSe_{2-x}S_x$ (*theory*)
  (b) Pd-intercalated RTe_3 (*expt & theory*)

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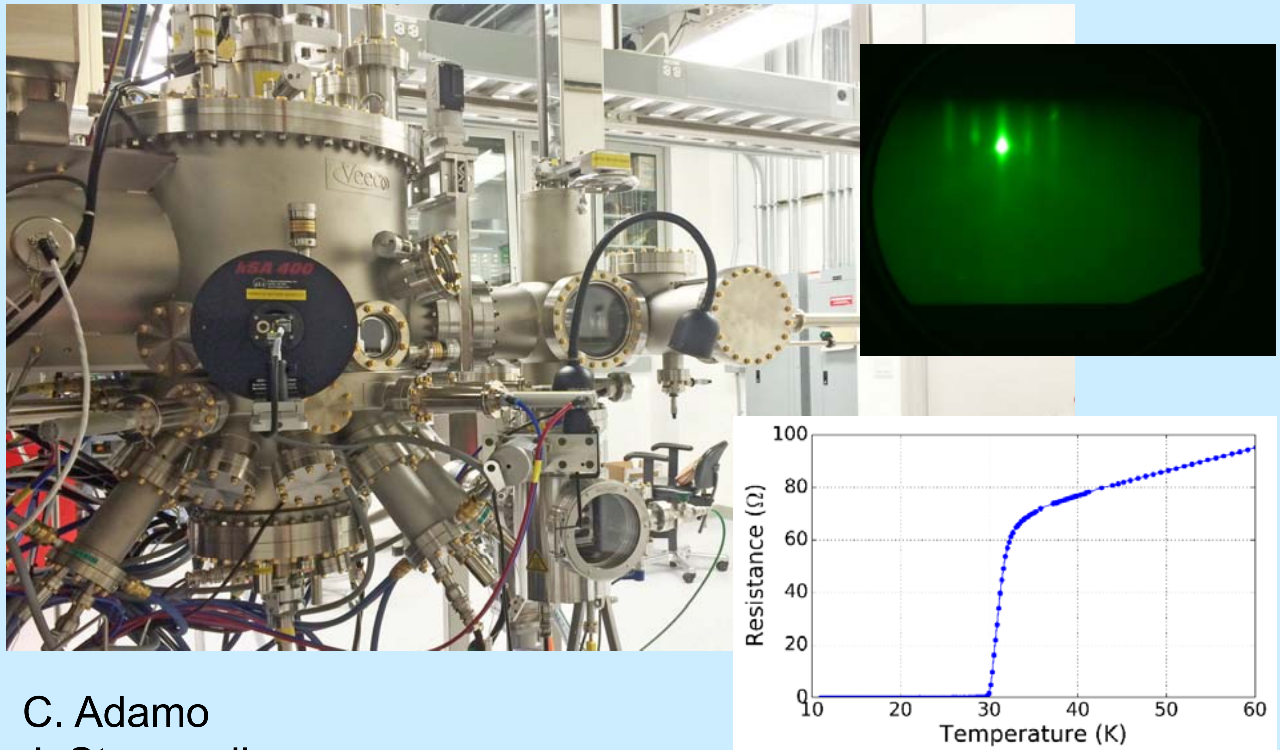
1. Model systems
- Role of valence skipp
- Role(s) played by dis

Commissioned new Veeco oxide MBE system:



C. Adamo
J. Straquadine

2. New experimental approaches (applied to known materials; LSCO)
- Evidence for nematic fluctuations ? (new probe!)
- Effect of anisotropic strain on phase diagram ? (new tuning parameter!)
- Evidence for stronger pairing near putative QCP ?

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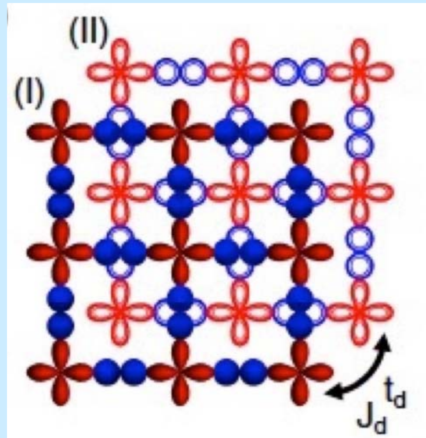
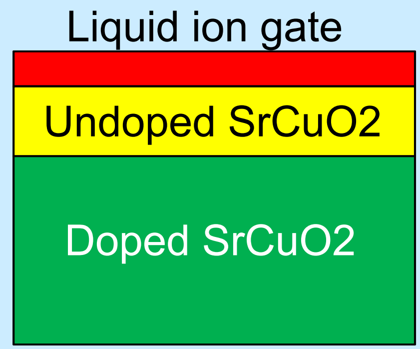


MBE of Quasi-2D Tetragonal CuO:



MBE of infinite layer material $SrCuO_2$ (pn junctions)

C. Adamo

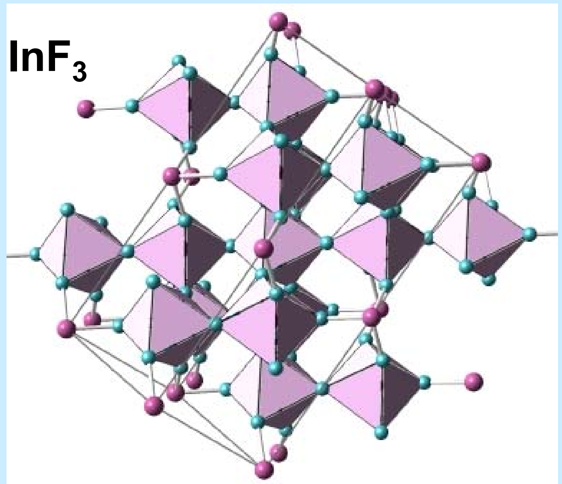
2. New experimental approaches (applied to known materials; LSCO)

- Evidence for nematic fluctuations ? (new probe!)
- Effect of anisotropic strain on phase diagram ? (new tuning parameter!)
- Evidence for stronger pairing near putative QCP ?

3. New materials

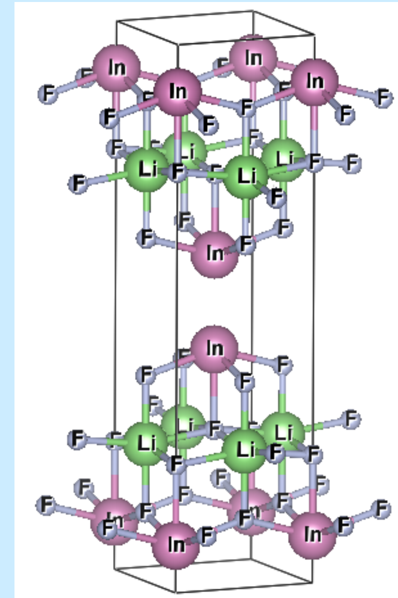
- Exploratory synthesis using MBE: new materials and new interfaces (*expt*)
- Towards an analog of $BaBiO_3$ and $CsTlF_3$ based on indium (*expt & theory*)

One promising candidate, inspired by chemical intuition and guided by theory (*Kotliar*) is $LiInF_3$…



Intercalate Li →

$LiInF_3$



Harlyn Silverstein
Chang-Jong Kang

Lowest energy candidate structure is tetragonal
With a unique indium site!

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For this presentation; two short stories…

- These materials are complicated, a ... ght even be unrelated
- For an improved understanding, w ... (2) new experimental approaches;
- For all cases, we incorporate material-spe ... y guidance

- Thallium impurity band causes enhanced DOS, and possibly an additional pairing interaction
- Design criterion for enhanced Tc in similar materials

established results

ongoing & future directions

1. Model systems
- Role of valence skipping elements: Tl-doped PbTe (*expt & theo*
- Role(s) played by disorder: (a) 2H $TaSe_{2-x}S_x$ (*theory*)
  (b) Pd-intercalated RTe_3

Candidate model system to study vestigial nematic order associated with an incommensurate unidirectional CDW (relevant to other superconductors of current interest, including cuprates)

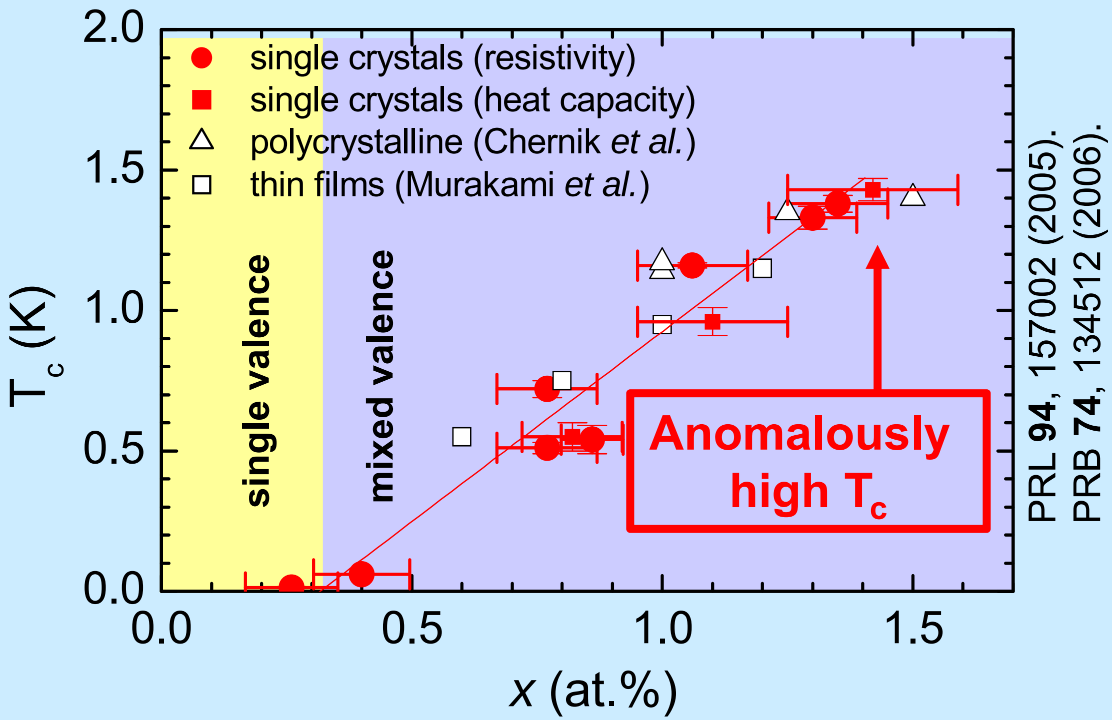
2. New experimental approaches (appli ... nown materials; ...)
- Evidence for nematic fluctuations ? (n
- Effect of a ... ng parameter!)
- Evidence f

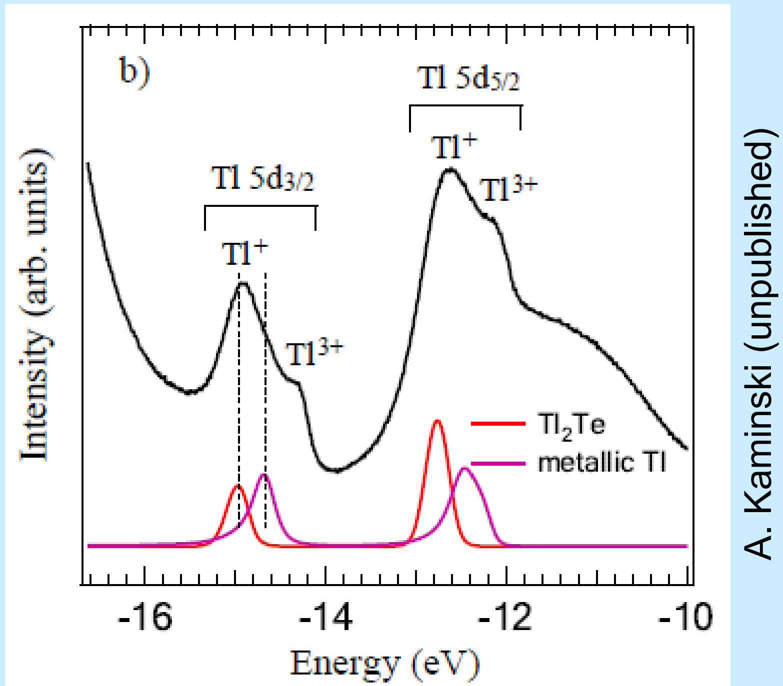
3. New mat
- Explorator ... interfaces (*expt*)
- Towards an ... um (*expt & theory*)

(1) Role(s) played by valence-skipping elements in CDW formation and superconductivity

- Charge disproportionation provides one possible avenue for CDW formation
- Bismuthates: correlation enhanced superconductivity (*Kotliar*)
- Group III impurities in IV-VI semiconductors are model systems, exhibiting charge disproportionation and in the case of $Pb_{1-x}Tl_xTe$, superconductivity…

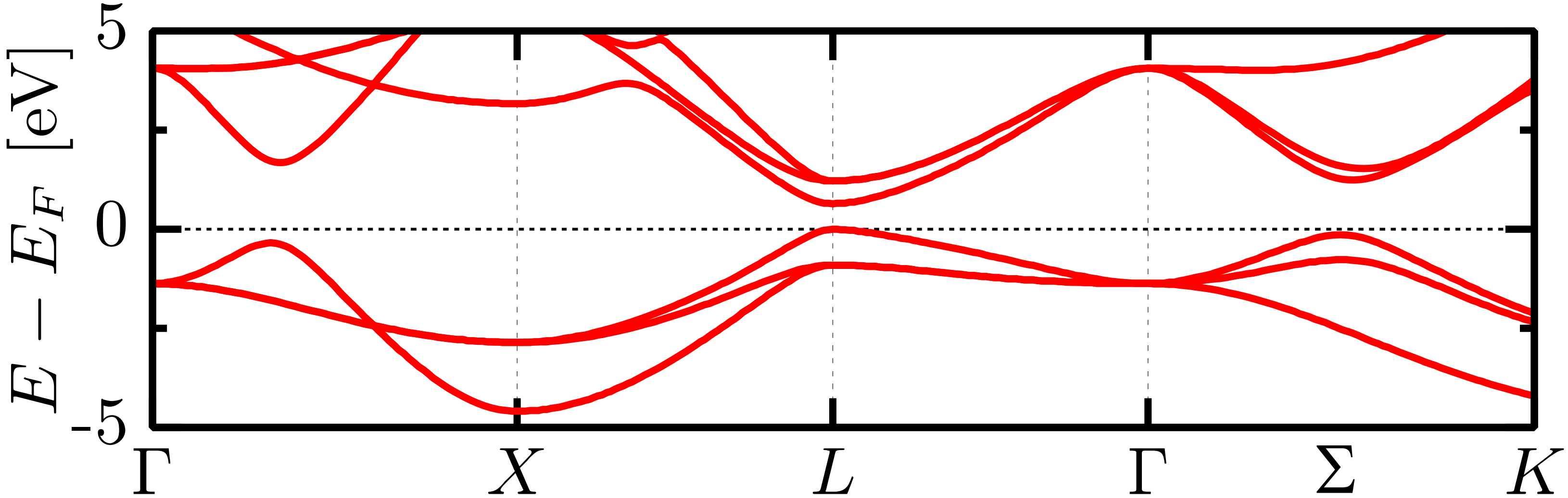
Tl-doped PbTe:





- Why is superconductivity seemingly associated with mixed Tl valence in PbTe?
- What is happening to the electronic structure?

