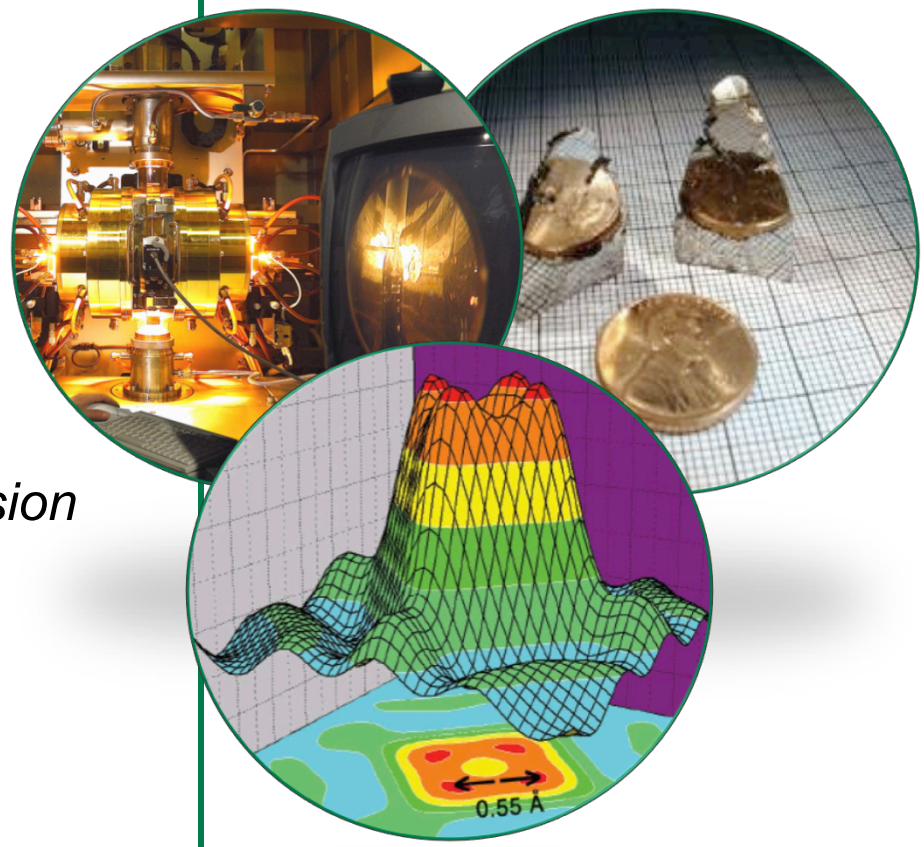
An Experimentalist's View of the Role of Theory in Moving Up the Materials Pyramid

Digital Design of Materials Workshop
Boston University
September 27-29

B. C. Sales
Correlated Electron Materials Group
Materials Science and Technology Division
Oak Ridge National Laboratory



U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Outline of Presentation

• Overview of Correlated Electron Materials Group- Who we are and what we do. (Where I am coming from)

• New Materials and The Materials Pyramid

•An experimentalist's perspective of the role of theoretical approaches in the discovery of new materials

• Issues with Digital Design of Materials

•Theoretical successes

• Examples of the importance of an accurate crystal structure and/or composition –Fe based superconductors

• Historical Example: A "new" Permanent Magnet $Nd_2Fe_{14}B$

• Importance of "Mesoscale" (metallurgy, microstructure, defects) in magnetic performance of $Nd_2Fe_{14}B$

• Screening guide for identifying superconductors with an unusual pairing mechanism

Our research

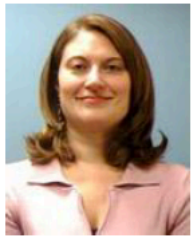
Correlated Electron Materials Group

Materials Science and Technology Division

Oak Ridge National Laboratory

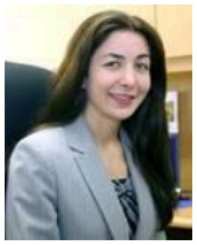
Brian Sales
Group Leader

David Mandrus

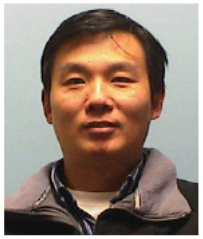


Claudia Cantoni

Michael McGuire



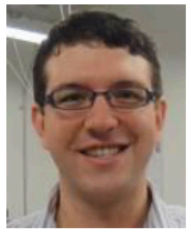
Athena Sefat



Jiaqiang Yan

Andrew May

Bayram Saparov



Jonathan Mitchell

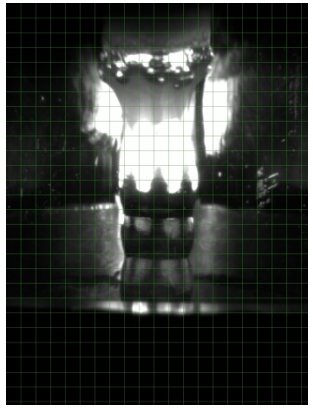
Complex electronic and magnetic materials relevant to energy technology:

- **thermoelectrics** (transition metal compounds, heat transport, phonons)
- **superconductors** (iron pnictides and selenides, cuprates, magnetism)
- **permanent magnets** (non-rare earth alternatives)
- **unusual magnetic ground states** (helimagnets, frustration)

Materials synthesis and single crystal growth; structural, thermal, magnetic, transport properties; chemical manipulation of physical properties; materials and samples relevant for neutron scattering experiments.

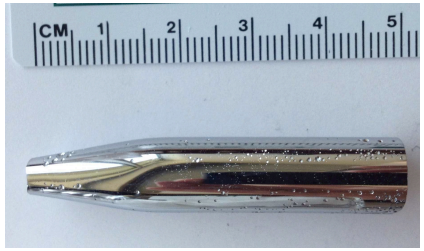
OAK RIDGE

We grow unique crystals:
Science Driven Synthesis



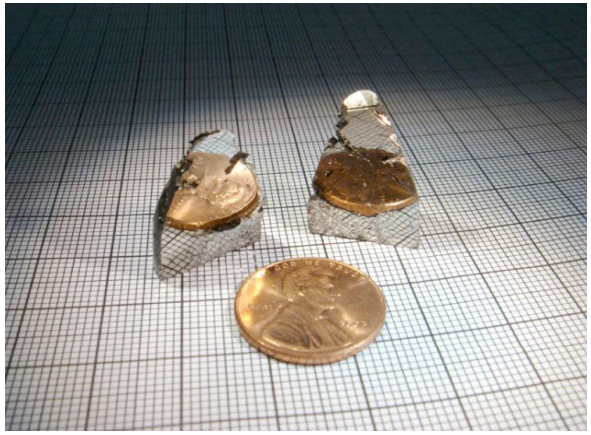
$BaFe_{12}O_{19}$
permanent magnet
room temp multiferroic
grown under 100 bar
oxygen pressure

Relationship between dielectric constant and carrier mobility?
Magnetic fluctuations and superconductivity?
Magnetic fluctuations and thermal conductivity?
Microscopic origin of low thermal conductivity in (Ag,Sb) Te crystals?
Why does $SrTcO_3$ magnetically order at such a high temperature? (T_N= 1000 K)