DFT results for the band structure of PbTe



B. Sangiorgio & N. Spaldin

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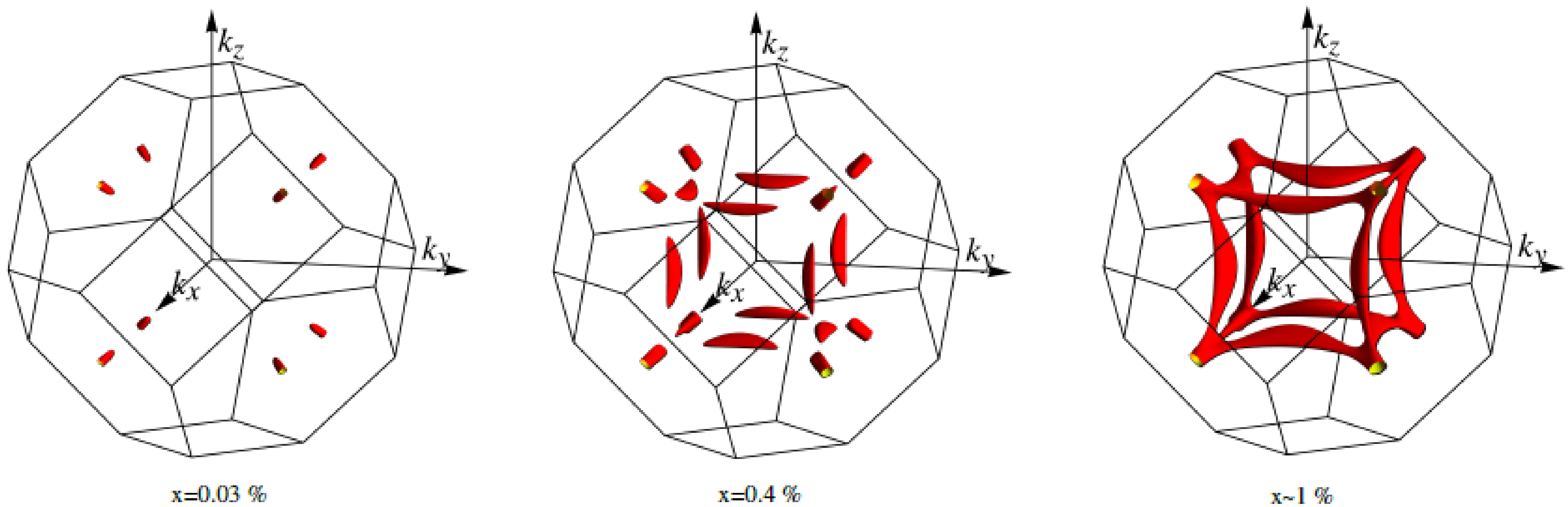


B. Sangiorgio & N. Spaldin

rigid band: 1 hole per dopant

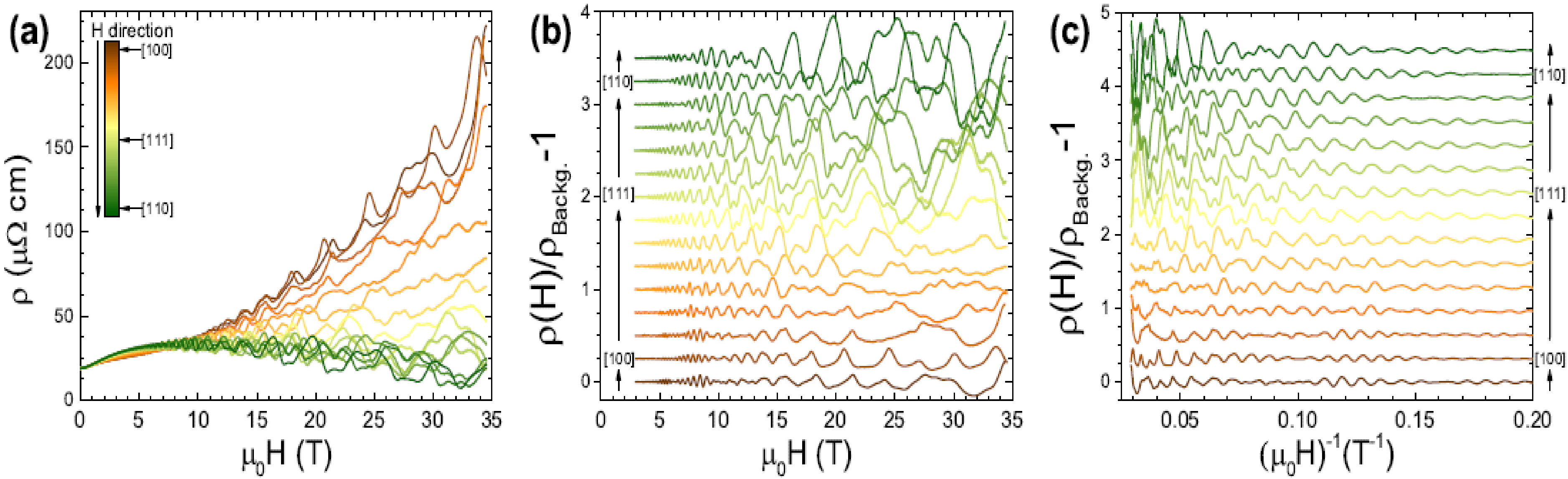
Questions:
- Does the FS of the actual material evolve like this? (esp. band offset)
- Is anomalously high T_c associated with these changes in FS morphology?
- How does the evolution of the FS relate to changes in thallium valence?
- Is there a "design criterion" that might be applicable to other materials?

Expts:
- Compare FS evolution for Tl (superconducting) & Na (non-superconducting)

Na-doped PbTe quantum oscillations

P. Giraldo-Gallo
P. Walmsley

p_H = 6.3 x 10^{19} cm^{-3}



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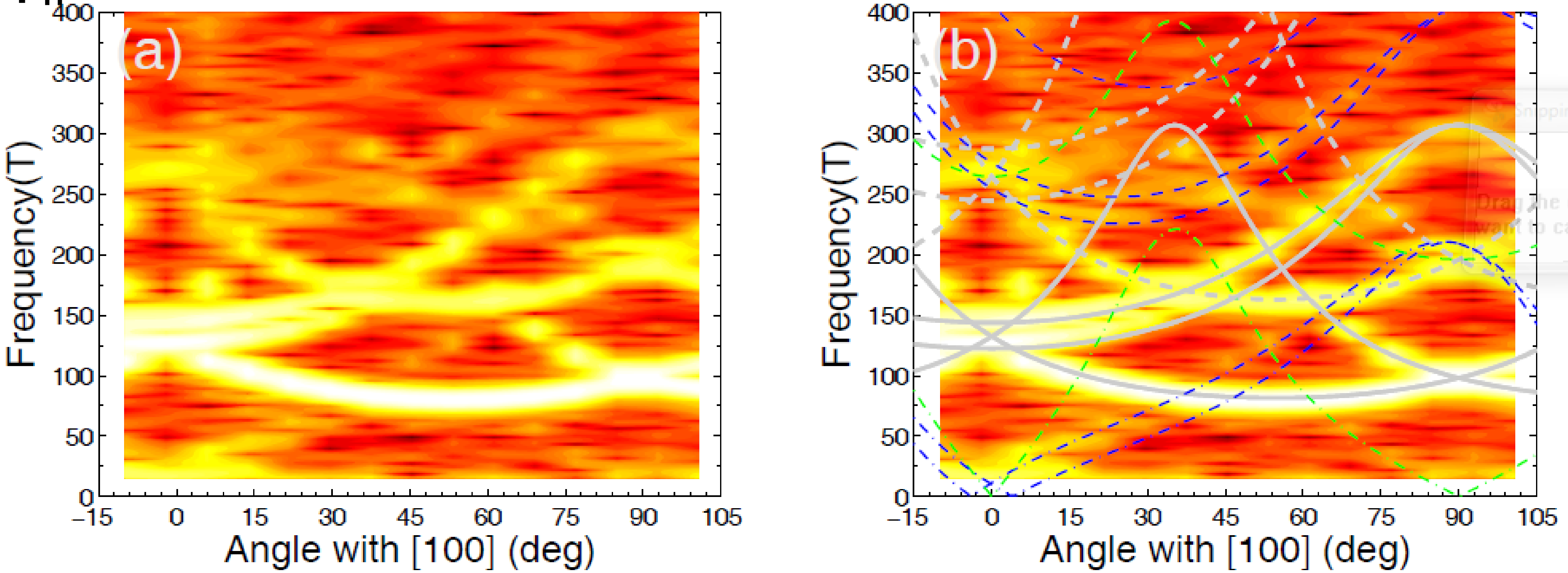

- For all Na concentrations measured (max = 9.4 x 10^{19} cm^{-3}), the FS is described by [111]-oriented ellipsoids

arXiv:1603.04414

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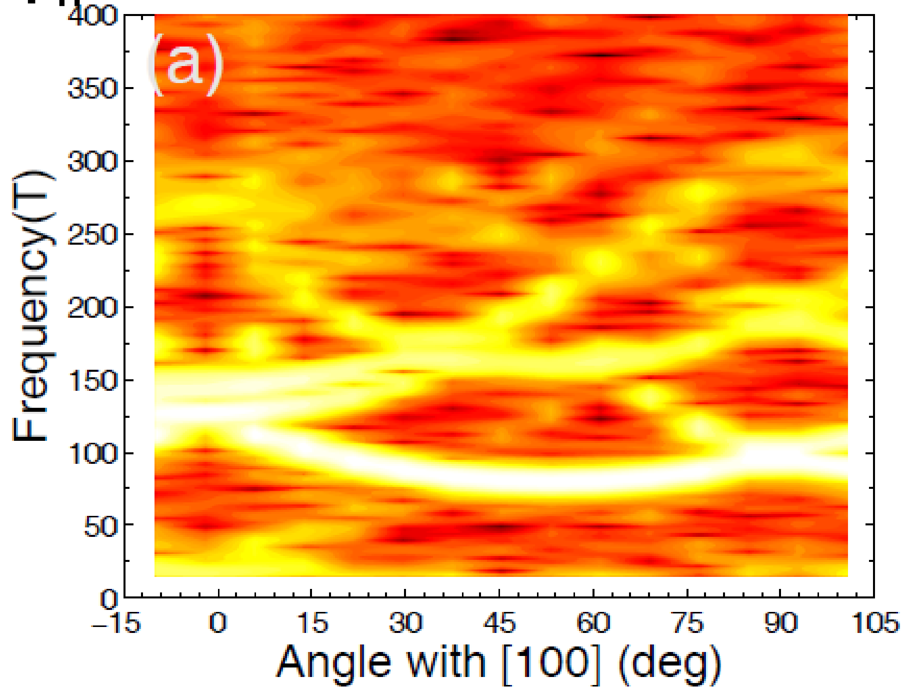

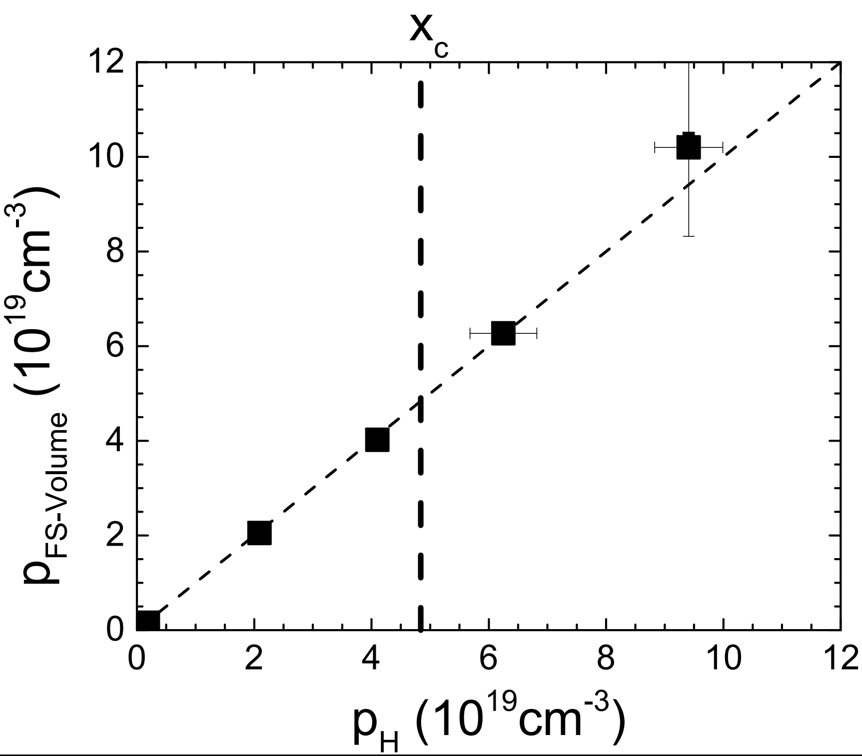

- For all Na concentrations measured (max = 9.4 x 10^{19} cm^{-3}), the FS is described by [111]-oriented ellipsoids
- Luttinger volume enclosed by 4 L-ellipsoids ***exactly*** accounts for Hall coeff
- Apparently the Sigma pocket is ***not*** occupied up to these high concentrations

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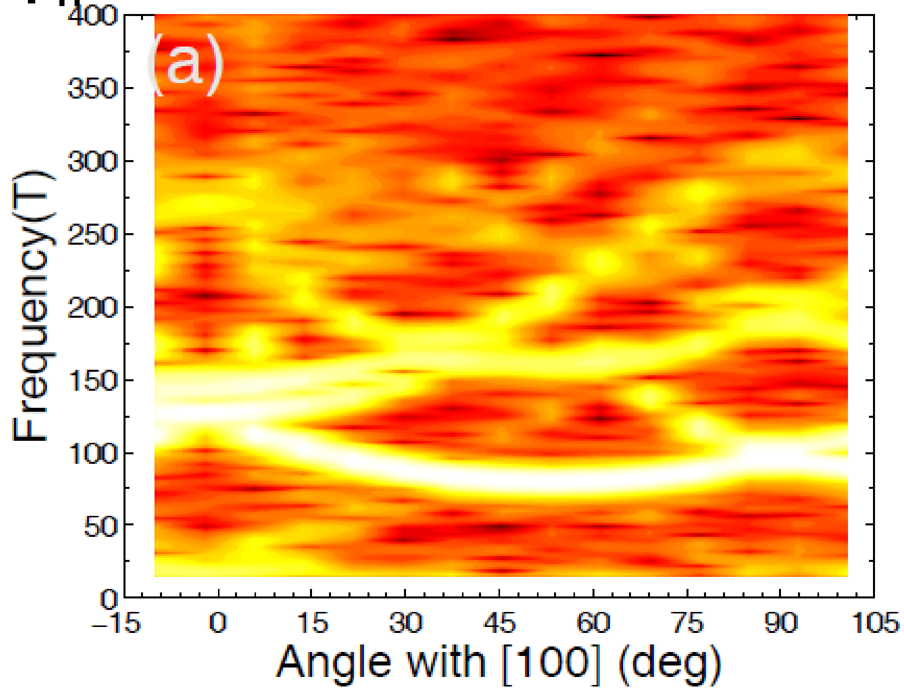