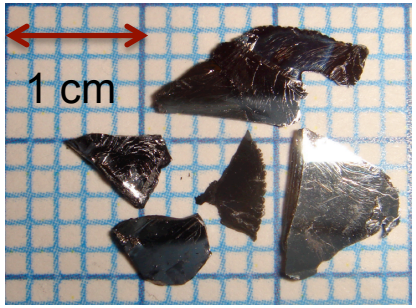


$AgSbTe_2$

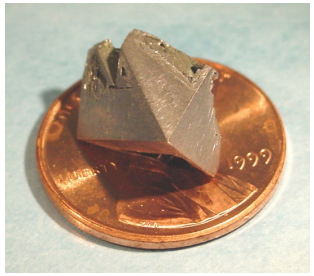
Mo_3Sb_7



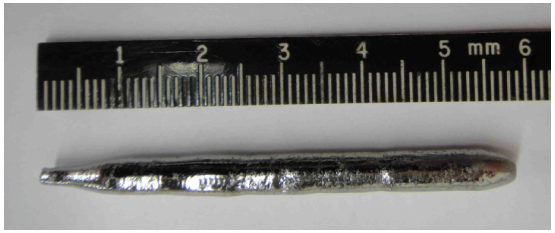
$FeTe_{0.75}Se_{0.25}$



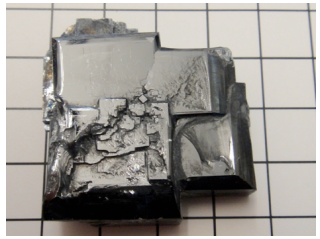
$TlFe_{1.6}Se_2$



$CrSb_2$



$Fe_{0.96}Ir_{0.04}Si$



$KTa_{1-x}Nb_xO_3$:Ca

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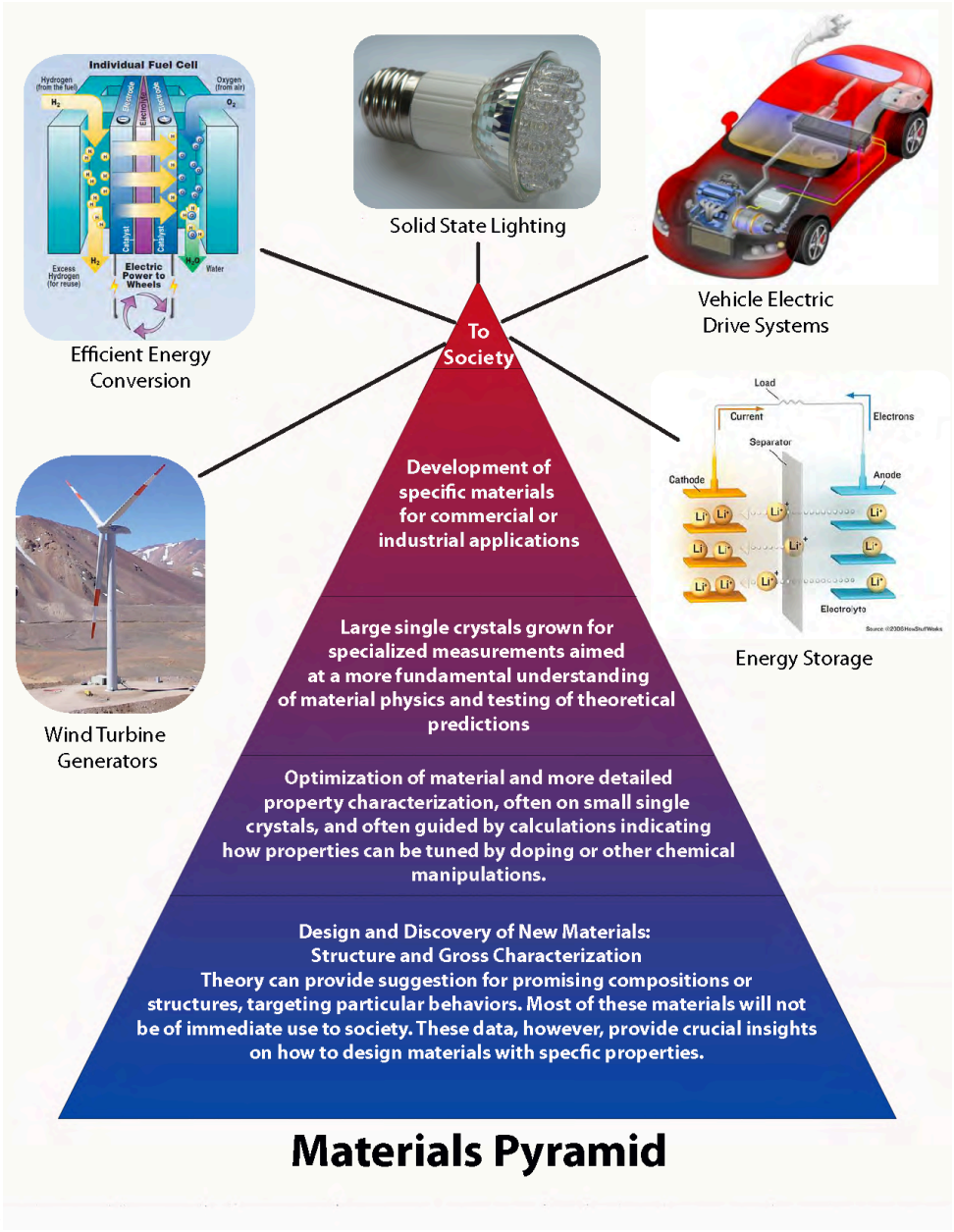
Where do new materials come from?

18 years



Moving up the Materials Pyramid

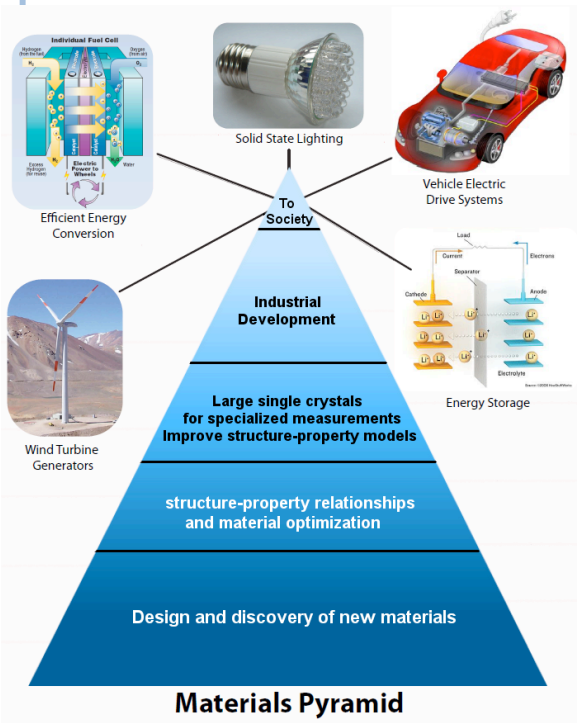
1. Identify a scientific or technological problem that would benefit from a new material

2. Study the literature to learn which materials do the job pretty well. Identify shortcomings and how those shortcomings might be addressed, and identify a candidate in the lower tier of the pyramid that might do it. (Crystal chemistry rules, phenomenological rules)

3. Form a team of researchers whose specialties and interests are complimentary, make the material and test to see if your idea is right. Include theory to help interpret your results.

4. Make the new material in the form needed to determine if the material has any chance of being useful in the device of interest.

5. Transfer new material to industry and eventually to society



Physics Viewpoint:
R. J. Cava
http://link.aps.org/doi/10.1103/Physics.4.7

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An Experimentalist perspective on theory and Materials Discovery

(Inorganic Crystalline Materials)

Different classes of theory and models:

a) **Density Functional Theory**- can sometimes predict properties (before experiments done!)- PbSe, some ferroelectric structures are example. Needs to know accurate positions of atoms and precise stochiometry (accurate crystal structure)

b) **LDA +U** - sometimes gives interesting results that helps interpret known experimental data. Results sometime suggest new experiments.

c) **Dynamical Mean Field Theory**- a serious attempt to develop techniques to treat strong correlations. Seems to stress correlations even when experimental data suggests otherwise. Helpful at understanding but not useful for finding new materials.

d) **Model Hamiltonians**- useful for providing insight into general behavior of complex correlated materials- not particularly useful at finding new materials

e) In general, theory not good at predicting new crystal structures- except perhaps in very simple cases- elements or simple cubic compounds. Some interesting results in literature- Zunger correctly accounted for 95% of structures of 565 binary AB compounds using pseudopotential radii [PRB **22** (1980) 5839] -crystal structure energy scale 10^{-3}-10^{-4} of cohesive energy

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Serious Real-World Issues With Computational Design of Materials

1. Defects (vacancies, twins, chemical inhomogeneities) often dominate many material properties- even more so for correlated materials

2. Many very useful, and not so exotic materials are not equilibrium phases and are metastable (phases will be missed in theoretical phase diagrams):

    - Steel
    - PZT (piezeoelectric)
    - Glass
    - Plastics
    - Most composites
    - Diamond
    - Highly doped Silicon
    - etc

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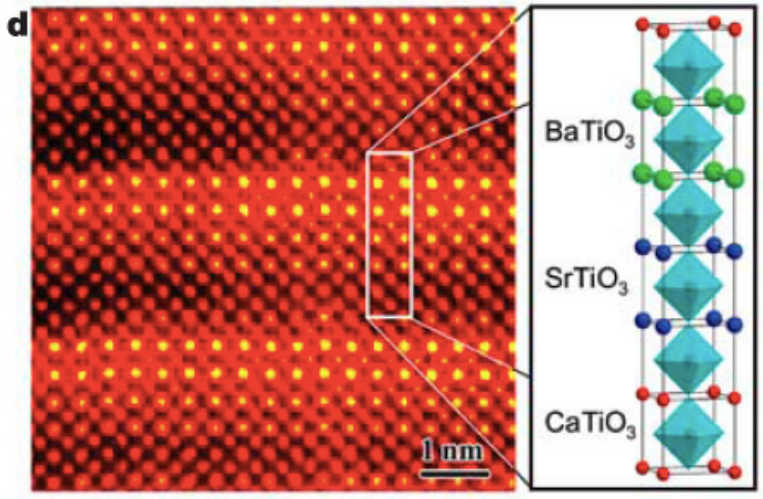
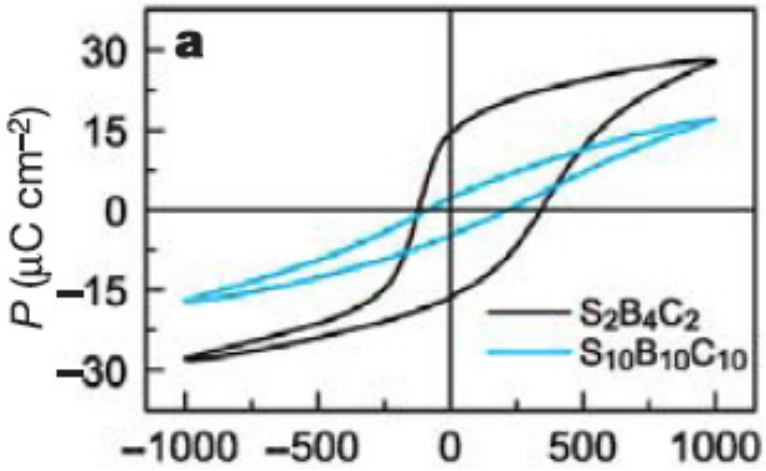
Some theoretical successes at predicting materials properties

1. PbSe is a good thermoelectric material at high temperatures (Singh)

2. Ferroelectric superlattices (Rabe, Vanderbilt, Spaldin)- polarization enhancement in asymmetric superlattices

3. Topological insulators, $Bi_{1-x}Sb_x$, Bi_2Se_3, etc.





HN Lee et al Nature **433** (2005) 395

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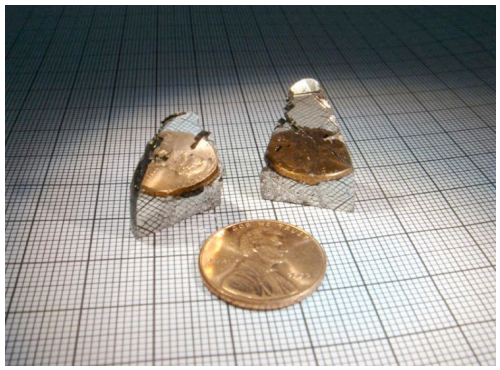
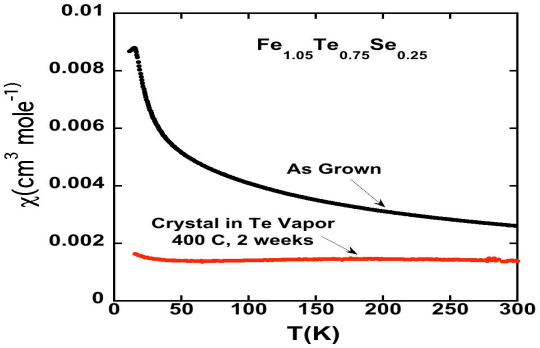
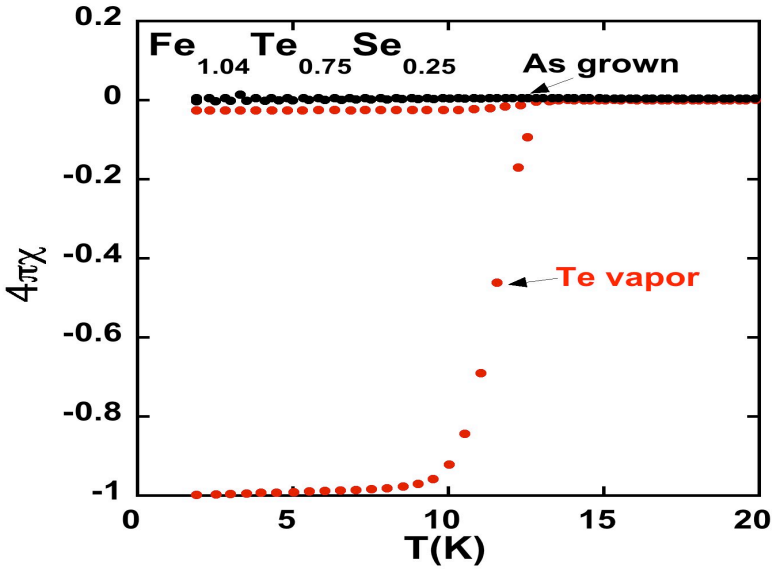
Importance of Correct Composition

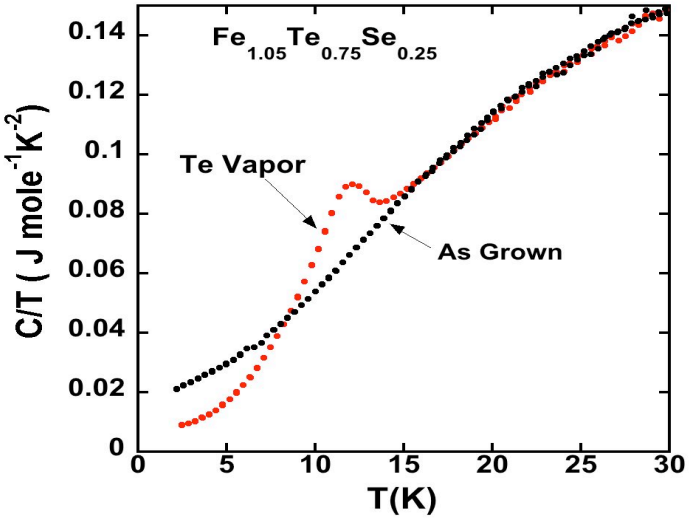
1. FeSe is a 7 K superconductor, initial electronic structure calculations suggested that FeTe should be a better superconductor- however FeTe doesn't exist- what forms is $Fe_{1.07}Te$

2. Can illustrate significance of excess Fe in $Fe_{1+x}Te_{0.75}Se_{0.25}$ exposing crystals to Te vapor at low temperatures.





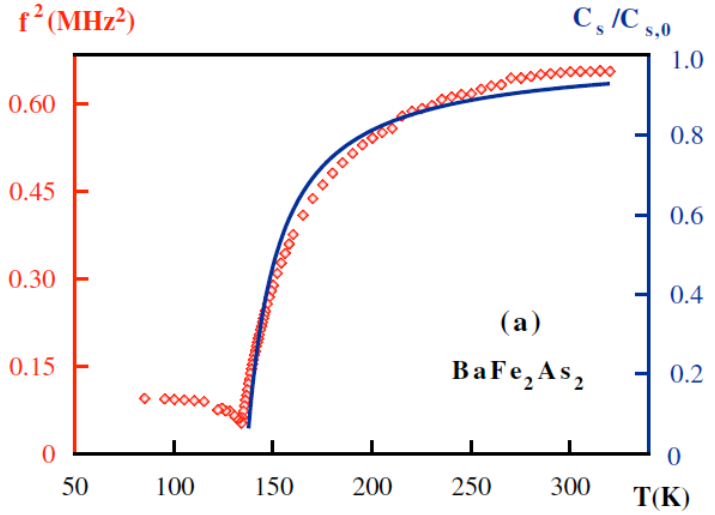




Importance of Correct Crystal Structure in Understanding/Predicting Properties

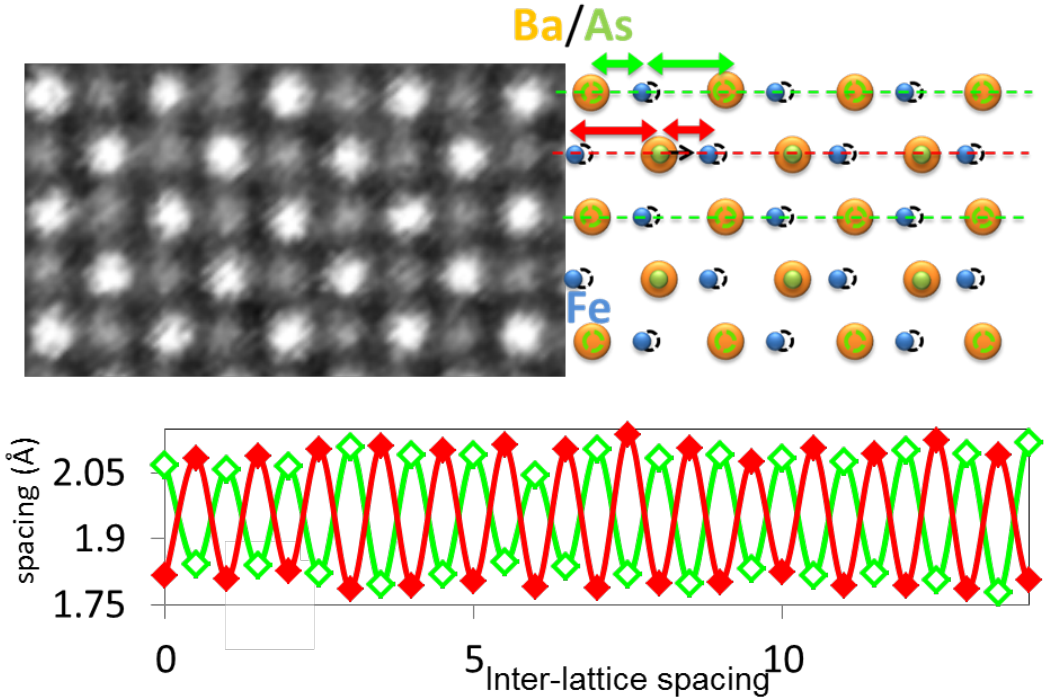
1. $BaFe_2As_2$ is the parent phase of several electron and hole doped Fe based superconductors ($BaFe_{2-x}Co_xAs_2$ or $Ba_{1-x}K_xFe_2As_2$)

2. Single crystal and powder structural data are consistent with $BaFe_2As_2$ having the tetragonal $ThCr_2Si_2$ structure- but this material has very strong magneto-elastic coupling a striking elastic properties- even at room temperature. What is the local structure of $BaFe_2As_2$ at room temperature.



Fernandes et al. PRL **105** (2010) 157003

Evidence that $BaFe_2As_2$ is not perfectly tetragonal at room temperature



Claudia Cantoni

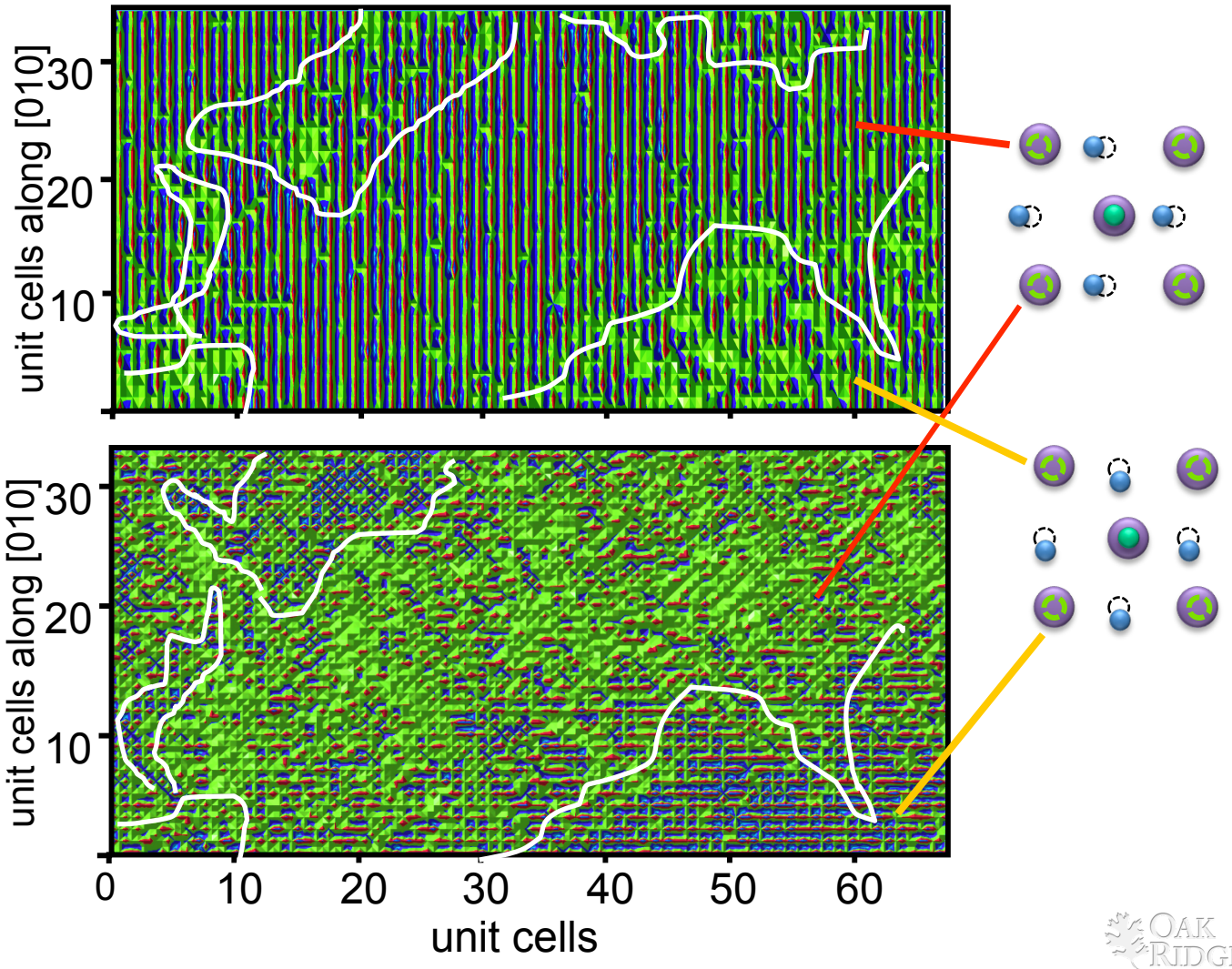
Careful Analysis of Images indicate Fe layer shifted about 0.1 Å along Either [100] or [010] directions- Domains ≈ 12 nm in size

Domains are ~ 10-20 nm in size!