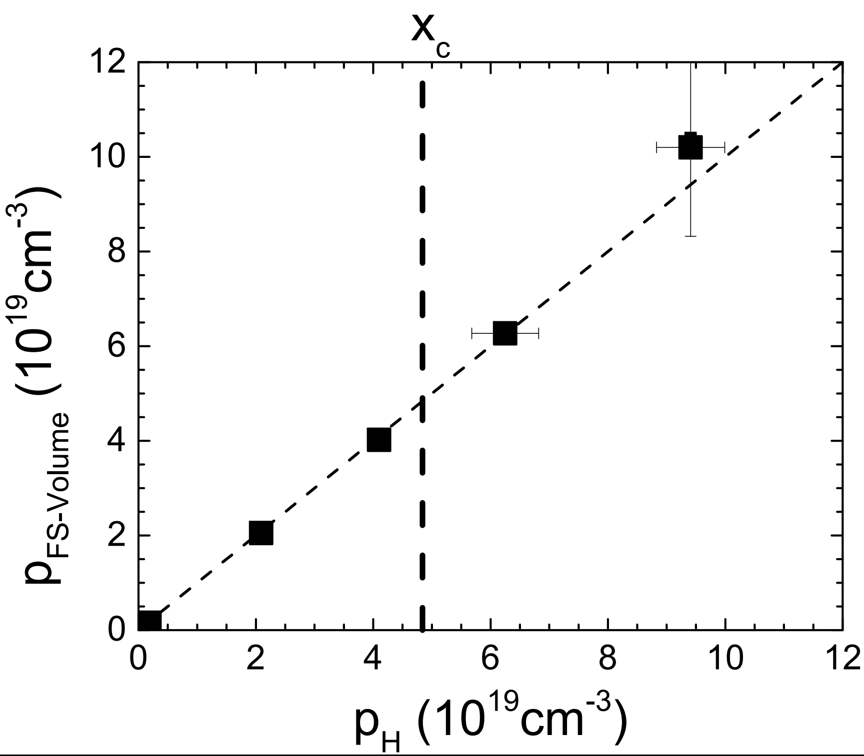

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- Luttinger volume enclosed by 4 L-ellipsoids ***exactly*** accounts for Hall coeff
- Apparently the Sigma pocket is ***not*** occupied up to these high concentrations

- Achieving a quantitative description of band structure is a challenge for DFT
- Important for PbTe: relevant to TEP as much as superconductivity (*Kotliar*)

arXiv:1603.04414

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P. Walmsley

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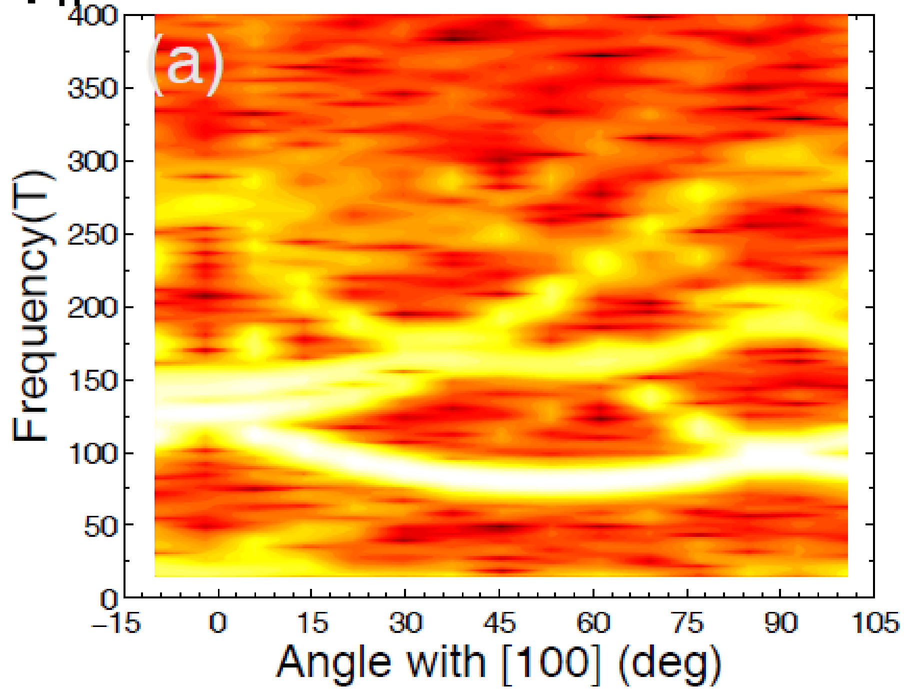

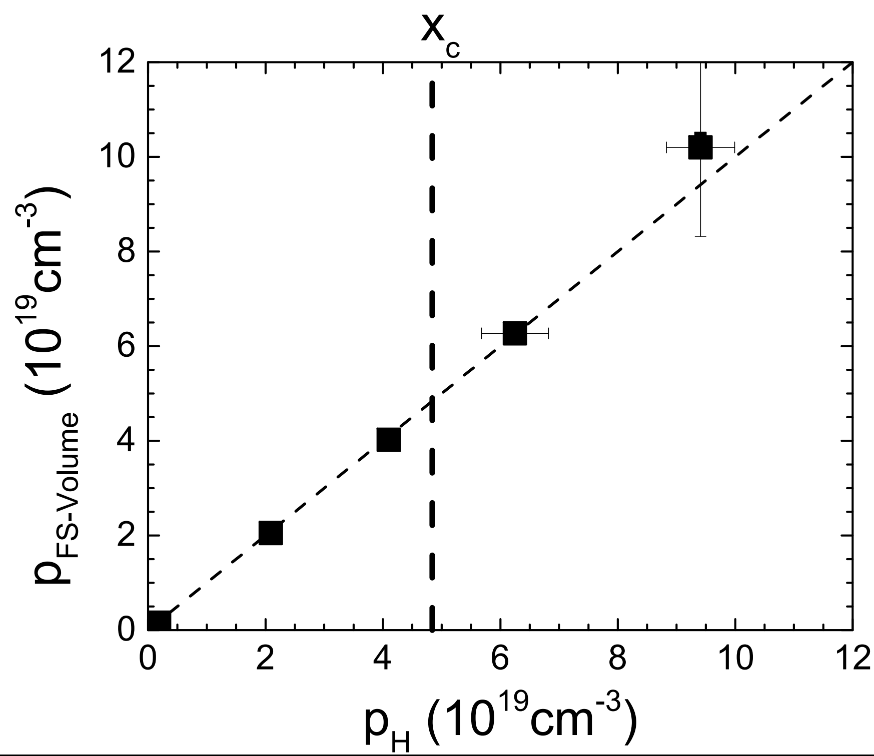

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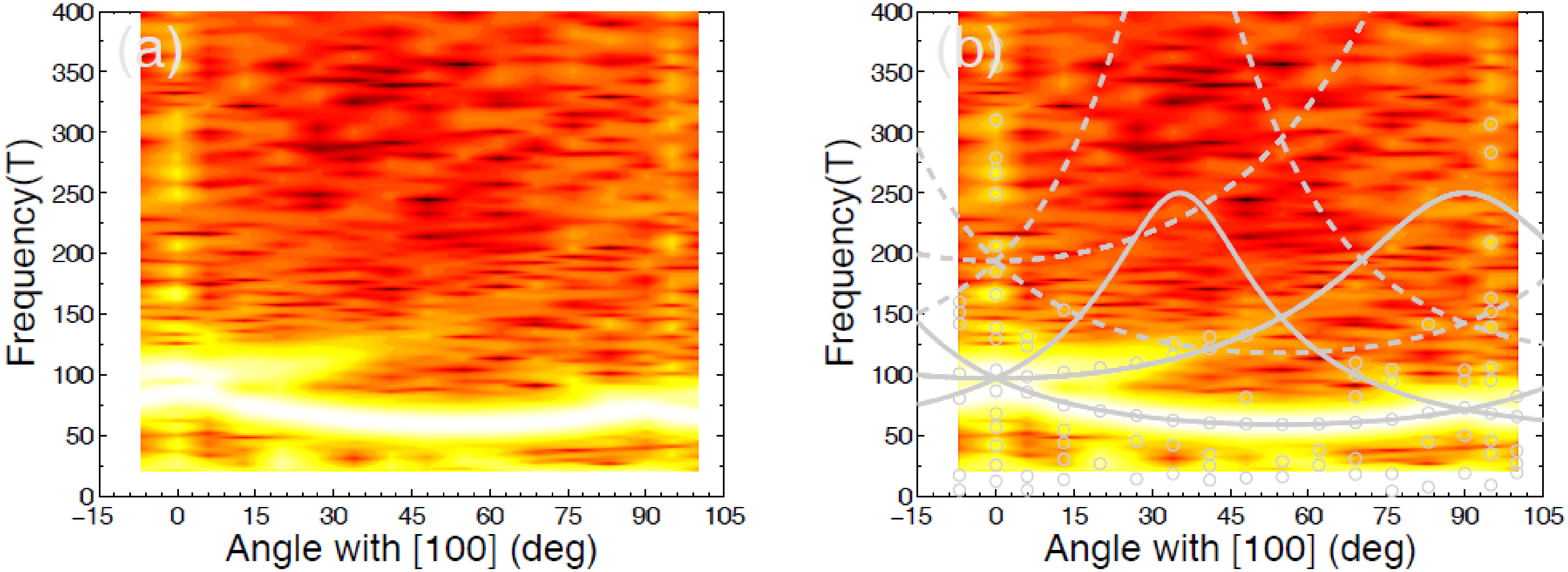
- Luttinger volume enclosed by 4 L-ellipsoids ***exactly*** accounts for Hall coeff
- Apparently the Sigma pocket is ***not*** occupied up to these high concentrations
- → the L-pocket on its own cannot be responsible for superconductivity
- i.e. for Tl-doped PbTe there must be ***either*** additional carriers, ***or*** an enhanced pairing interaction (or perhaps both)

arXiv:1603.04414

Tl-doped PbTe quantum oscillations

P. Giraldo-Gallo
P. Walmsley

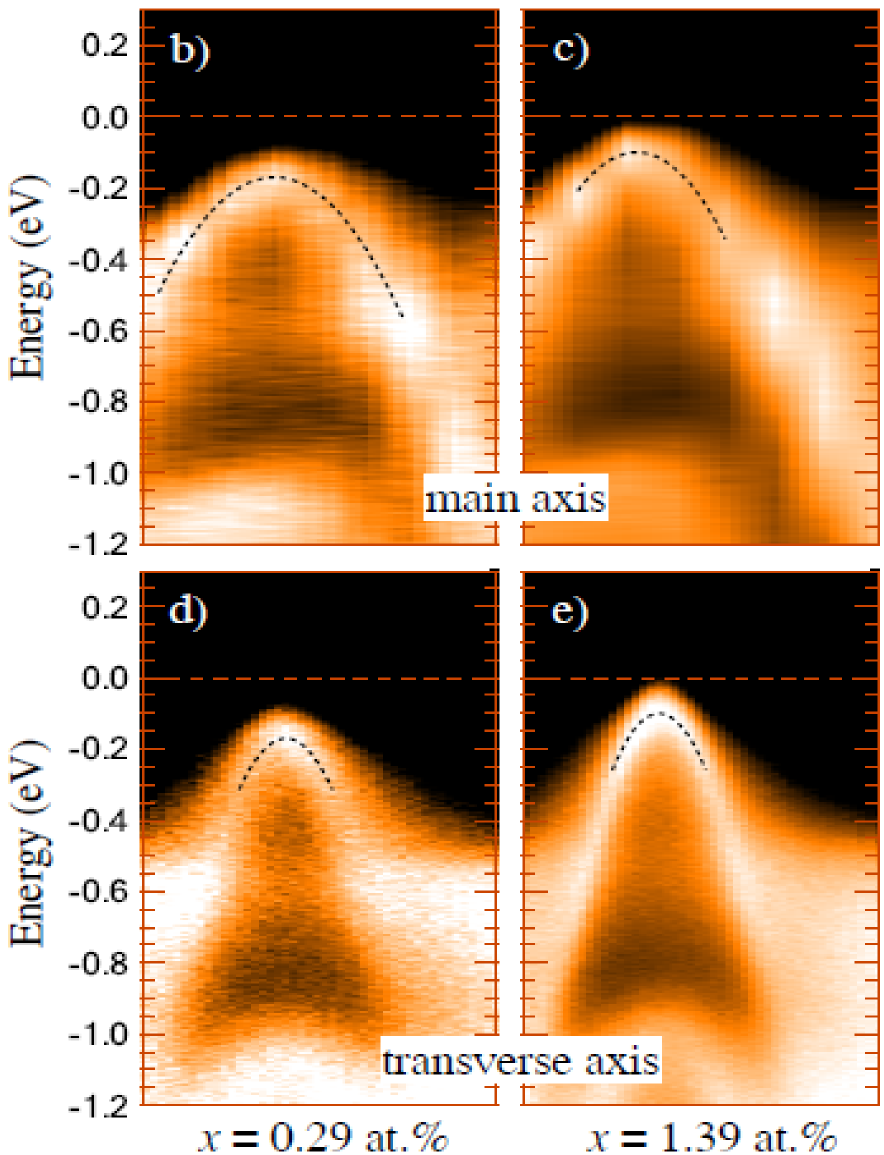
p_H = 4.8 x 10^{19} cm^{-3}



- Significantly increased scattering rate for the same E_F compared to Na
- But can still clearly resolve QO from ellipsoidal pocket (same as Na-doping)
- No evidence for any other coherent FS pockets
- Confirmed by ARPES…

Tl-doped PbTe ARPES (A. Kaminski)

Σ pocket:



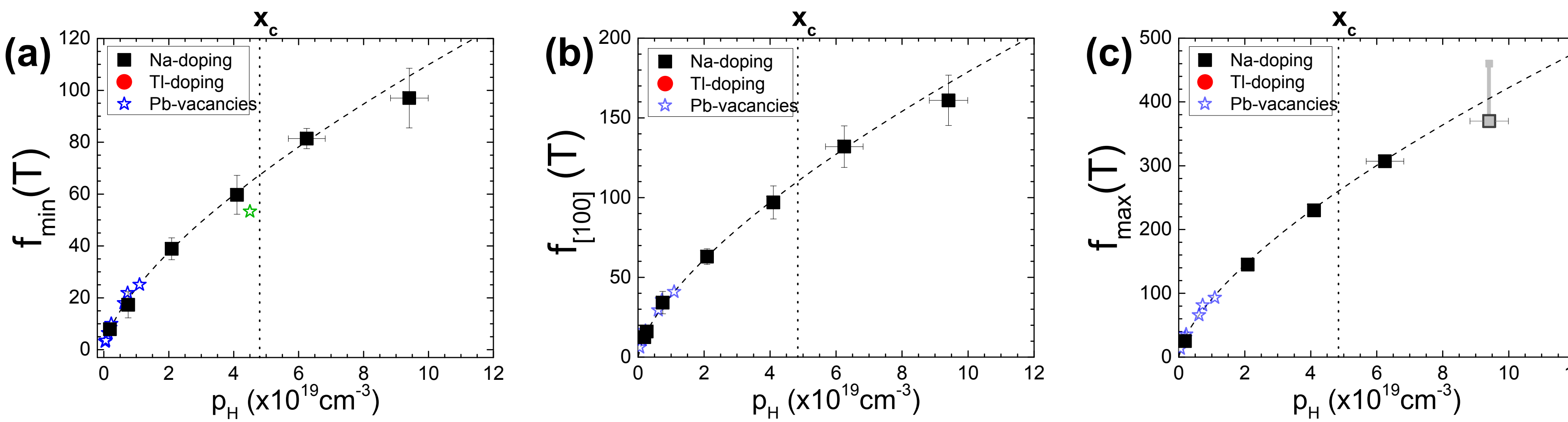
- The Σ pocket remains well below E_F up to at least 1.39% Tl, well beyond the onset of superconductivity

- But we know that the L pocket on it's own does not superconduct

- So Tl-doped PbTe must have ***either*** additional ***incoherent*** carriers (for instance an impurity band) ***or*** an additional pairing interaction, ***or*** perhaps both…