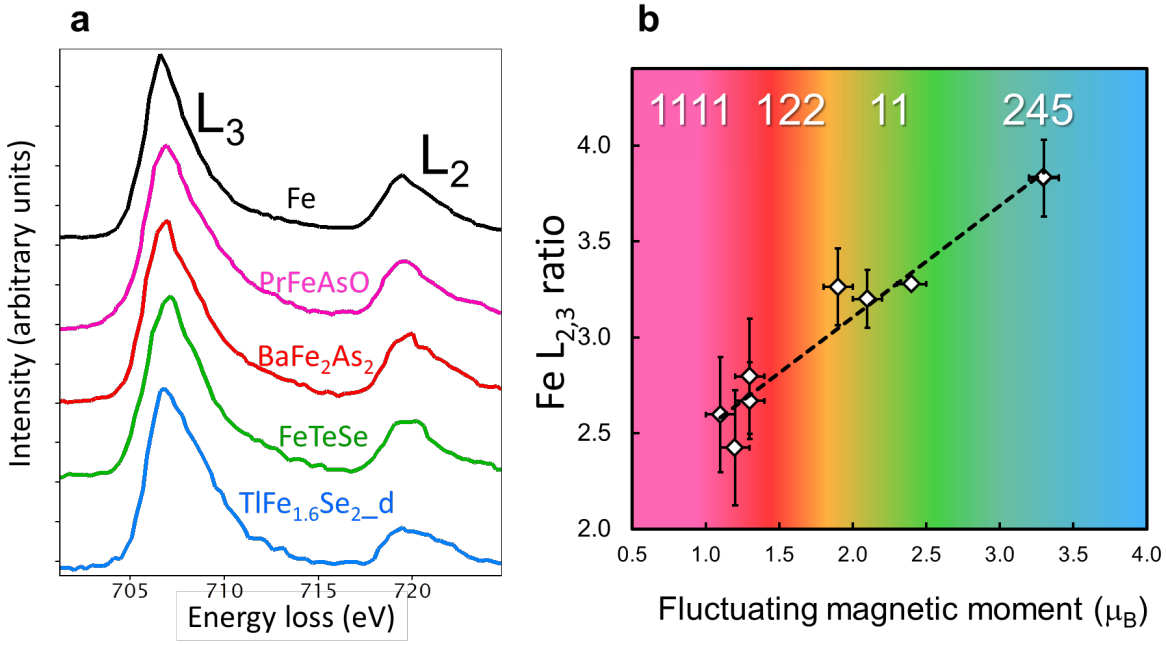
blue ordered regions: modulated interlattice spacing along the probed direction
green, disordered regions: non-modulated interlattice spacing along the probed direction

Map of distortions along [100] →

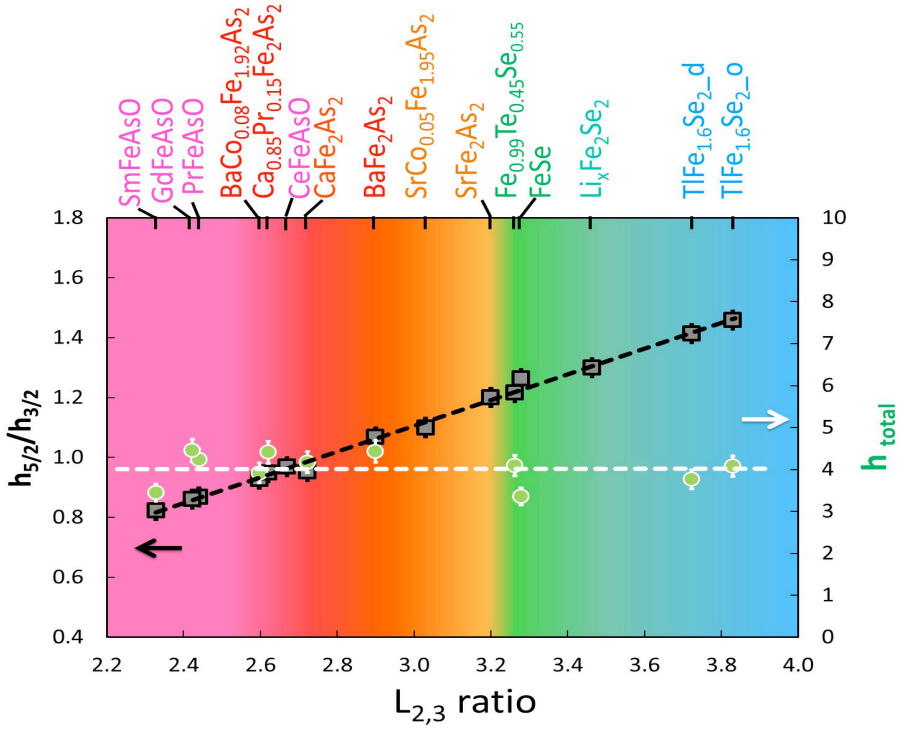
Map of distortions along [010] ↓



Empirical Correlation between L_3/L_2 Ratio, as measured with EELS and Fe Magnetic Moment -useful for family of similar Fe compounds with same formal oxidation state and local environment

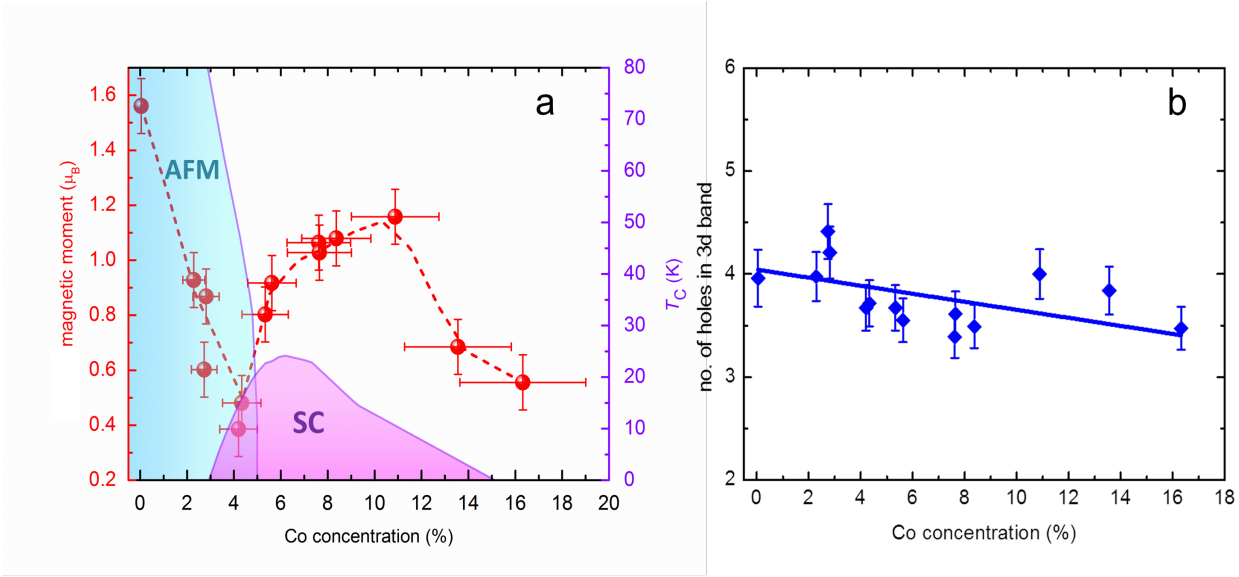


Better theoretical justification for using L_{23} Edge Spectra to obtain (1) Total number of holes in d band and (2) changes in distribution of same number of electrons within 3d orbitals



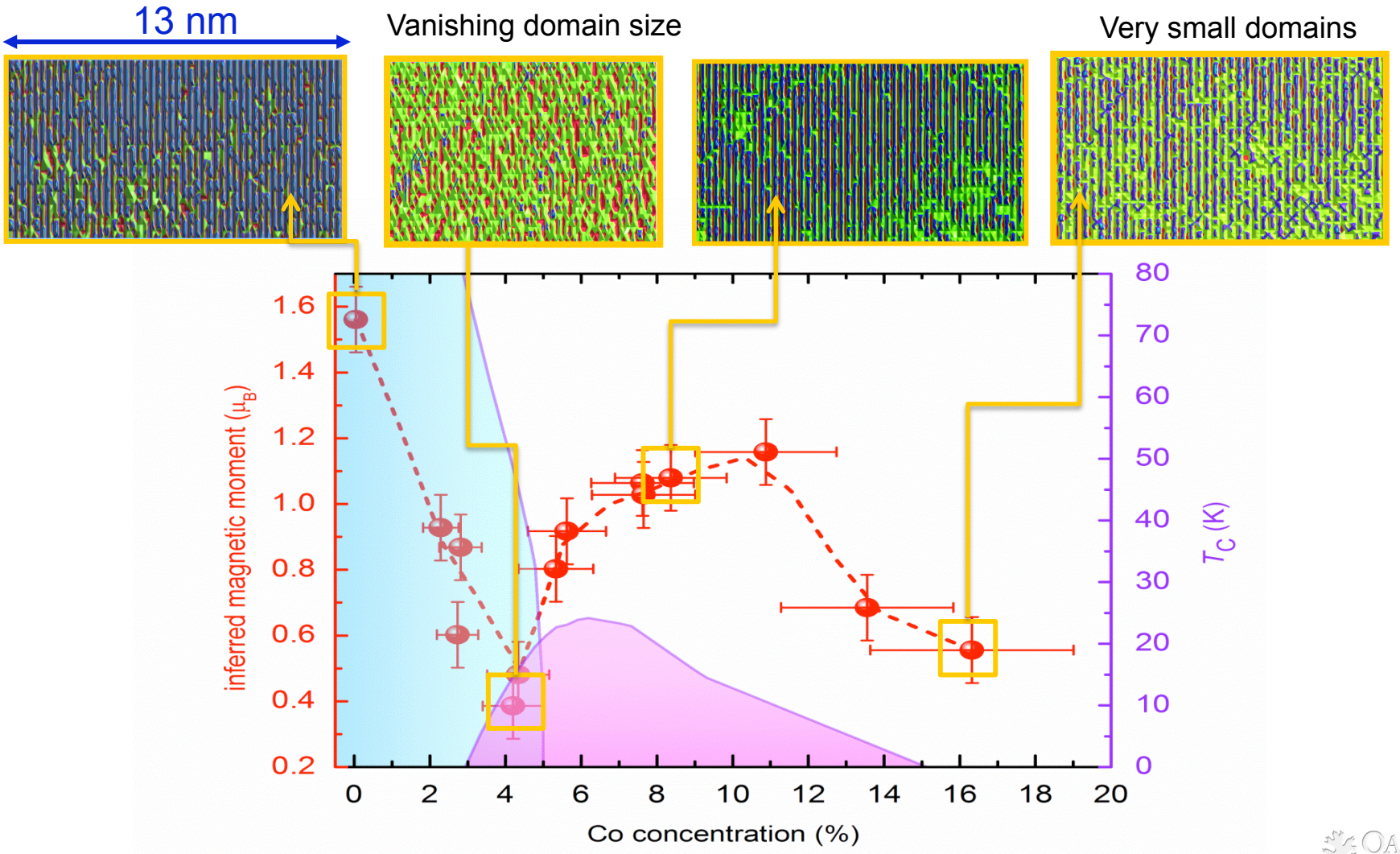
$$\frac{h_{5/2}}{h_{3/2}} = \frac{1}{6}\left[\frac{5I_{L_3}\omega_{L_2}}{2I_{L_2}\omega_{L_3}} - 1\right]$$