Tl-doped PbTe: impurity band

P. Giraldo-Gallo
P. Walmsley



- Na substitution: E_F falls deeper in to band for every hole added

Tl-doped PbTe: impurity band

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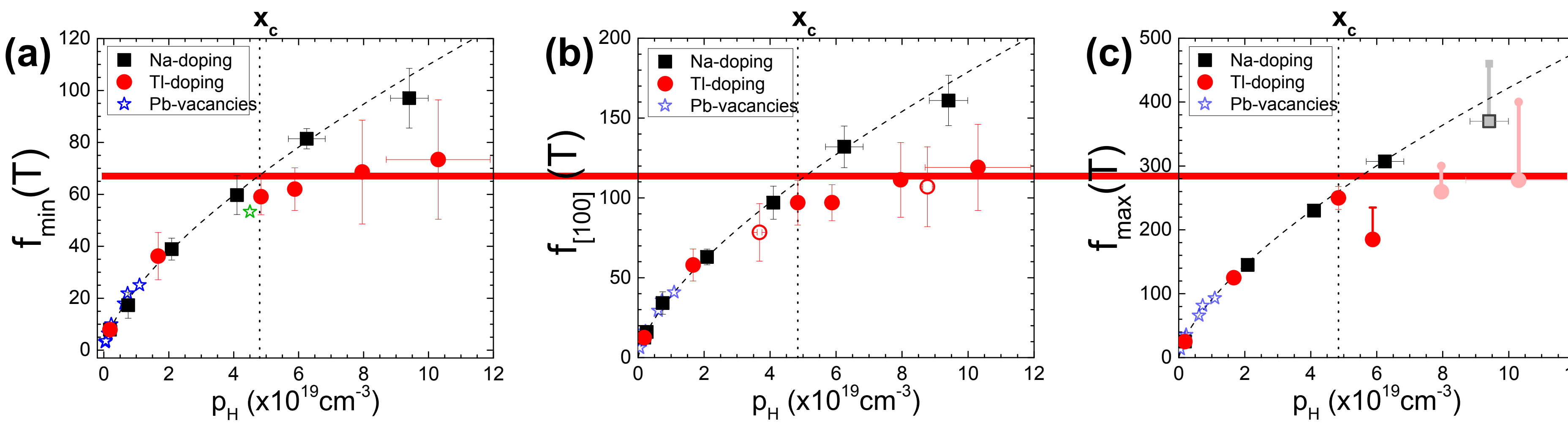
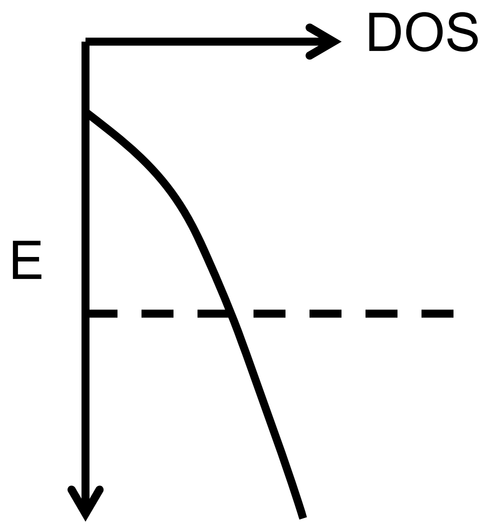


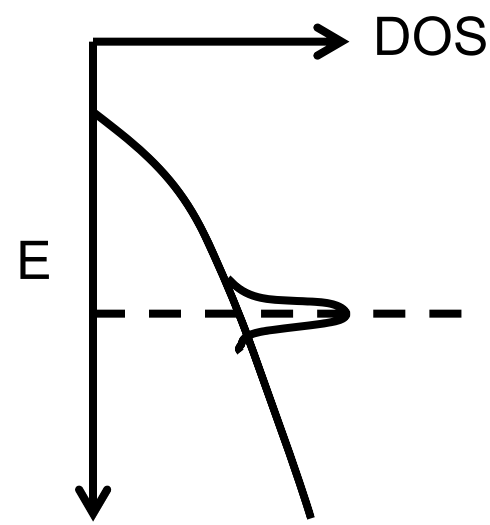
- Na substitution: E_F falls deeper in to band for every hole added
- Tl substitution: even though additional carriers are added, E_F is "pinned" (and the number of additional carriers is ***less than*** 1 per Tl, consistent with observation of mixed Tl valence)
- Clear evidence for an impurity band…

Resonant impurity states

Na substitution:



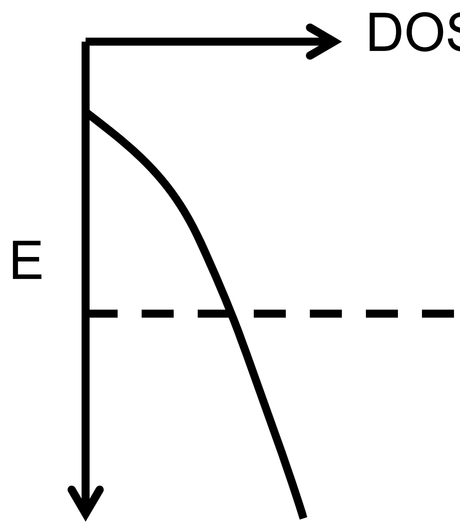
Tl substitution:



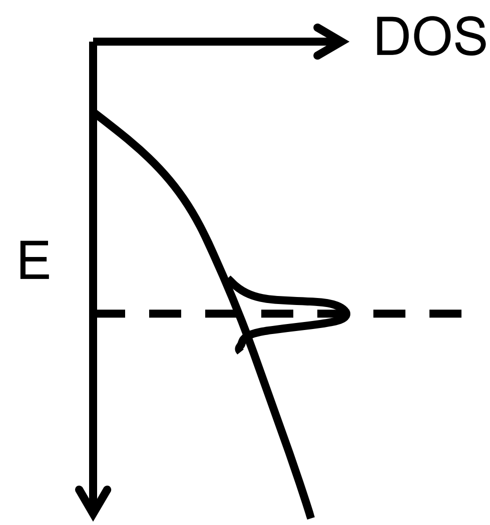
- Group III impurities in PbTe known to yield deep & resonant states
- Pin E_F, increase scattering rate, and contribute additional incoherent carriers
- The presence of these states seems to be the distinguishing characteristic of the “high” Tc superconductor in this case: enhance $N(E_F)$ (good for sc & TEP)
- Points towards a potential “design criterion” for enhancing Tc…

Resonant impurity states

Na substitution:



Tl substitution:



Ongoing & future experiments:

- Tune E_F in/out of resonance for fixed Tl concentrations

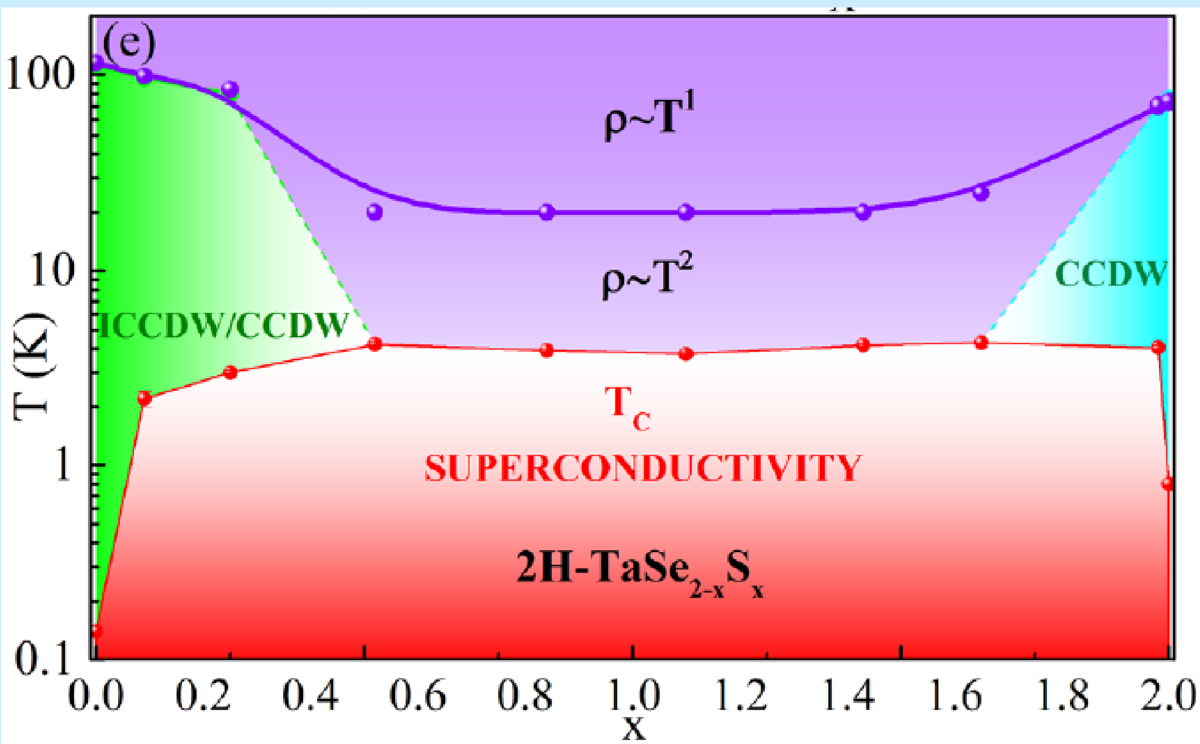
Open questions for theory:

- Do these states also contribute an enhanced pairing interaction, similar to the correlation effects in bismuthate superconductors?
- Requires further theoretical work (*Kotliar*), but tantalizing possibility…
- Which impurities will work for which host systems? Add quantitative accuracy to qualitative "design criterion" : theoretical guidance for materials discovery…

(2) Role(s) played by disorder in optimizing T_c in the presence of CDW correlations

- For materials that exhibit a tendency towards both CDW formation and superconductivity, ***disorder*** presents some new opportunities to optimize T_c
- Ongoing & future work explores two paradigms that haven't been extensively investigated before, and some candidate model systems…

1. Competing order: eg 2H-$TaSe_{2-x}S_x$



- Disorder suppresses CDW
- Leaves superconductivity to thrive for conventional superconductors (saved by Anderson's theorem)
- 2H-$TaSe_{2-x}S_x$ is a model system for theory (isoelectronic substitution) - *Kotliar*

arXiv 1608.06275 (expt: Petrovic ; **theory: *Kotliar***)

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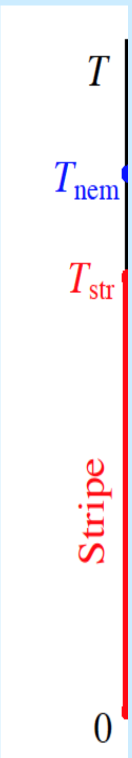
2. Vestigial nematic order:



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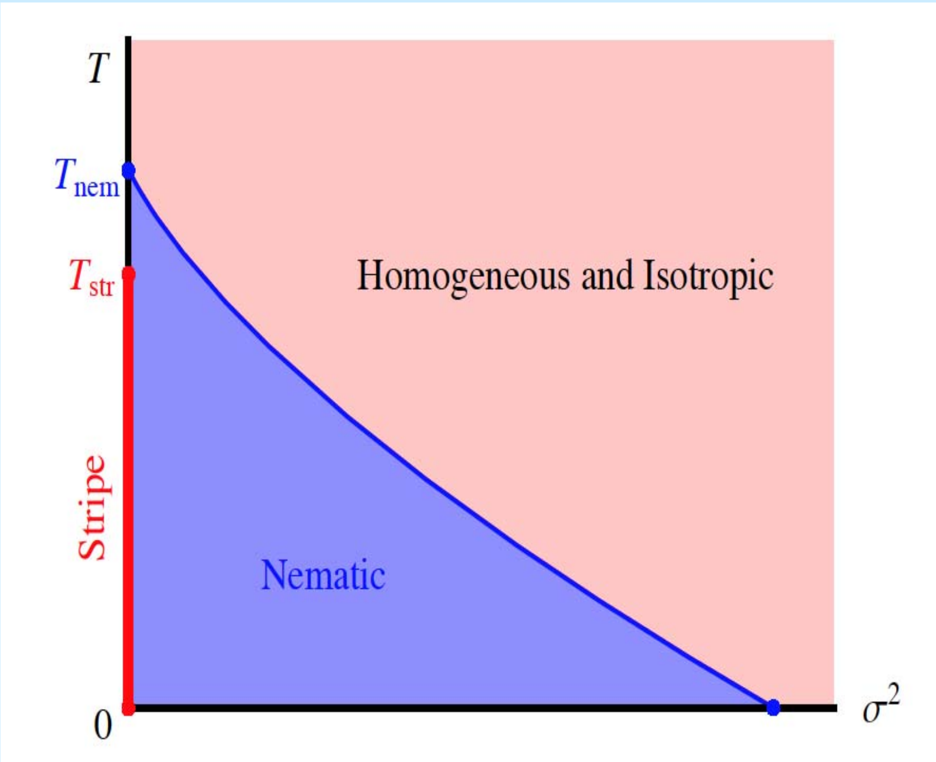
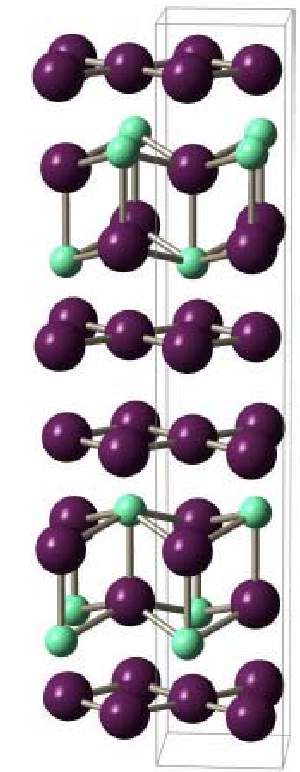


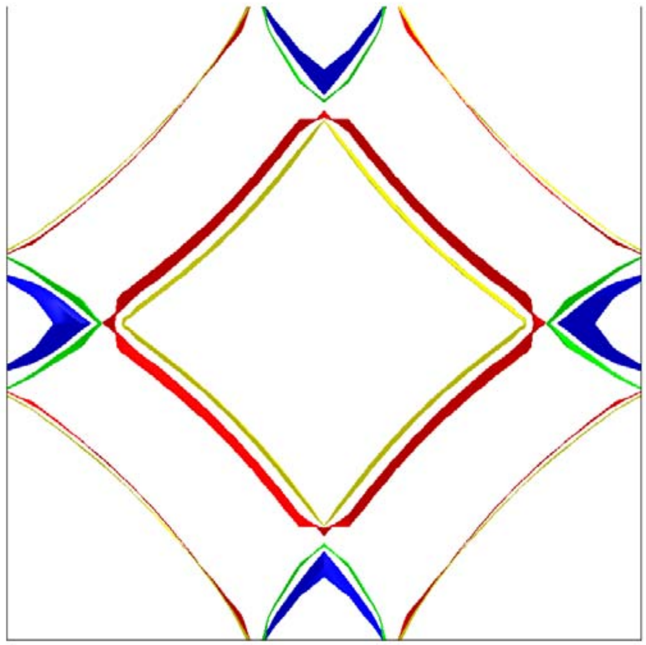
Kivelson et al, PNAS, **111**, 7980-7985 (2014)

- Strictly speaking, for a unidirectional iCDW, the CDW transition is destroyed by even weak disorder
- However, ***nematic*** order can survive, and such systems can potentially be tuned to a nematic QCP
- Open question as to whether nematic fluctuations can contribute an effective pairing interaction (goes beyond paradigm of competing order)
- Would like to find a model system to test these ideas…

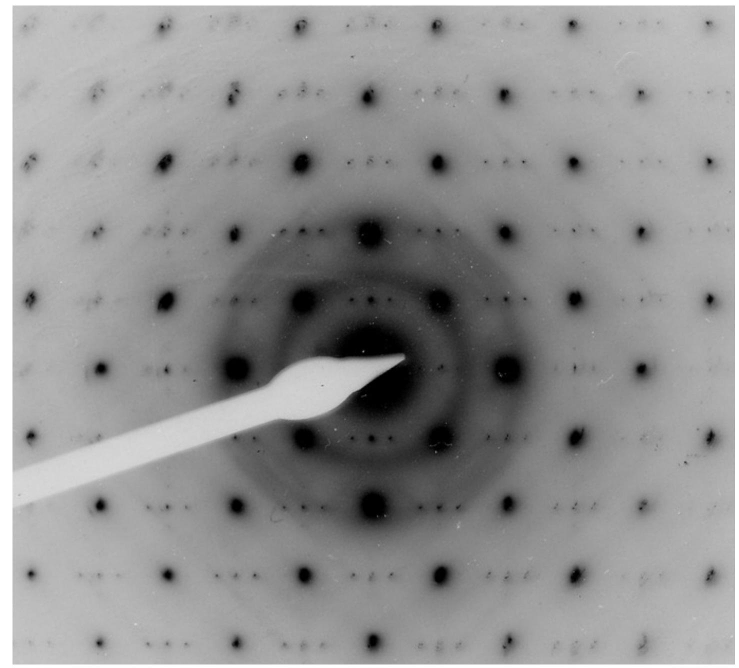
A possible model system: Pd-intercalated RTe_3

J. Straquadine





J. Laverock, IRF et al., PRB **71**, 085114 (2005).



RTe_3:

- Unidirectional incommensurate CDW breaks approximate C_4 symmetry

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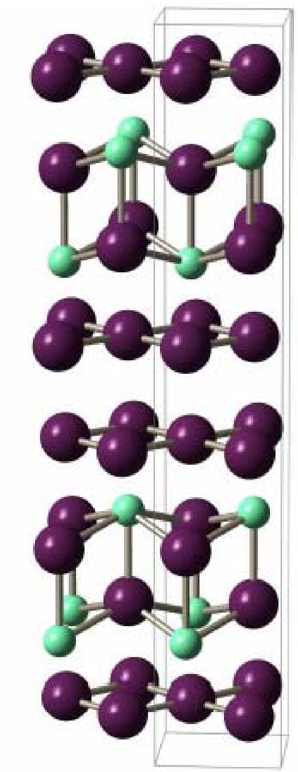

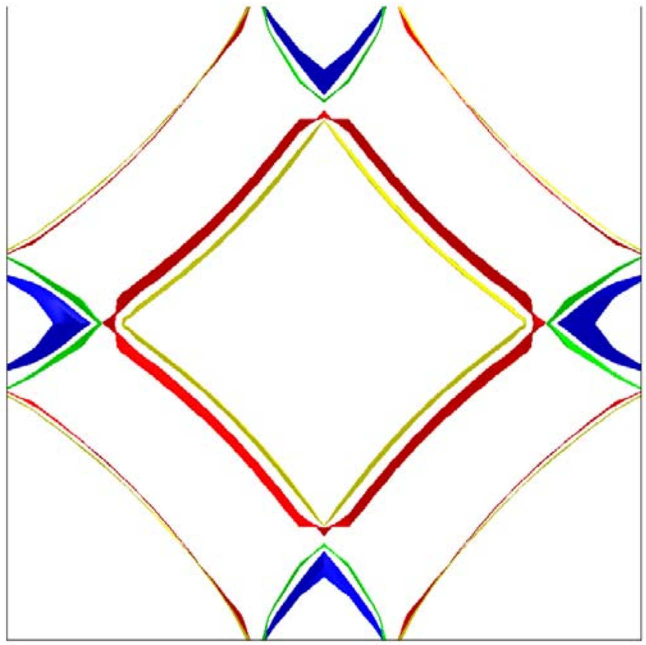

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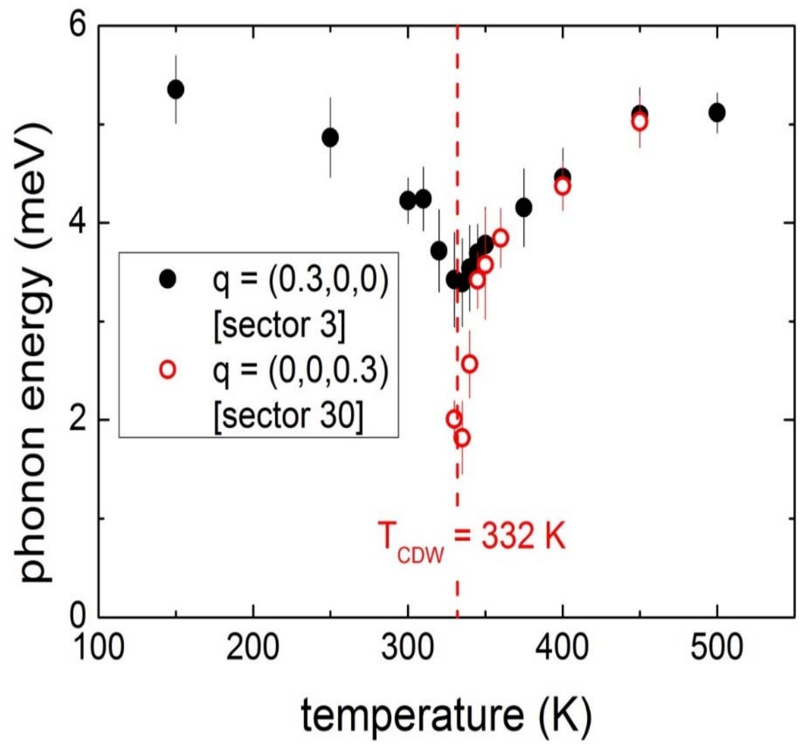

F. Weber, S. Rosenkranz, IRF (unpublished)

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- Kohn anomaly observed in both directions (weak orthorhombicity selects one)

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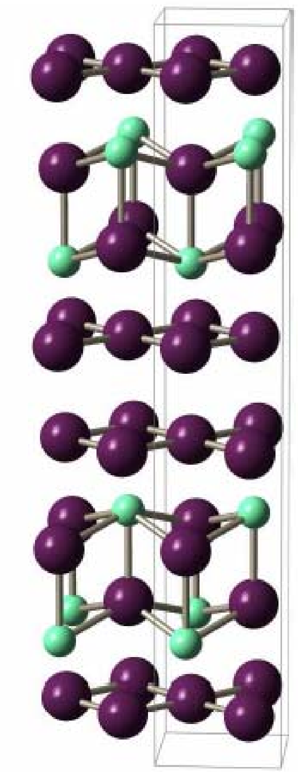

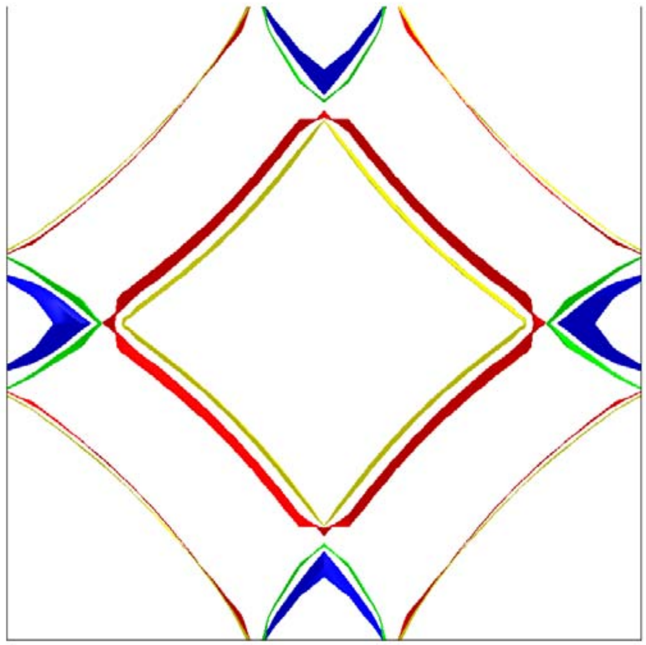

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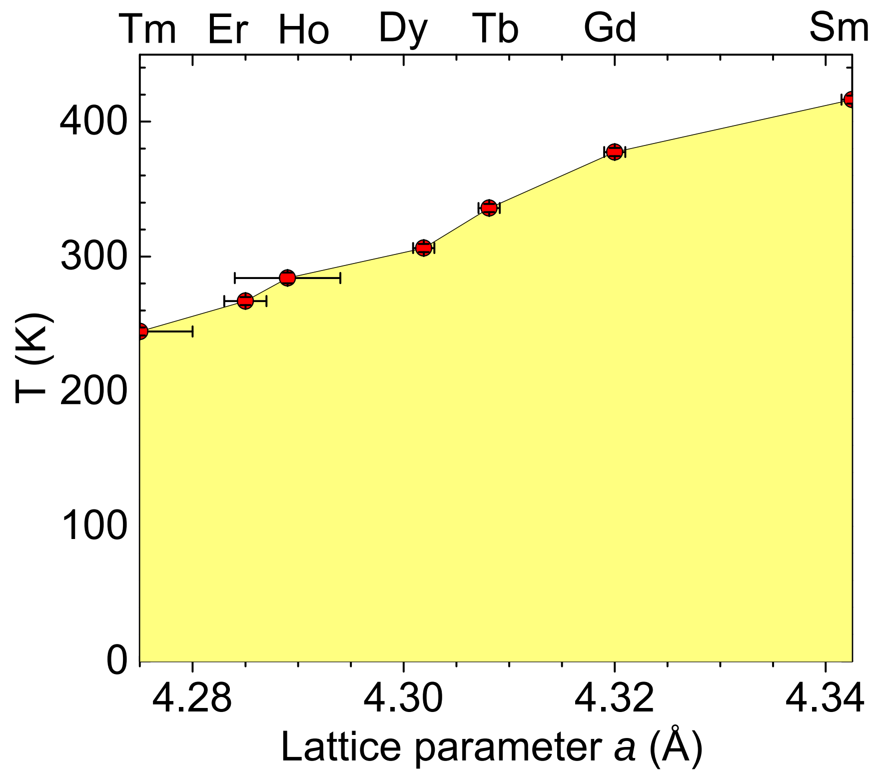

N. Ru, IRF *et al*. Phys. Rev. B **77**, 035114 (2008).

RTe_3:

- Unidirectional incommensurate CDW breaks approximate C_4 symmetry
- Kohn anomaly observed in both directions (weak orthorhombicity selects one)
- Tune critical temperature by varying lattice parameter

A possible model system: Pd-intercalated RTe_3

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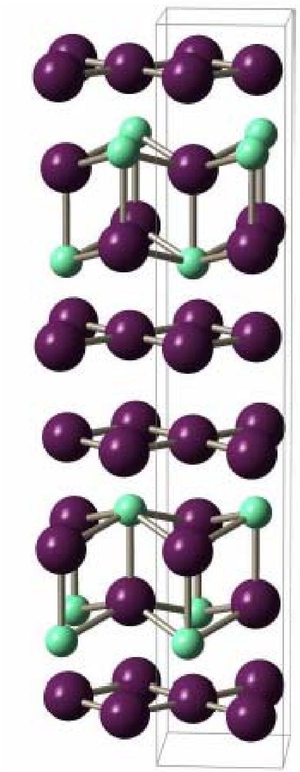
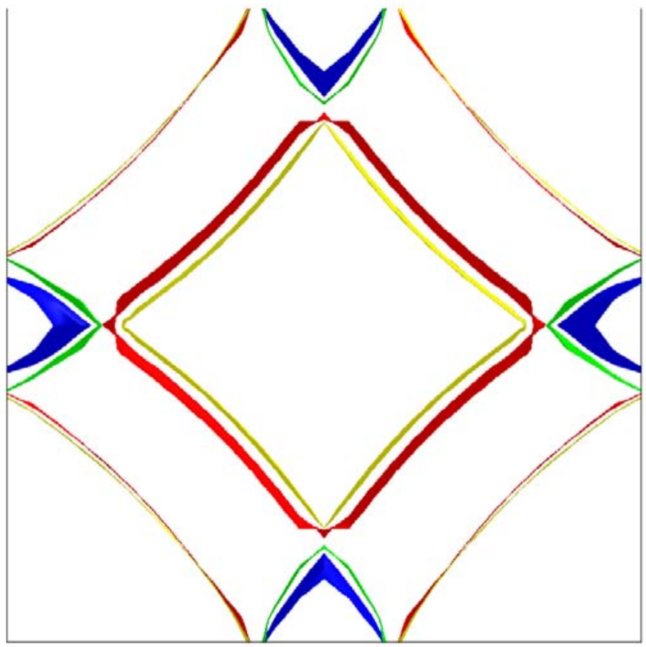
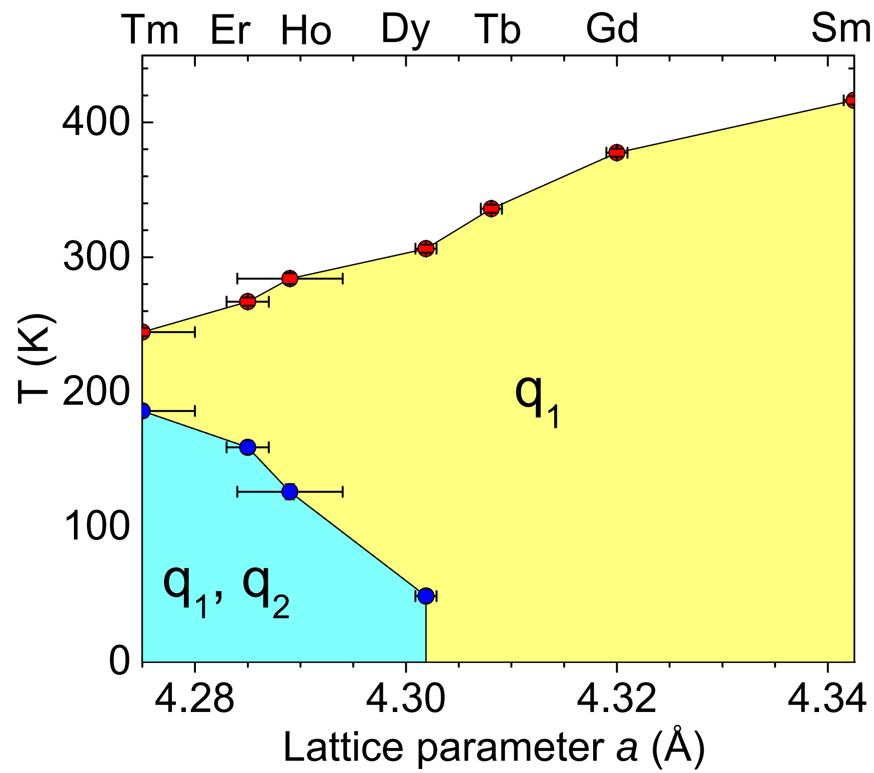




J. Laverock, IRF et al., PRB **71**, 085114 (2005



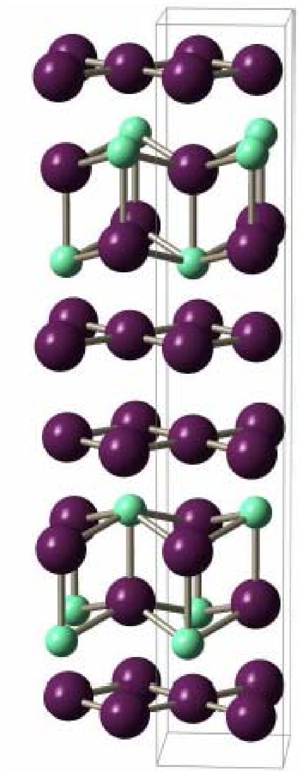
N. Ru, IRF *et al*. Phys. Rev. B **77**, 035114 (2008).