Careful Examination of EELS data from Series of $Ba(Fe_{1-x}Co_x)_2As_2$ Crystals



Minimum in variation of Fe moment with Co doping
minimum value near “Lifshitz concentration”

Distorted domains correlate with Fe local magnetic moment



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Case Study (circa 1980): New Permanent Magnet to Replace $SmCo_5$

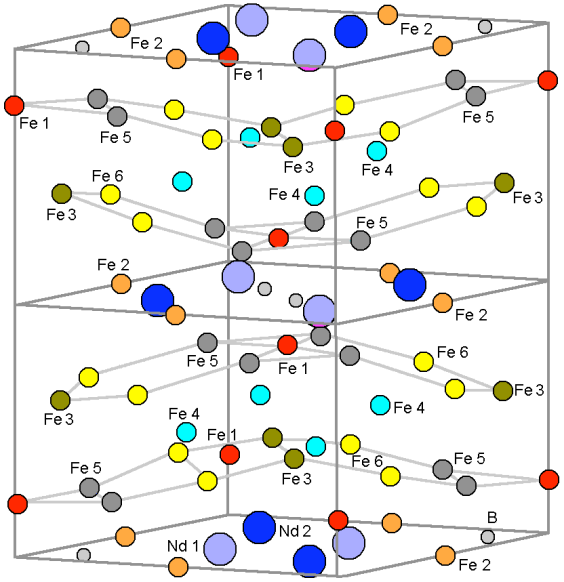
1. Sm and Co too expensive, supply of Co uncertain due to political instability in Zaire.

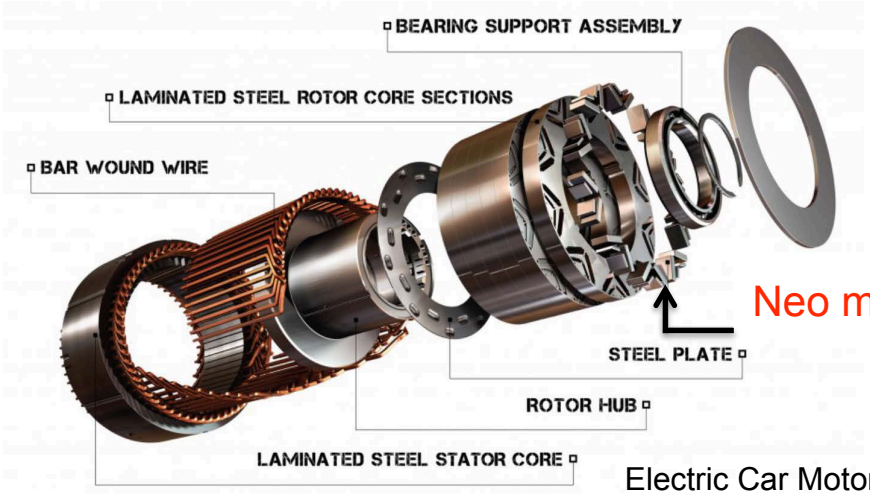
2. Compounds with same structure as $SmCo_5$ don't form with Fe (which is much cheaper). In analogy with $SmCo_5$ want uniaxial compound with large amount of Fe and a more abundant light rare earth.

3. In rare earth compounds with iron, spin of iron couples antiferromatically with spin on rare earth ion. For rare earths orbital moment is often much larger (than spin part) and for lighter rare earths is in direction opposite to spin moment. For light rare earths the net magnetic moment is in the same direction as the transition metal.

4. Based on these considerations one should look for a Nd-Fe magnet- but no suitable binary compounds. Thus want small amount of third element to stabilize new crystal structure. Boron works well- $Nd_2Fe_{14}B$ discovered 1984 – 68 atoms in conventional tetragonal unit cell

Current Rare Earth Permanent Magnets based on $Nd_2Fe_{14}B$

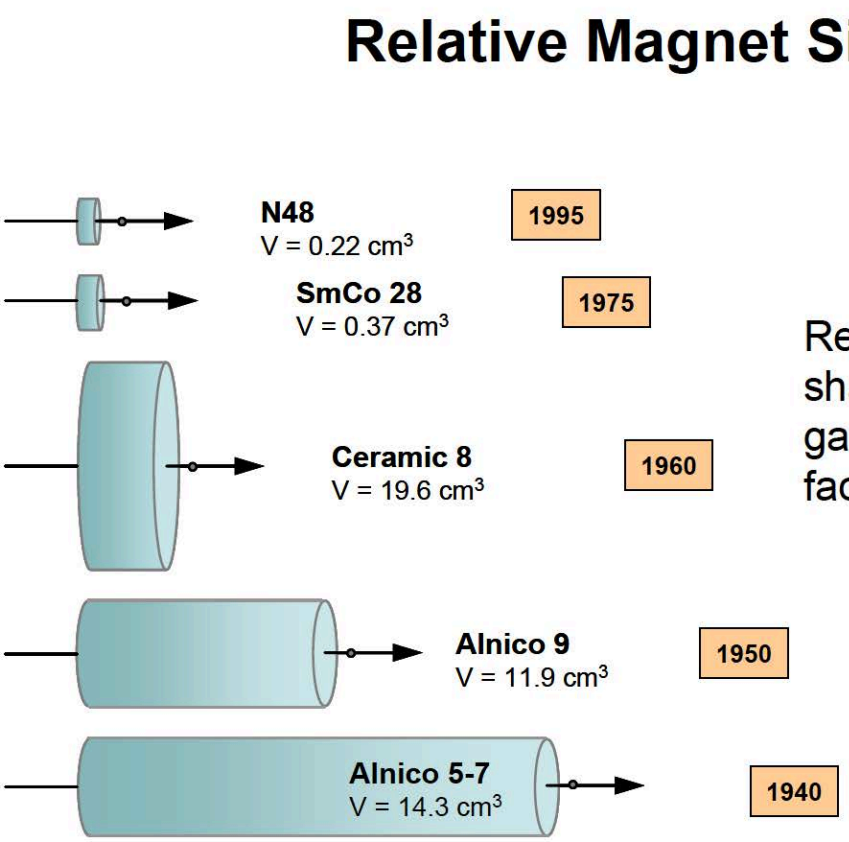




Electric Car Motor (GM)

- $Nd_2Fe_{14}B$ discovered/developed in 1984 to replace $SmCo_5$- partially as response to instability of cobalt supply from Zaire
- An expensive heavy rare earth, Dy, is added to improve magnet performance in electric motors and generators
- Both Nd and Dy in short supply

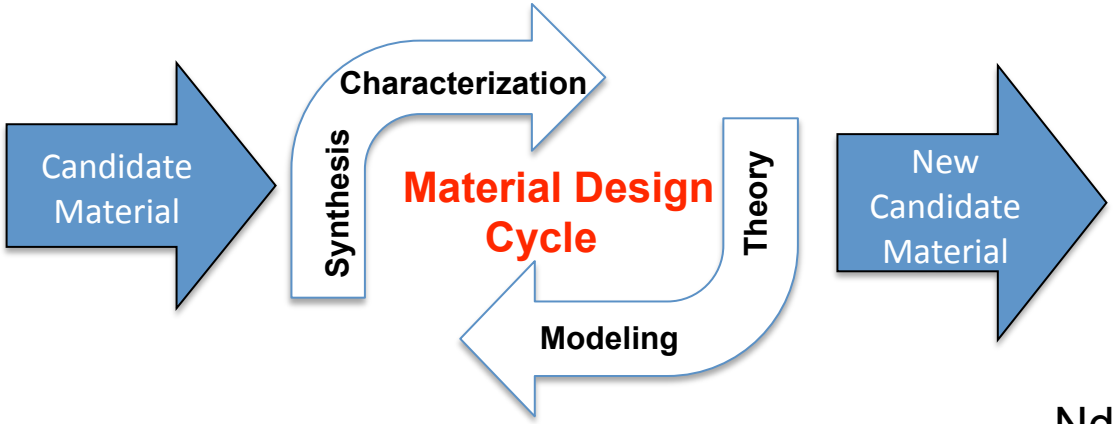
Why is a new stronger permanent magnet such a big deal?

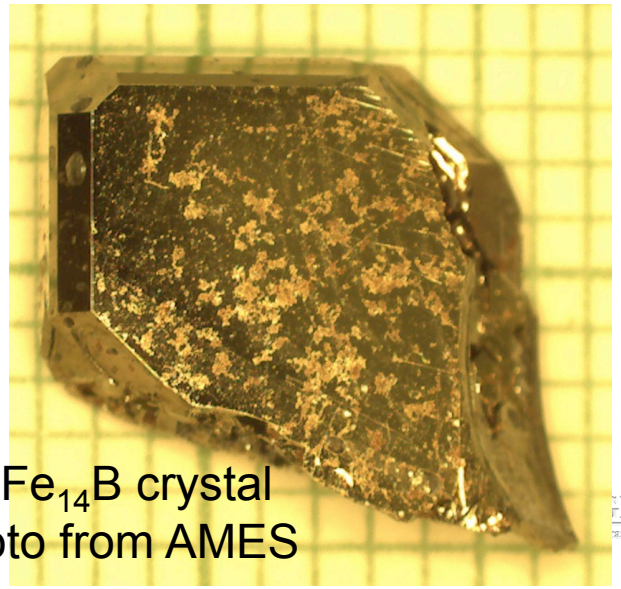


Relative magnet size and shape to generate 1000 gauss at 5 mm from the pole face of the magnet.

Solution: Develop/Discover New Permanent Magnets That Use Less Rare Earths

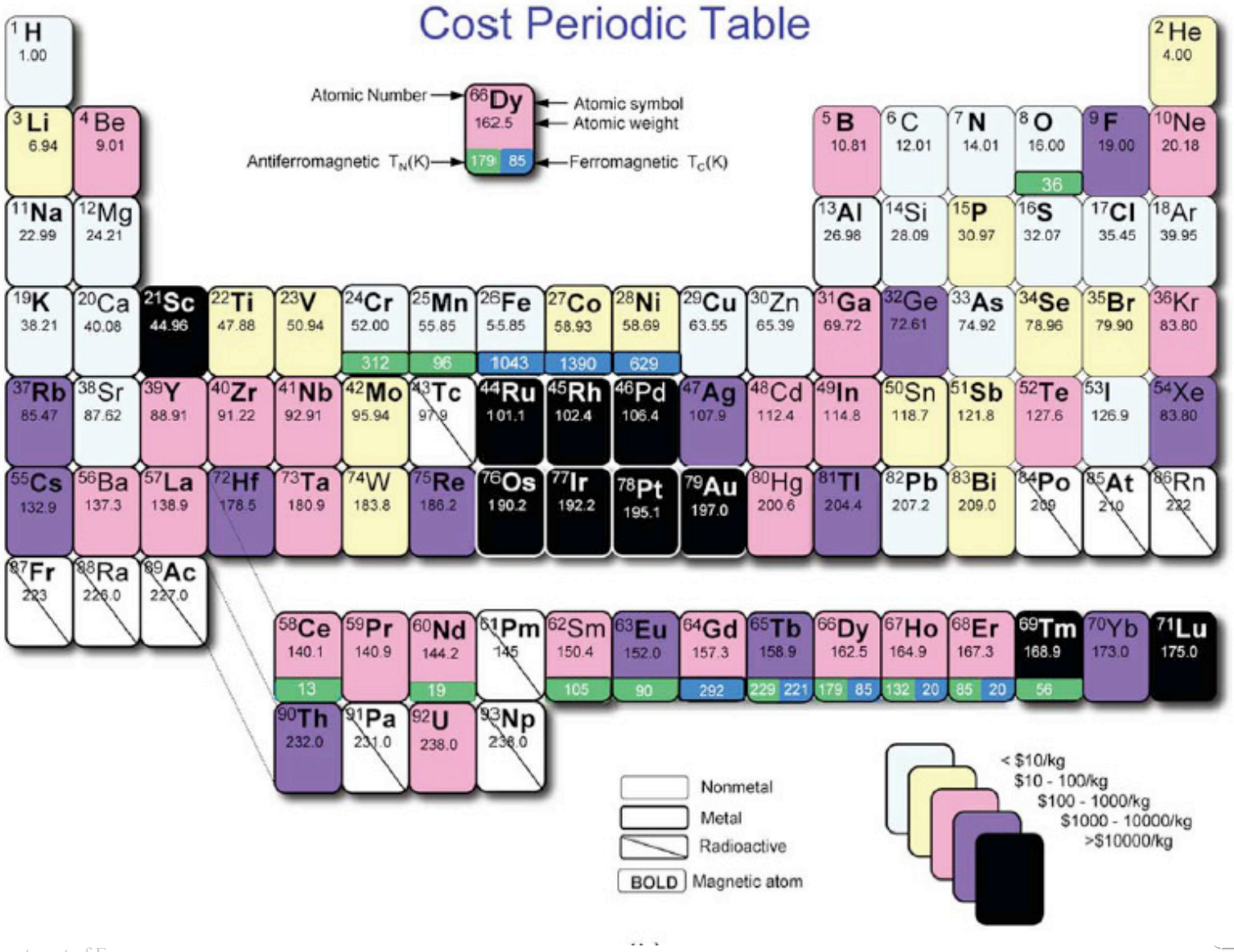
- Integrated synthesis and theory at Ames and Oak Ridge.
- Explore selected ternary phase compositions for transition metal rich magnets
- Theory used to understand results and suggest improved compositions
- New magnets with reduced rare earth content licensed to US manufacturers





$Nd_2Fe_{14}B$ crystal
Photo from AMES

Cost Constraints for New Materials



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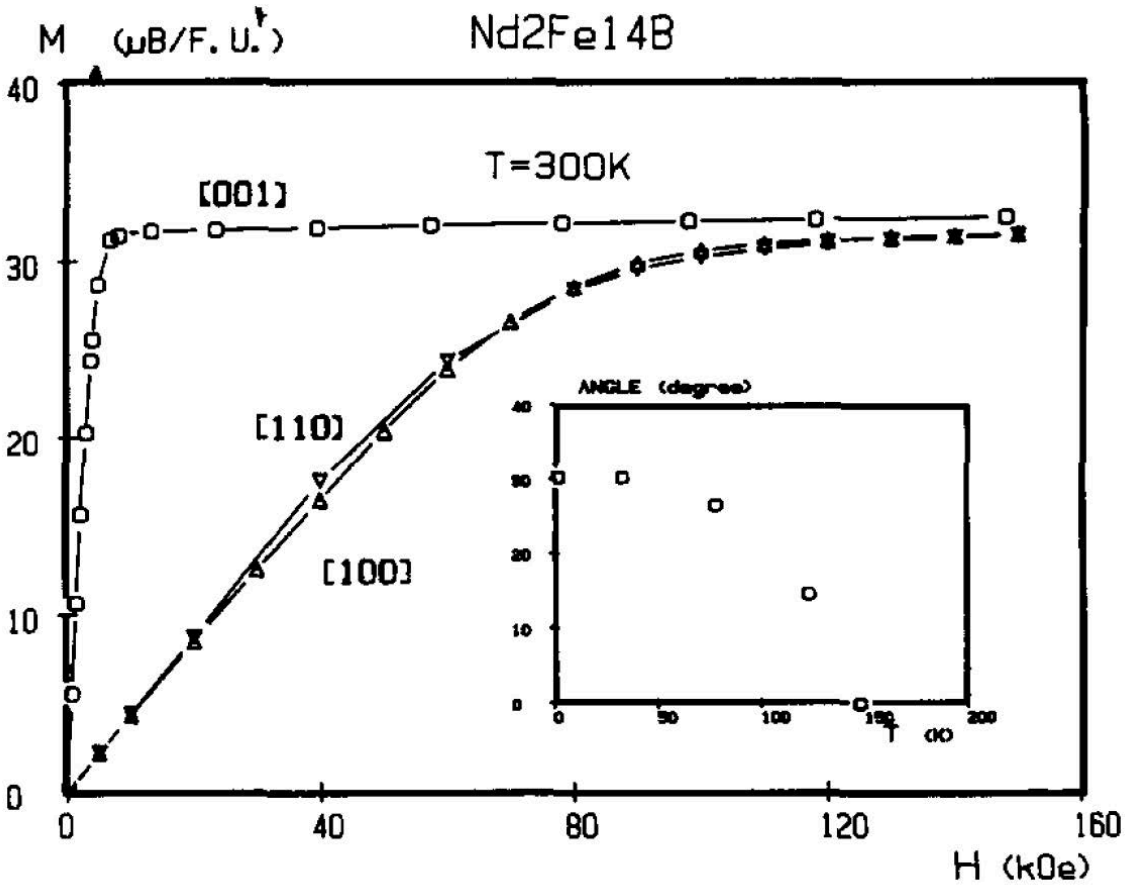
Importance of "mesoscale" in permanent magnets

Large single crystals are useless as permanent magnets (multiple domain formation demagnetizes most of sample)



Single Crystal Magnetization Data for $Nd_2Fe_{14}B$

Importance of "mesoscale" in permanent magnets

- **Ideal microstructure for $Nd_2Fe_{14}B$: grains should be near 0.3 micron in size, with relatively smooth surface and grain boundary layer between grains. This microstructure is suppose to increase resistance to demagnetization and reduce nucleation of domain walls.**
- **In theory, a better control of the microstructure could increase the energy product (performance) by a factor of 2 or 3.**

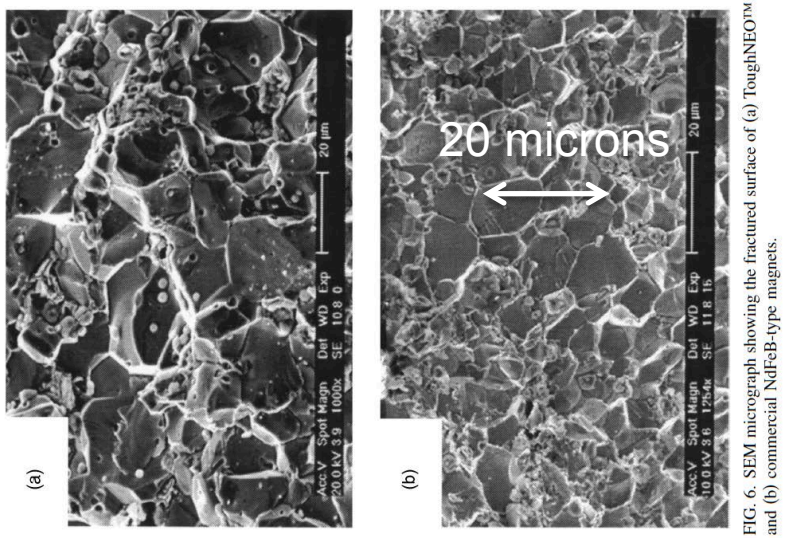


FIG. 6. SEM micrograph showing the fractured surface of (a) ToughNEO™ and (b) commercial NdFeB-type magnets.

Modeling could help understand the role of microstructure and defects

Liu et al. J Appl. Phys. 2005

Structure of Presentation

• Overview of Correlated Electron Materials Group- Who we are and what we do. (Where I am coming from)

• New Materials and The Materials Pyramid

•An experimentalist's perspective of the role of theoretical approaches in the discovery of new materials

• Issues with Digital Design of Materials

•Theoretical successes

• Examples of the importance of an accurate crystal structure and or composition –Fe based superconductors

• Historical Example: A "new" Permanent Magnet $Nd_2Fe_{14}B$

• Importance of "Mesoscale" (metallurgy, microstructure, defects) in magnetic performance of $Nd_2Fe_{14}B$

• Screening guide for identifying superconductors with an unusual pairing mechanism

Thermal Conductivity of Superconductors

Hypothesis:

"Normal" SC's- electron-phonon pairing- Kappa decreases below T_c

"Exotic" SC's with pairing partially due to magnetic fluctuations Kappa increases below T_c