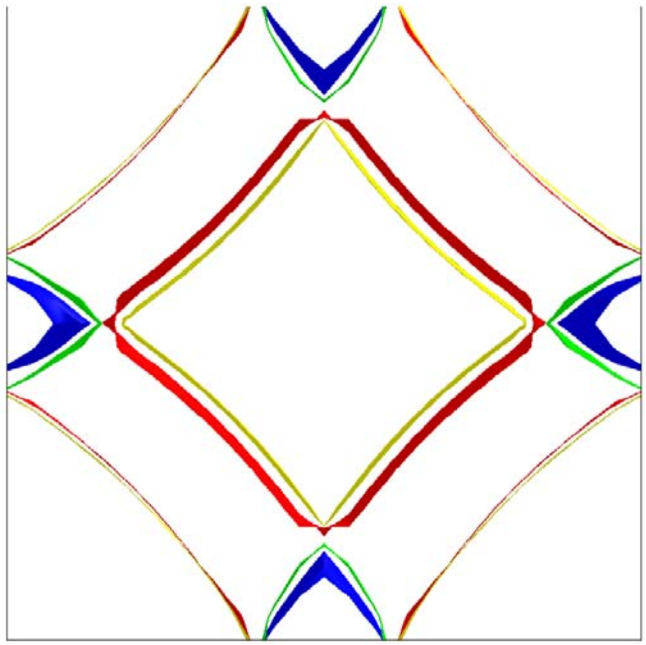
RTe_3:

- Unidirectional incommensurate CDW breaks approximate C_4 symmetry
- Kohn anomaly observed in both directions (weak orthorhombicity selects one)
- Tune critical temperature by varying lattice parameter
- For heavier rare earths, 2^{nd} (transverse) CDW competes with the first

A possible model system: Pd-intercalated RTe_3

J. Straquadine





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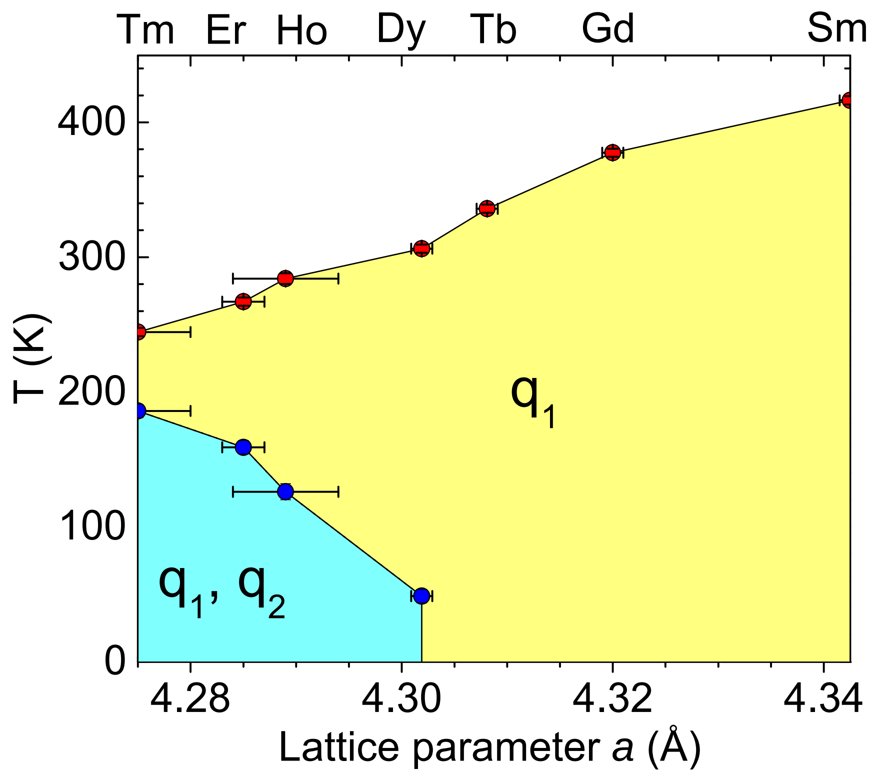
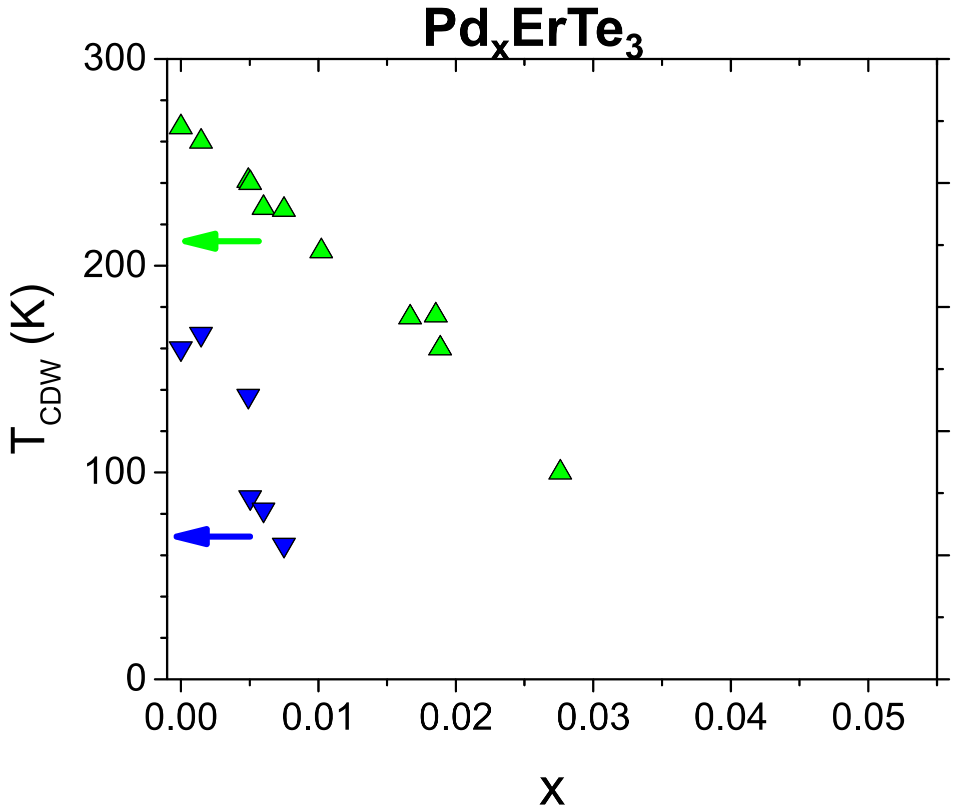


N. Ru, IRF *et al*. Phys. Rev. B **77**, 035114 (2008).

Pd intercalation:
- XRD: expands b-axis lattice parameter; likely intercalates between Te bilayers
- TEM: q_{CDW} remains incommensurate and is essentially unaltered
- not yet clear if a doping effect…
- …. but for sure, introduces disorder

A possible model system: Pd-intercalated RTe_3

J. Straquadine



- ***Both*** CDWs suppressed by Pd (even though these are competing phases)
- Consistent with a disorder-driven effect

A possible model system: Pd-intercalated RTe_3

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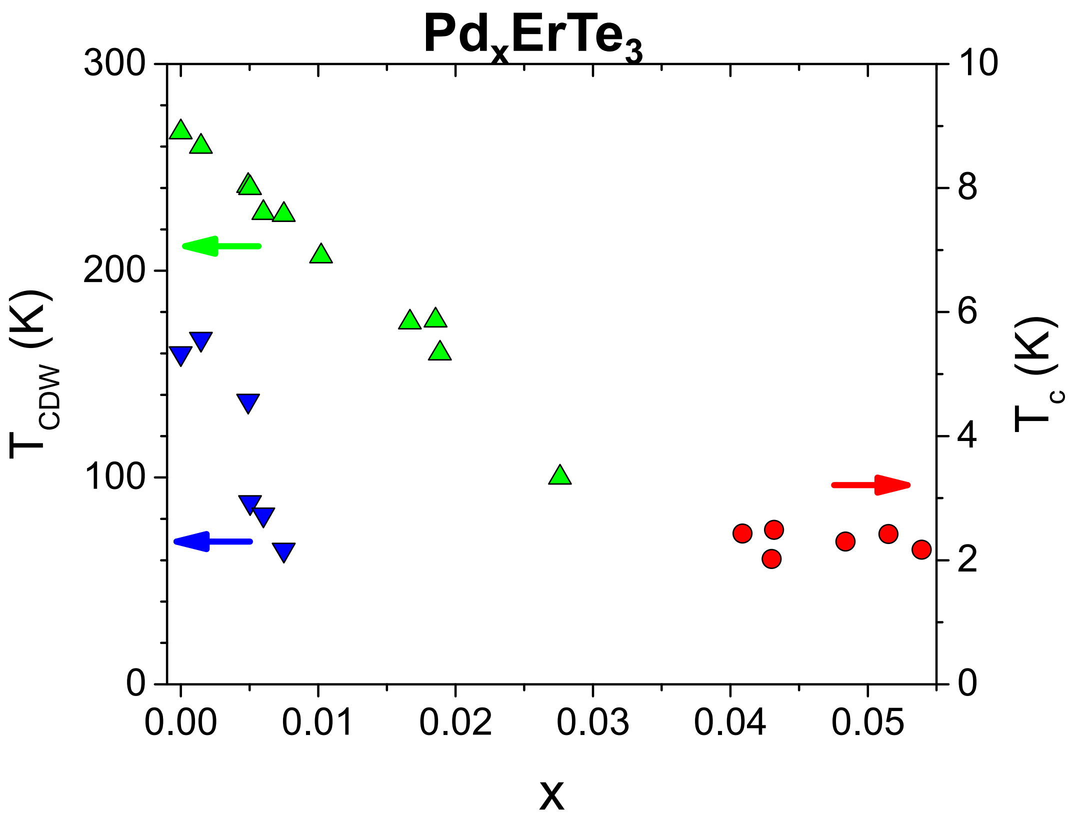
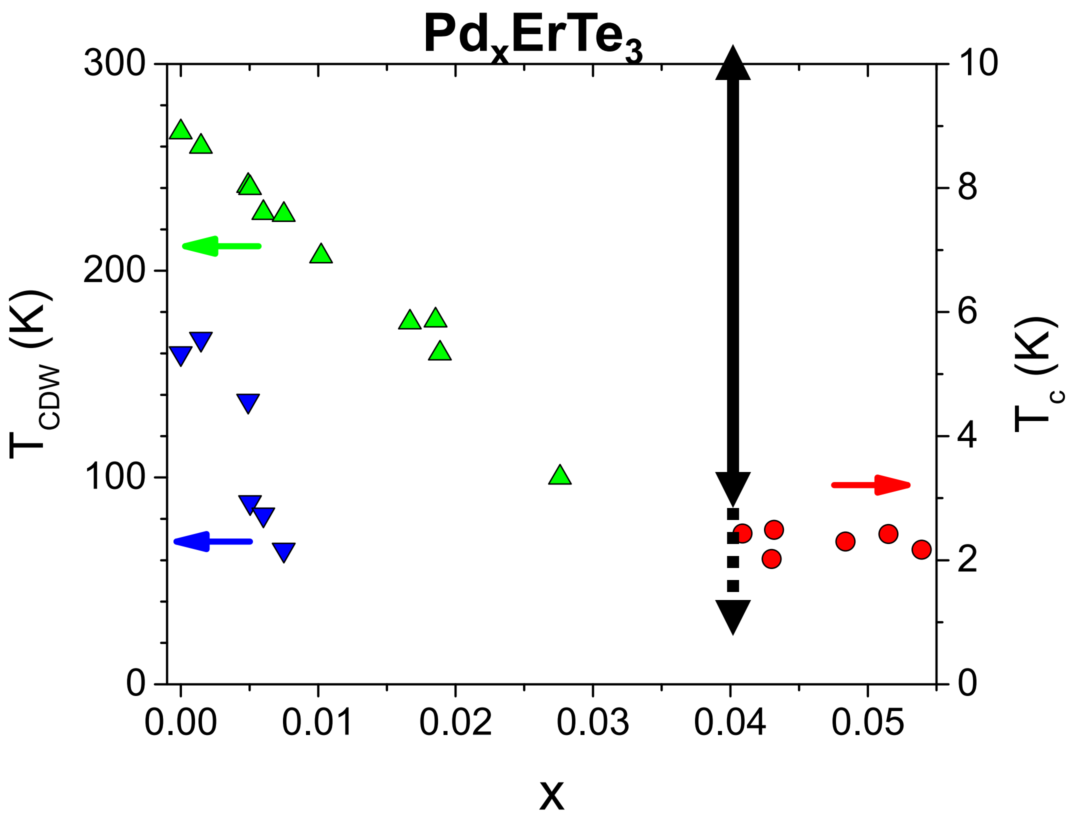
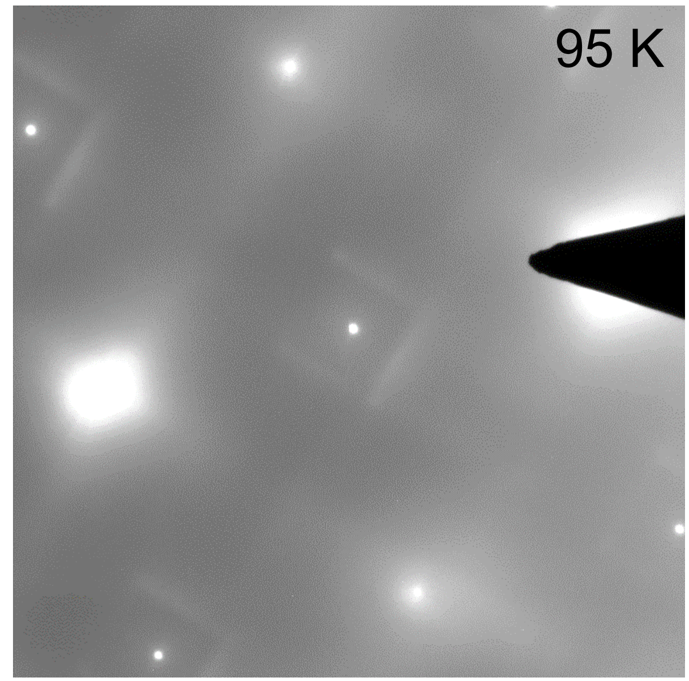


- ***Both*** CDWs suppressed by Pd (even though these are competing phases)
- Consistent with a disorder-driven effect
- Superconducts when CDW suppressed
- This might just be another example of competing phases…
  … but it is also possible that vestigial (nematic) order plays a role…