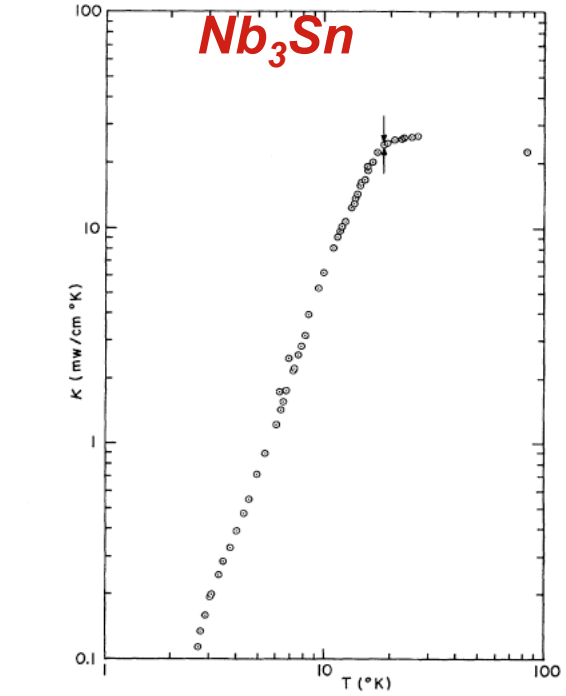
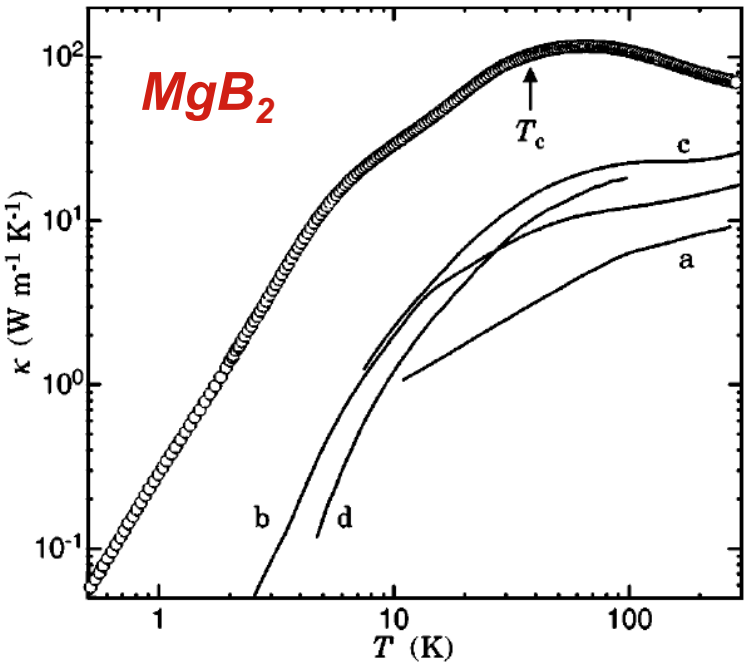


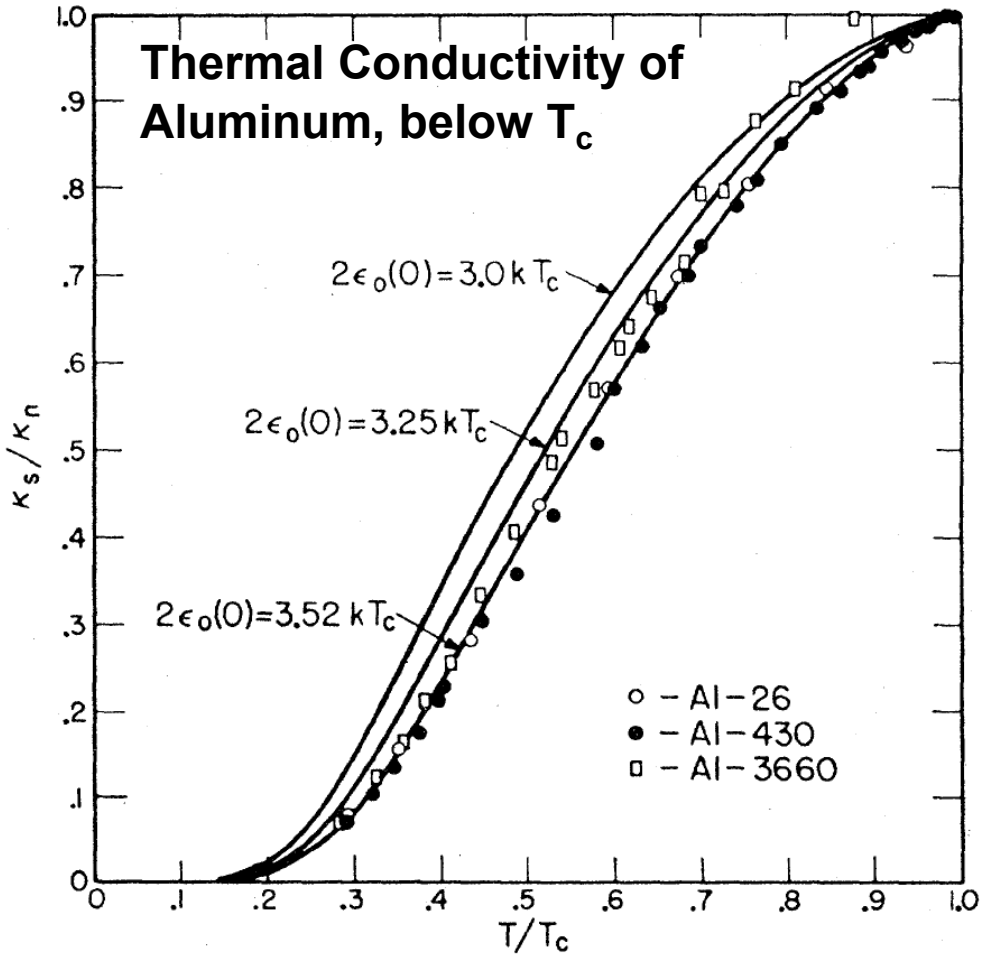
FIG. 1. Thermal conductivity of Nb_3Sn (sample FS14) as a function of temperature.

Cody&Cohen, Rev. Mod Phys. 1964

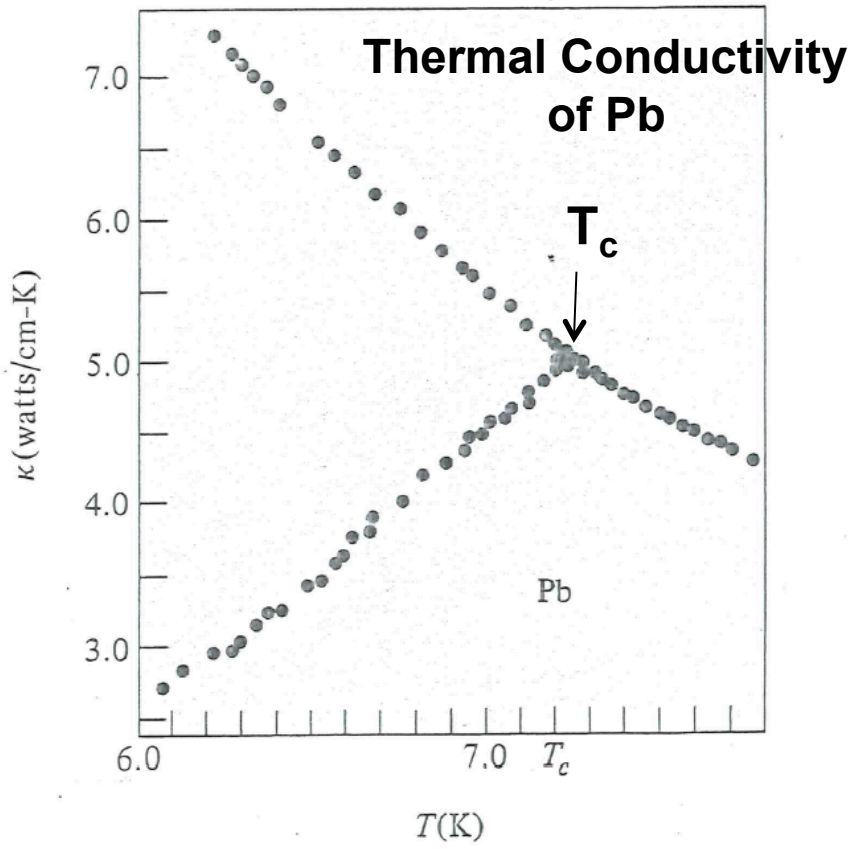


Sologubenko et al. PRB 66 (2002) 014504

Normal Superconductors (cont'd)



C. B. Satterthwaite, PRB, **125**,873 (1962)

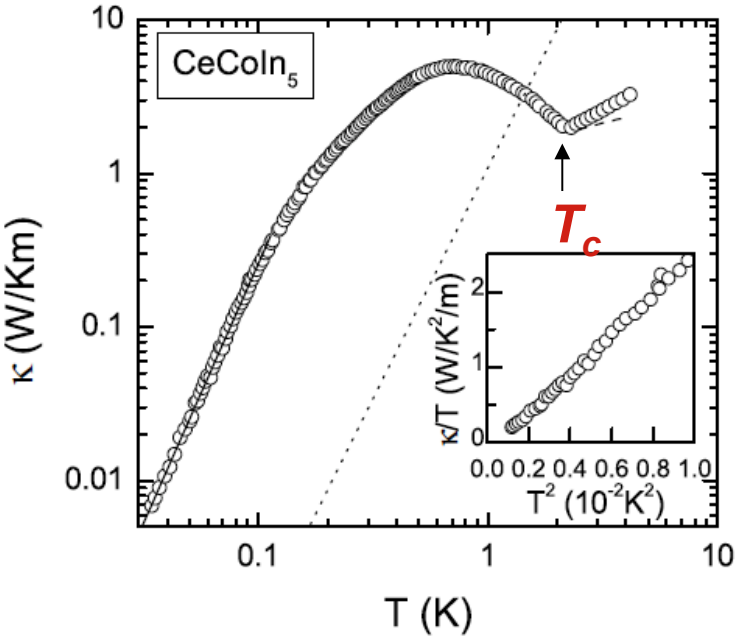


Watson and Graham, Can. J. Physics **41**, 1738 (1963)

Thermal Conductivity of Superconductors

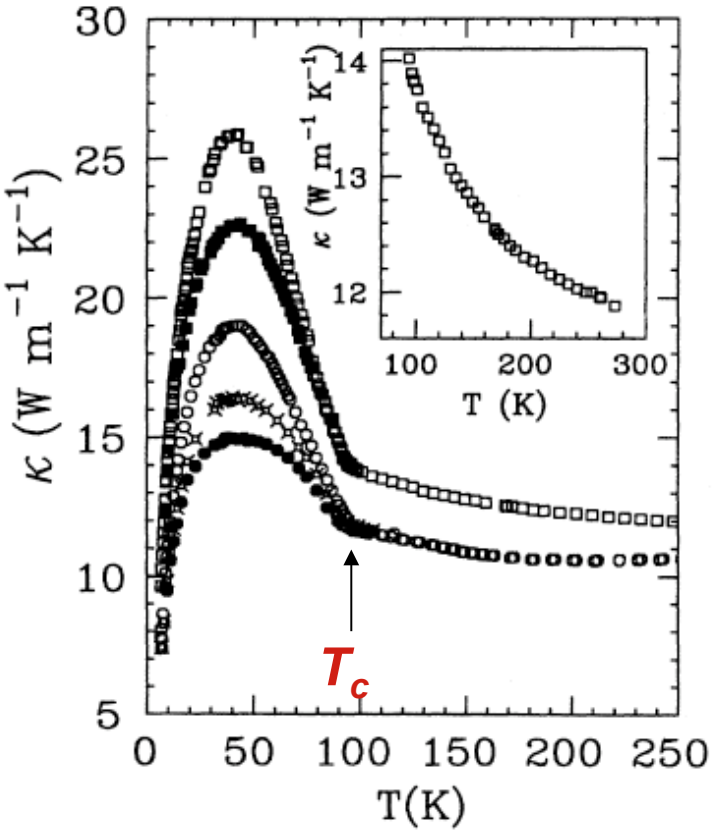
"Exotic" SC's with pairing partially due to magnetic fluctuations
Kappa increases below T_c