A possible model system: Pd-intercalated RTe_3

J. Straquadine

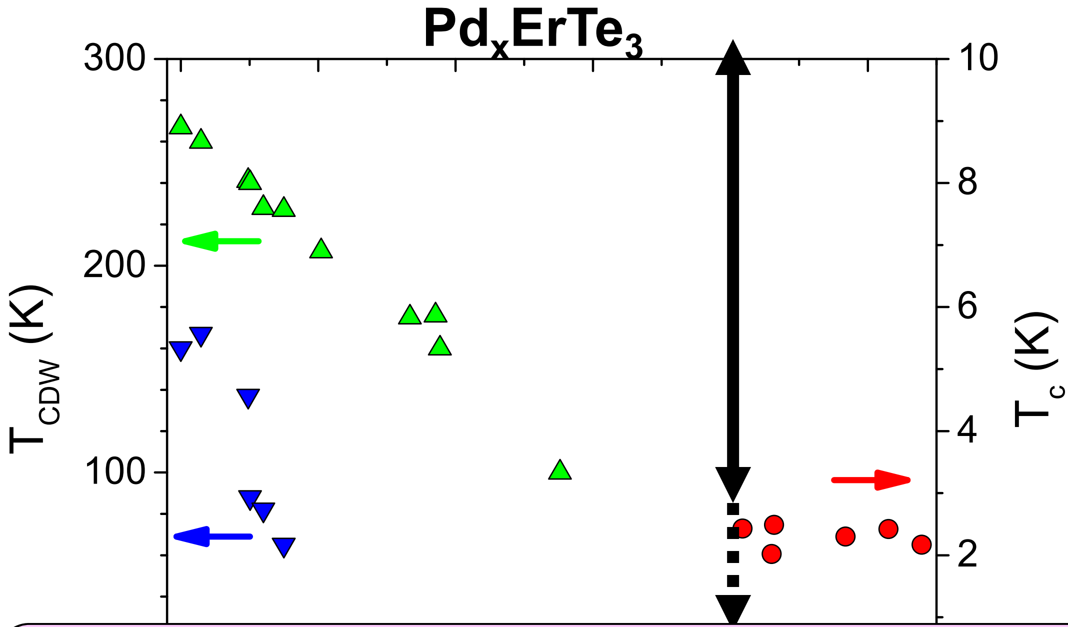


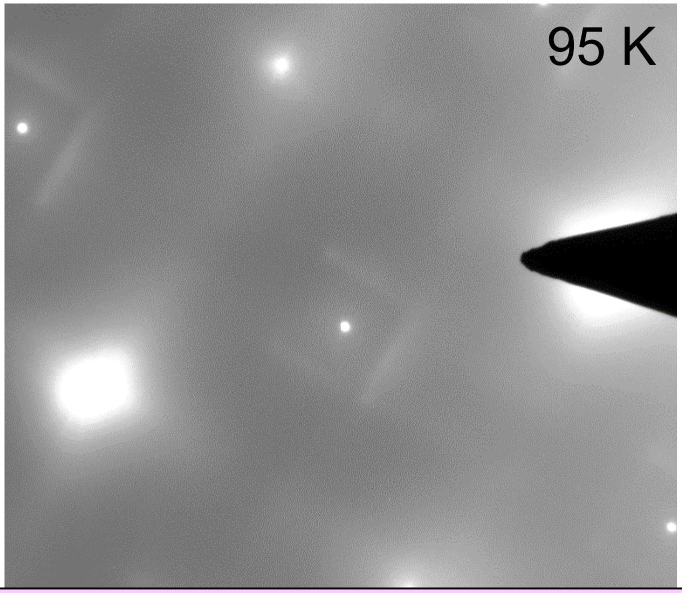


- Superconducting compositions exhibit short range CDW correlations over an enormous temperature range (to higher T even than parent $ErTe_3$)
- Disorder induces local CDW correlations, **but in *both* directions!**
- This is an anticipated result for nematic order in a ***tetragonal*** material
- Appears disorder has caused material to overcome weak orthorhombicity
- i.e. Pd_xRTe_3 ***might*** provide an approximate realization of Kivelson's model…

A possible model system: Pd-intercalated RTe_3

J. Straquadine



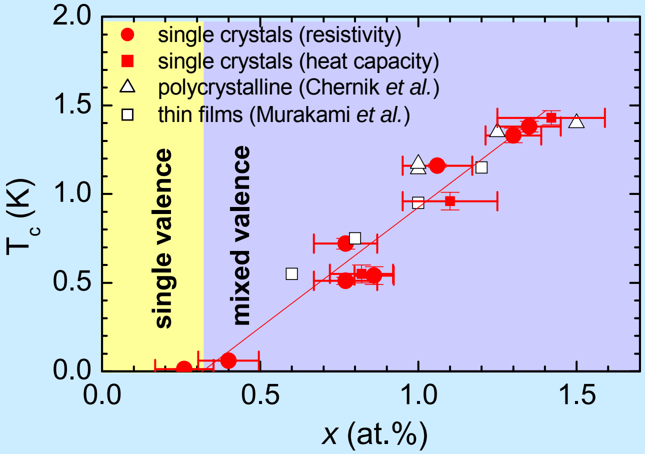


Ongoing & future experiments:

- Establish details of phase diagram & nature of short range correlations (diffraction & STM; note possible correspondence to cuprates)
- ***If*** these correspond to local puddles of nematic order, can we infer an equilibrium nematic critical temperature for a putative tetragonal analog?
- Can we make the material "even less orthorhombic" so it more closely corresponds to theoretical models? (e.g. induce anisotropic strain)
- Is there evidence for stronger nematic fluctuations for superconducting compositions? (i.e. measure nematic susceptibility)

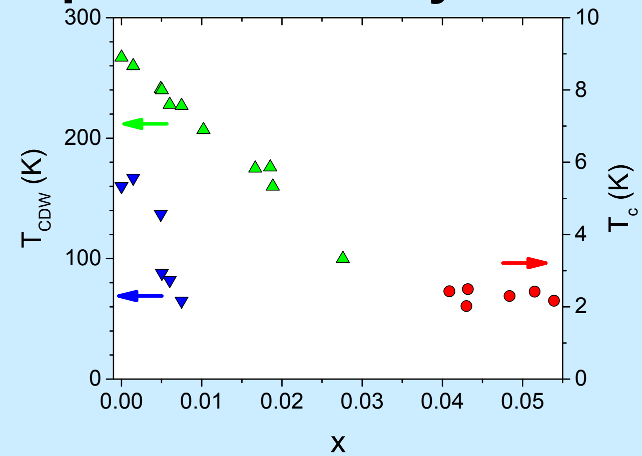
Summary

Role of valence skipping elements



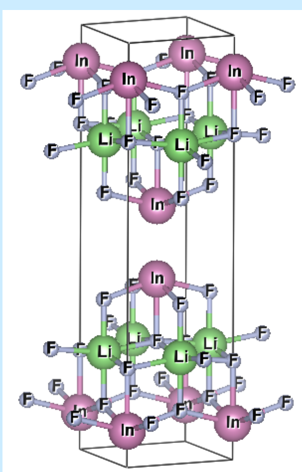
$Pb_{1-x}Tl_xTe$

Disorder & interplay of CDW & superconductivity



Pd_xRTe_3

New materials guided by theory



$LiInF_3$

New experiments on old friends

LSCO

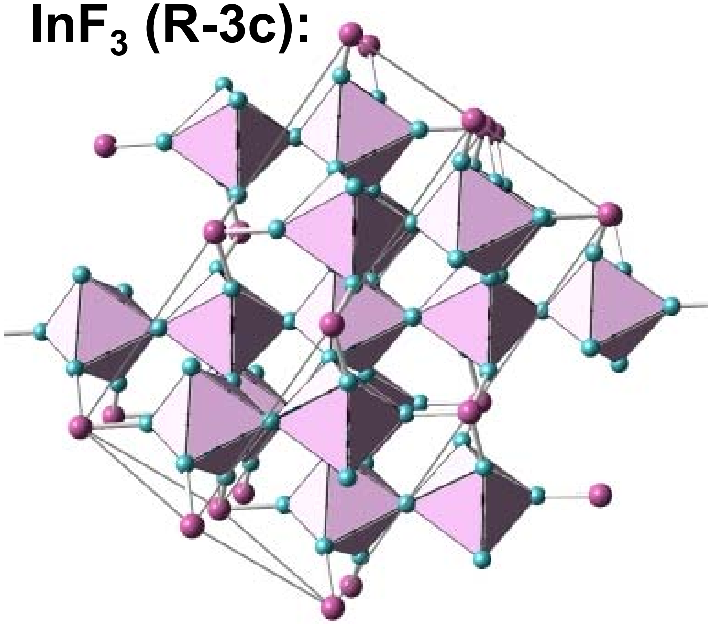
Additional slides

(3) New materials: exploratory synthesis guided by theory

Harlyn Silverstein
Chang-Jong Kang

- Can we find an indium analog of $BaBiO_3$ and $CsTlF_3$? (i.e. charge disproportionated CDW)
- One promising candidate, inspired by chemical intuition and guided by theory (*Kotliar*) is Li-intercalated InF_3…

InF_3 (R-3c):



Intercalate Li →

?

(3) New materials: exploratory synthesis guided by theory

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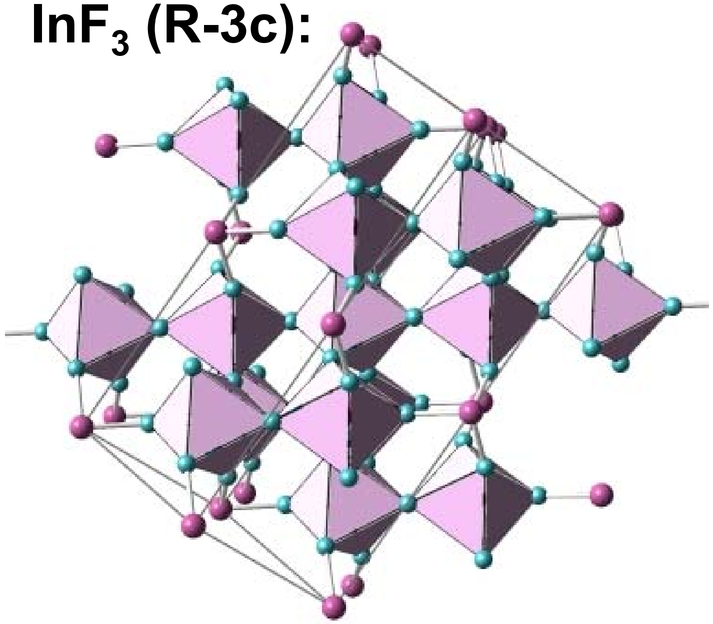
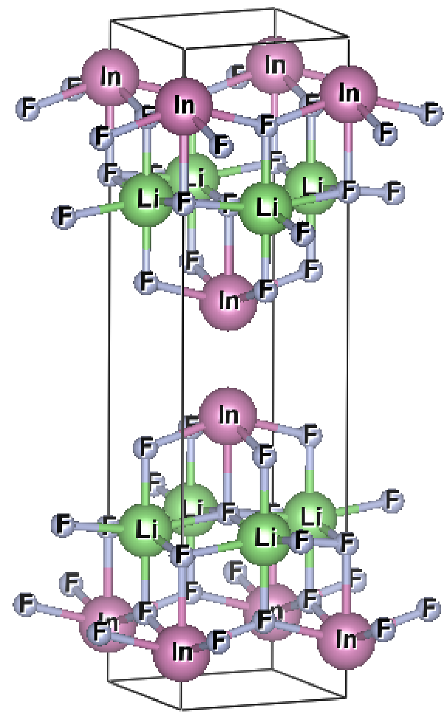


Intercalate Li →



$LiInF_3$:
Lowest energy candidate structure is tetragonal (I4/mmm)
$a = b = 4.23$ Å
$c = 15.619$ Å
With a unique indium site!

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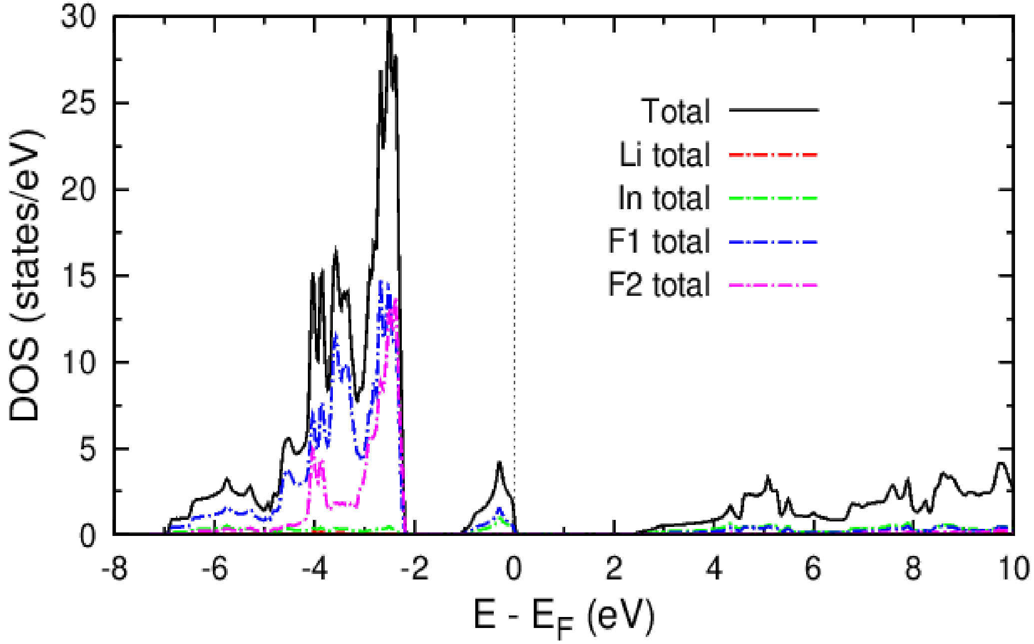

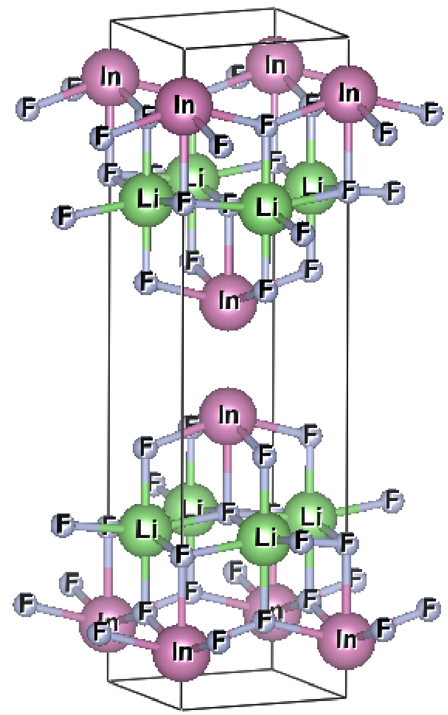

$LiInF_3$:
Lowest energy candidate structure is tetragonal (I4/mmm)
a = *b* = 4.23 Å
c = 15.619 Å
With a unique indium site!

- LDA is very promising: In states form a simple band near the Fermi energy

(3) New materials: exploratory synthesis guided by theory

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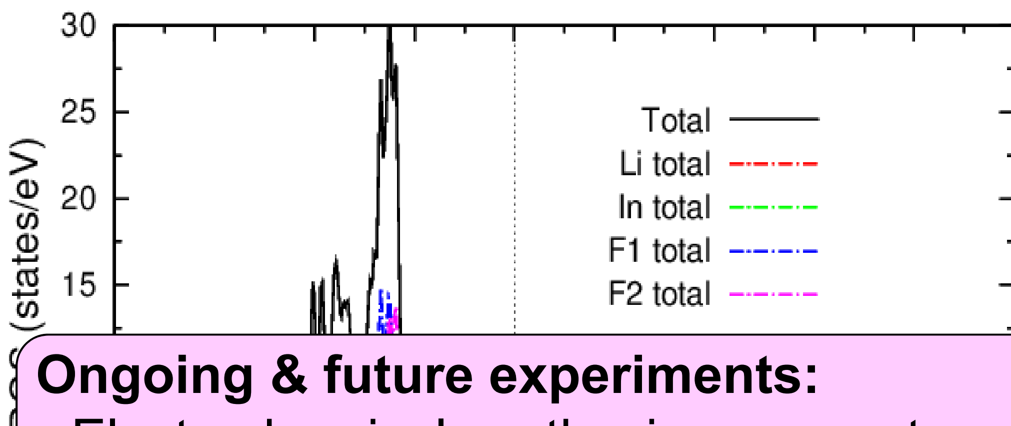
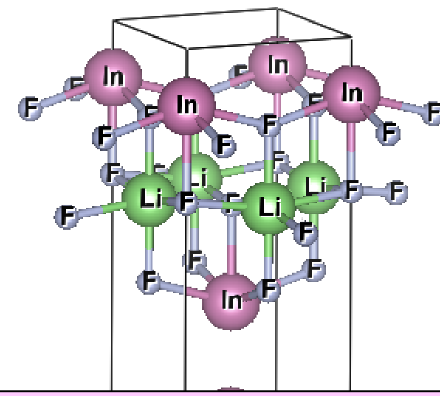




$LiInF_3$: Lowest energy candidate structure is tetragonal

Ongoing & future experiments:
- Electrochemical synthesis appears to work (with Zhiyi Lu & Yi Cui, Stanford); other avenues might also be possible
- Currently collecting high resolution data for a full structural refinement…
- Can this be doped to metallicity? (some obvious avenues to pursue…)

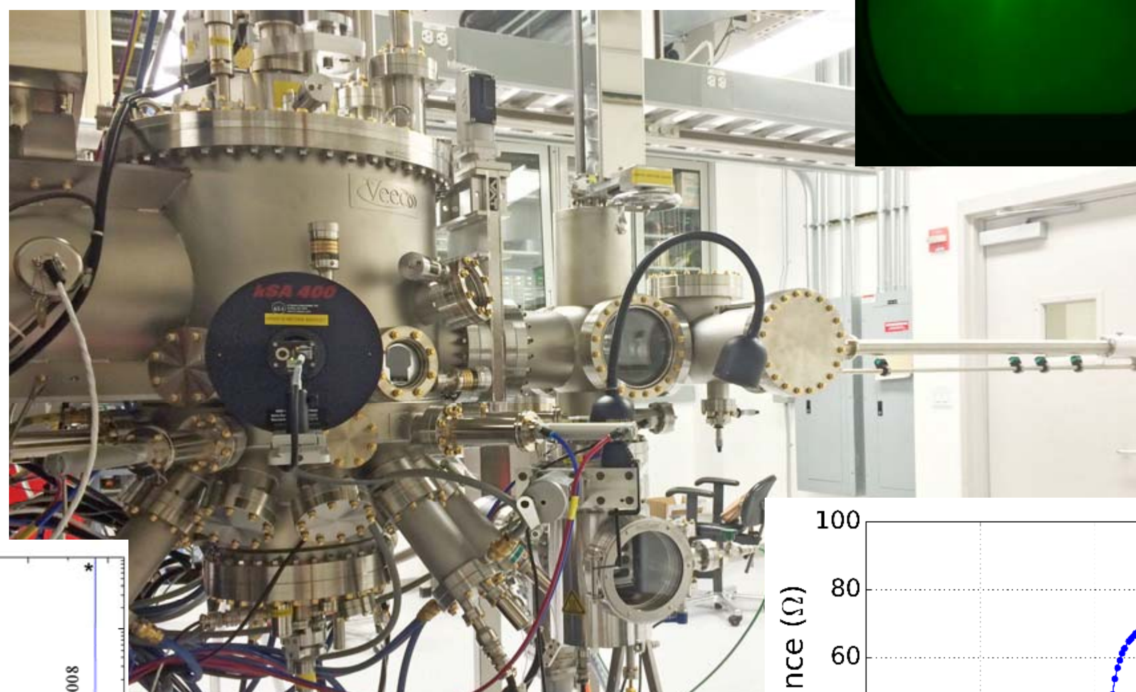
Theory:
- Determine e-ph coupling (for this and other nearby-in-energy candidates)
- Explore instabilities: CD-CDW and superconductivity
- Related materials? (continue theme of theory-inspired materials discovery…)

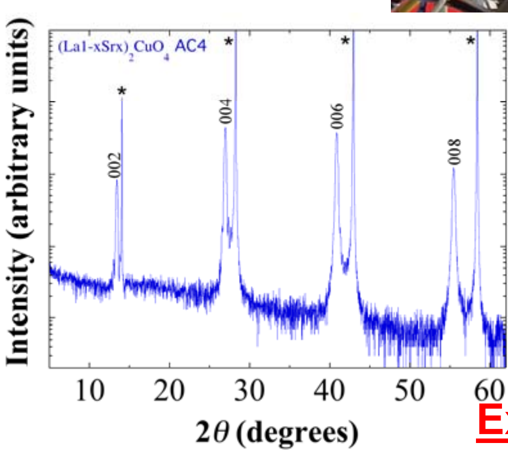
Final note: we have commissioned the new oxide MBE system…

C. Adamo
& J. Straquadine

Example: growth of $La_{1.83}Sr_{0.17}CuO_4$ by MBE:
(motivation: new classes of experiments probing nematic fluctuations in HTSC cuprates)

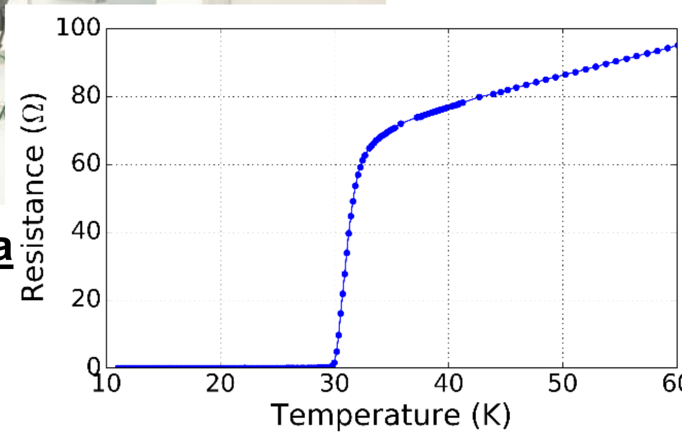
In-situ: Reflection high-energy electron diffraction (RHEED)





Ex-situ: X-ray diffraction

Ex-situ: Transport data

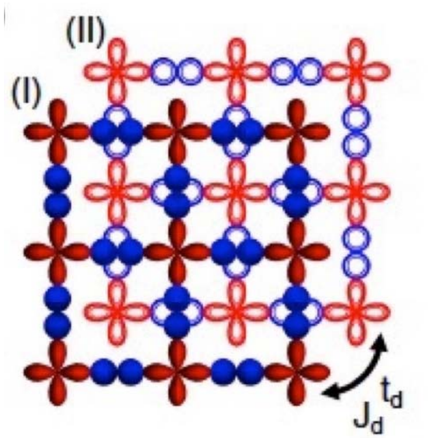


Final note: we have commissioned the new oxide MBE system…

C. Adamo

In addition to the main thrust of our program, we also make use of the new MBE to explore other related new materials and interfaces…

PRL **113**, 187001 (2014)

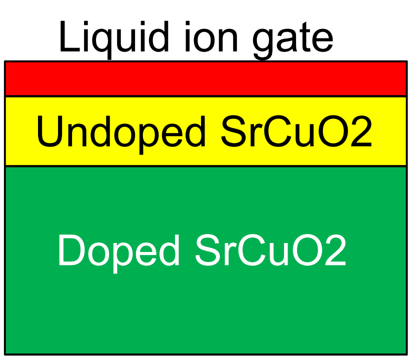


Single CuO layer

MBE of Quasi-2D Tetragonal CuO[1] (c/a>1):

- Study the AFI/N proximity effect[2] on tetragonal CuO and other transition metal monoxides (possible avenue to superconductivity)
- Synthesize the sister structure (c/a<1) that was recently predicted (tune effective dimensionality and T_N)

[1] PRB **79**, 195122 (2008)
[2] PRB **84**, 161405 (2011)



p/n heterostructure

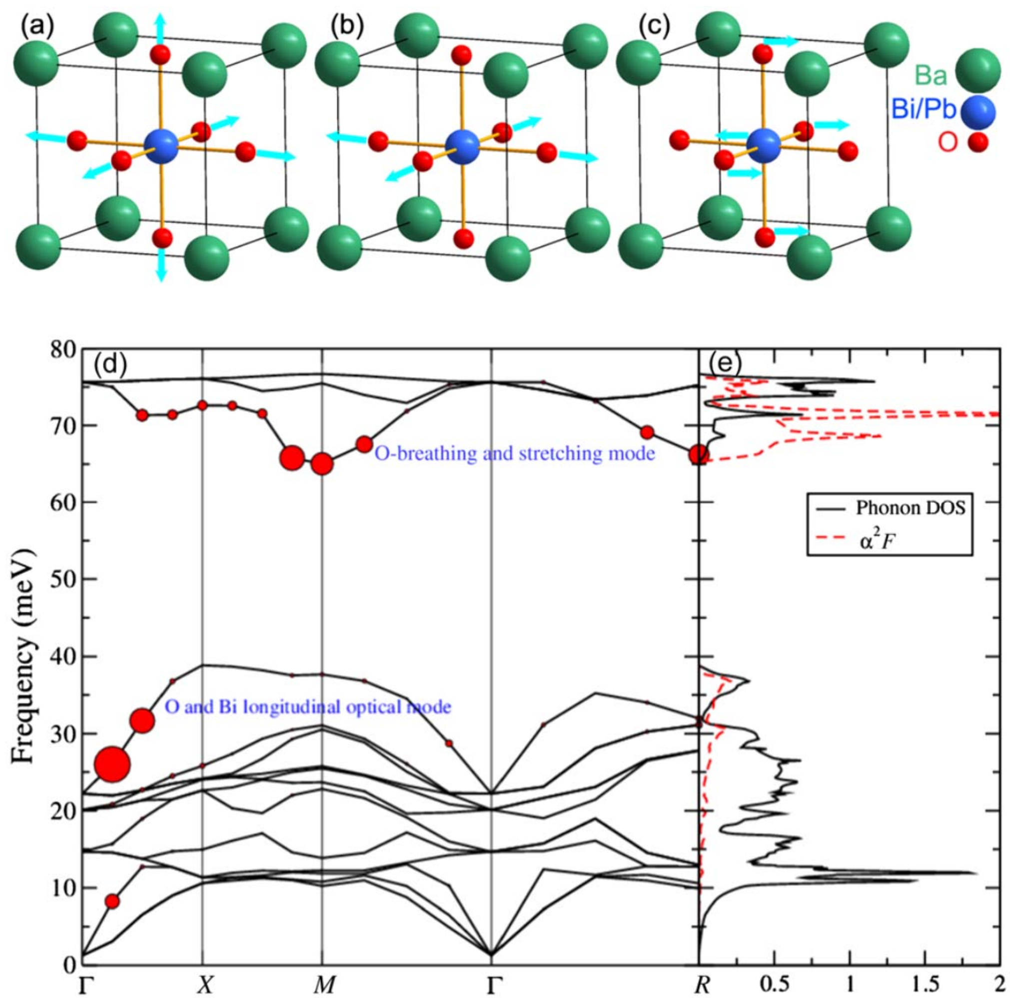
MBE of infinite layer material $SrCuO_2$:

- Synthesize novel hetero-structures
- Use liquid ion gate doping to create p/n junctions* (possible avenue to realise exciton BEC in a strongly correlated system)

** In collaboration with Harold Hwang (Stanford)*

Correlation-enhanced e-ph coupling in BKBO & BPBO

Nourafkan, Marsiglio & Kotliar, Phys. Rev. Lett. **109**, 017001 (2012);
Yin, Kutepov, and Kotliar, PRX **3**, 021011 (2013).

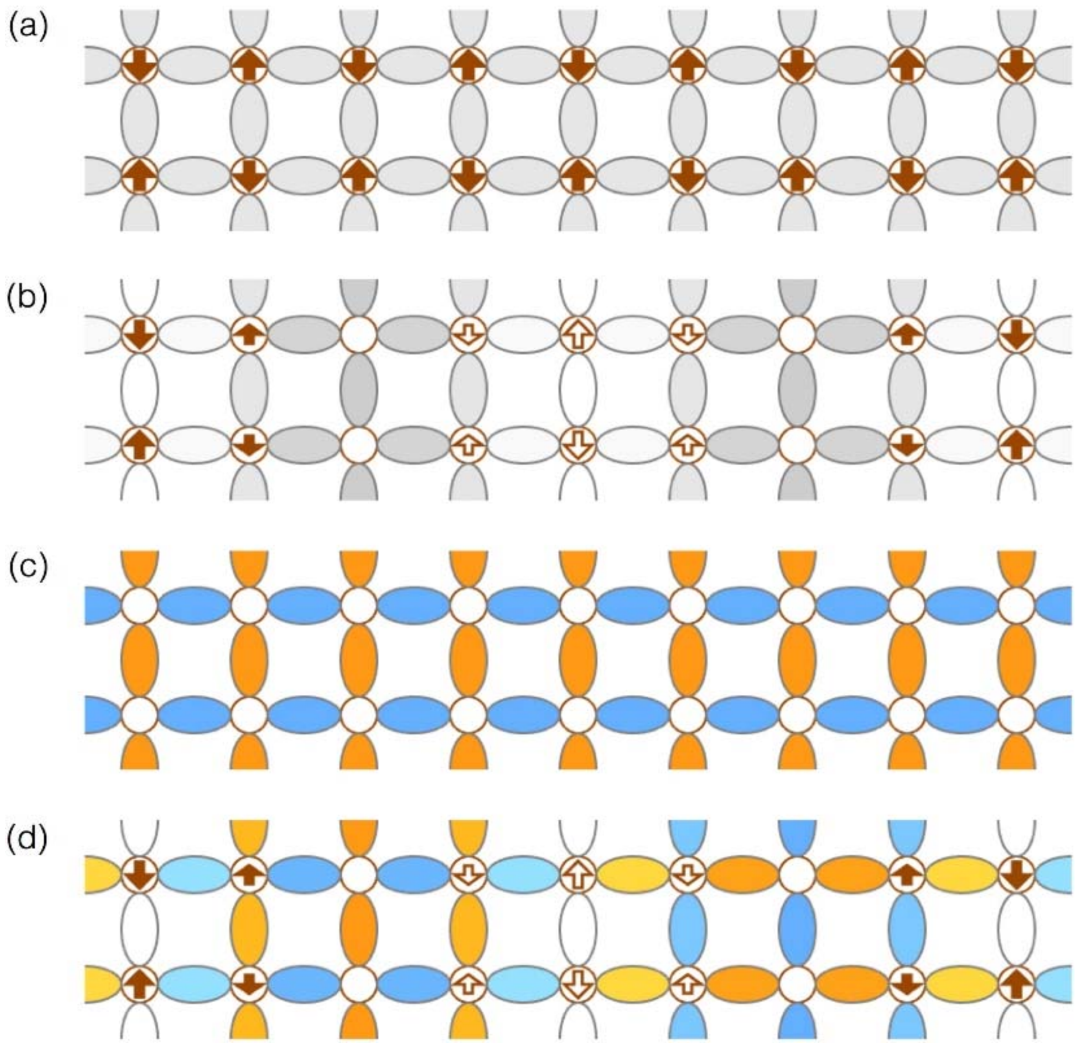


0.4 hole-doped cubic $BaBiO_3$

New understanding:

- Improved functional includes non-local ***dynamic correlation effects***, and yields:
  (a) correct CDW gap for $BaBiO_3$
  (b) strong-coupled T_C ~ 30K for doped system
- Nature of crucial correlations intimately connected to proximity to CDW state, affecting the Bi 6s orbital

Pair Density Wave as an example of intertwined order



AF Mott insulator

Doped Mott insulator
→ charge and spin stripes

D-wave superconductor

Pair density wave

J. Tranquada (BRN doc)