$CeCoIn_5$



Movshovich et al. PRL 86 (2001) 5152

$YBa_2Cu_3O_7$

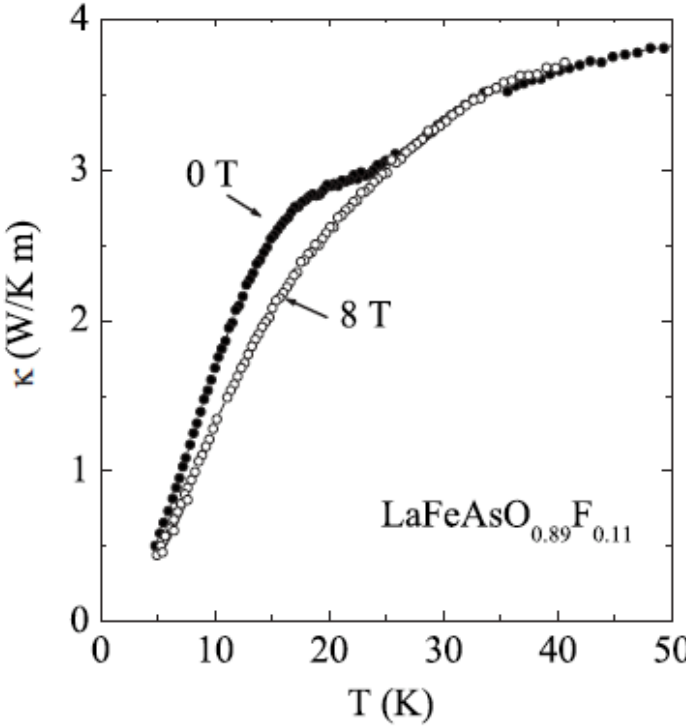


Peacor,Uher, PRB 43 (1991) 8721

Thermal Conductivity of Superconductors

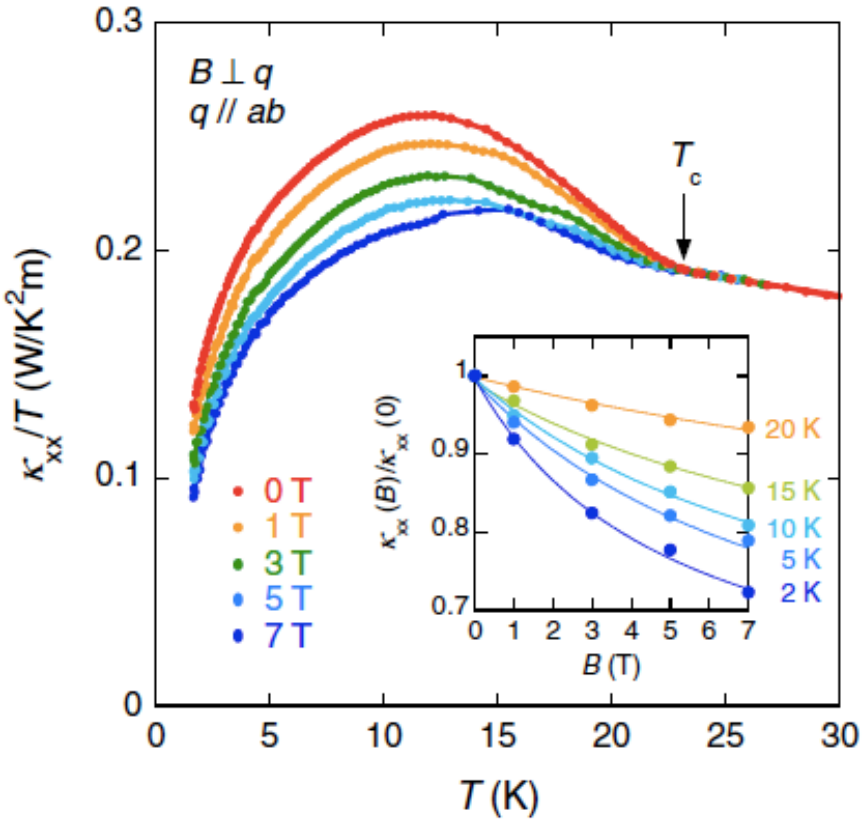
"Exotic" SC's with pairing partially due to magnetic fluctuations
Kappa increases below T_c

$LaFeAsO_{0.89}F_{0.11}$



Sefat et al. PRB 77 (2008) 174503

$Ba(Fe_{0.92}Co_{0.08})_2As_2$

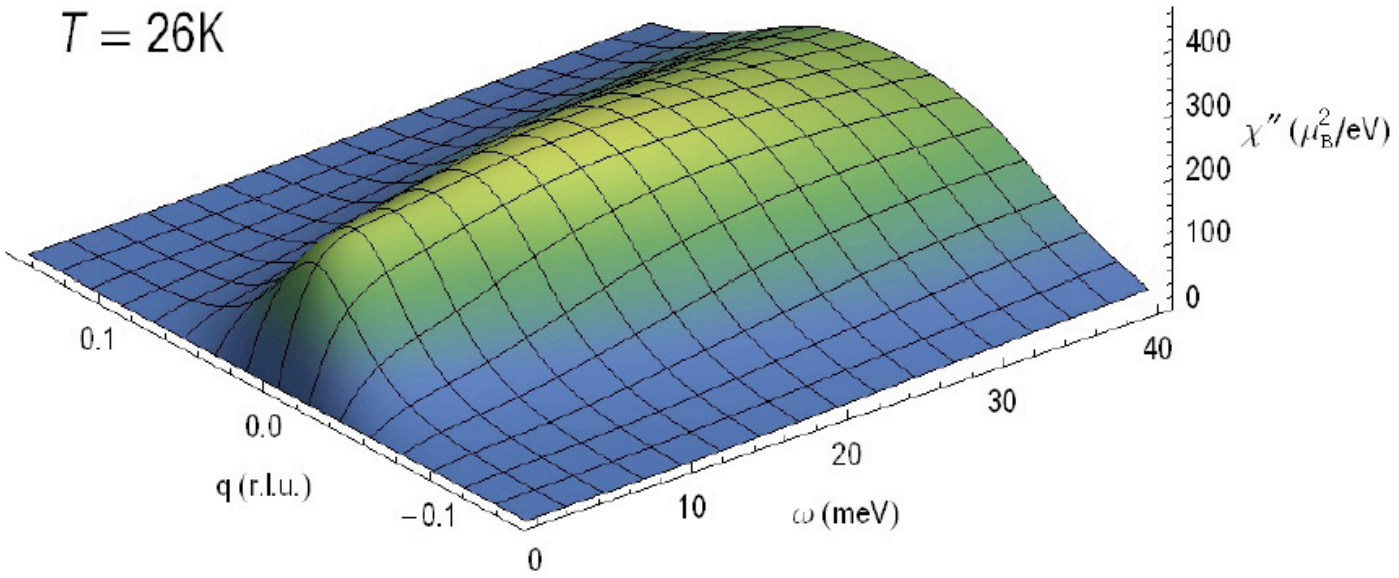


Machida et al. 78 (2009) 073705

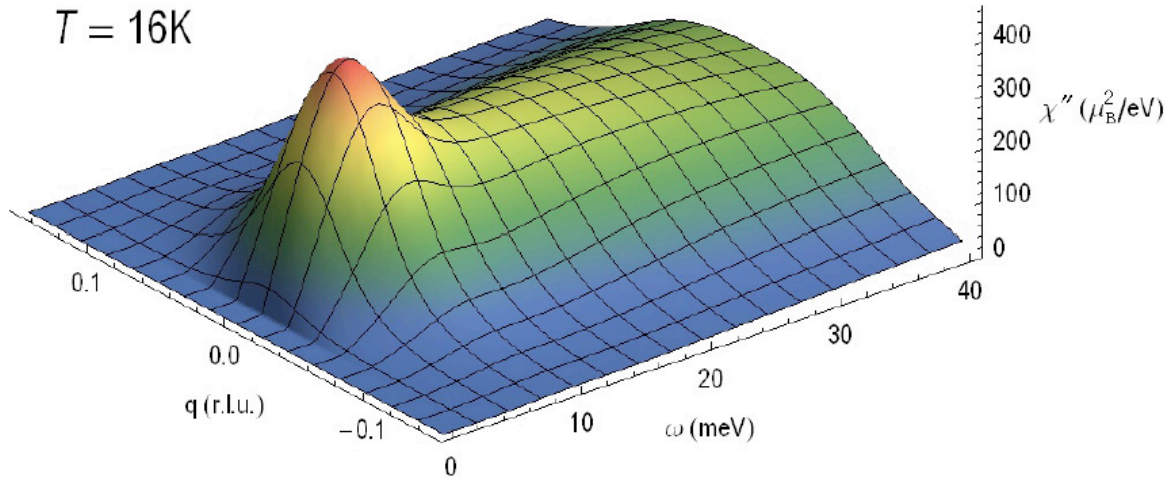
Table 1. Thermal conductivity data for a variety of superconductors. There is a clear correlation between an increase in κ just below T_c and the observation of a spin resonance with neutron scattering.

Compound	T_c (K)	κ just below T_c Up (U) or Down (D)?	Observation of Spin resonance? [20-24]	Thermal Conductivity Data References
Al	1.17	D	-	[8]
Pb	7.2	D	-	[9]
Nb_3Sn	18	D	-	[10]
MgB_2	39	D	N	[11]
$CeCoIn_5$	2.1	U	Y	[12]
$YBa_2Cu_3O_7$	92	U	Y	[13]
$LaFeAsO_{0.89}F_{0.11}$	26	U	Y	[14]
$Ba(Fe_{0.93}Co_{0.07})_2As_2$	22	U	Y	[15]
$MgCNi_3$	8	D	N	[16]
UPd_2Al_3	2	D	N	[17]
$PrOs_4Sb_{12}$	1.82	D	-	[5]
YNi_2B_2C	15.5	D	N	[5]
Sr_2RuO_4	1.4	D	N	[18]
κ - $(ET)_2Cu(NCS)_2$	10	U	-	[19]
Mo_3Sb_7	2.1	U	-	This Work

D. S. Inosov et al. Nature Physics 6 (2010) 178



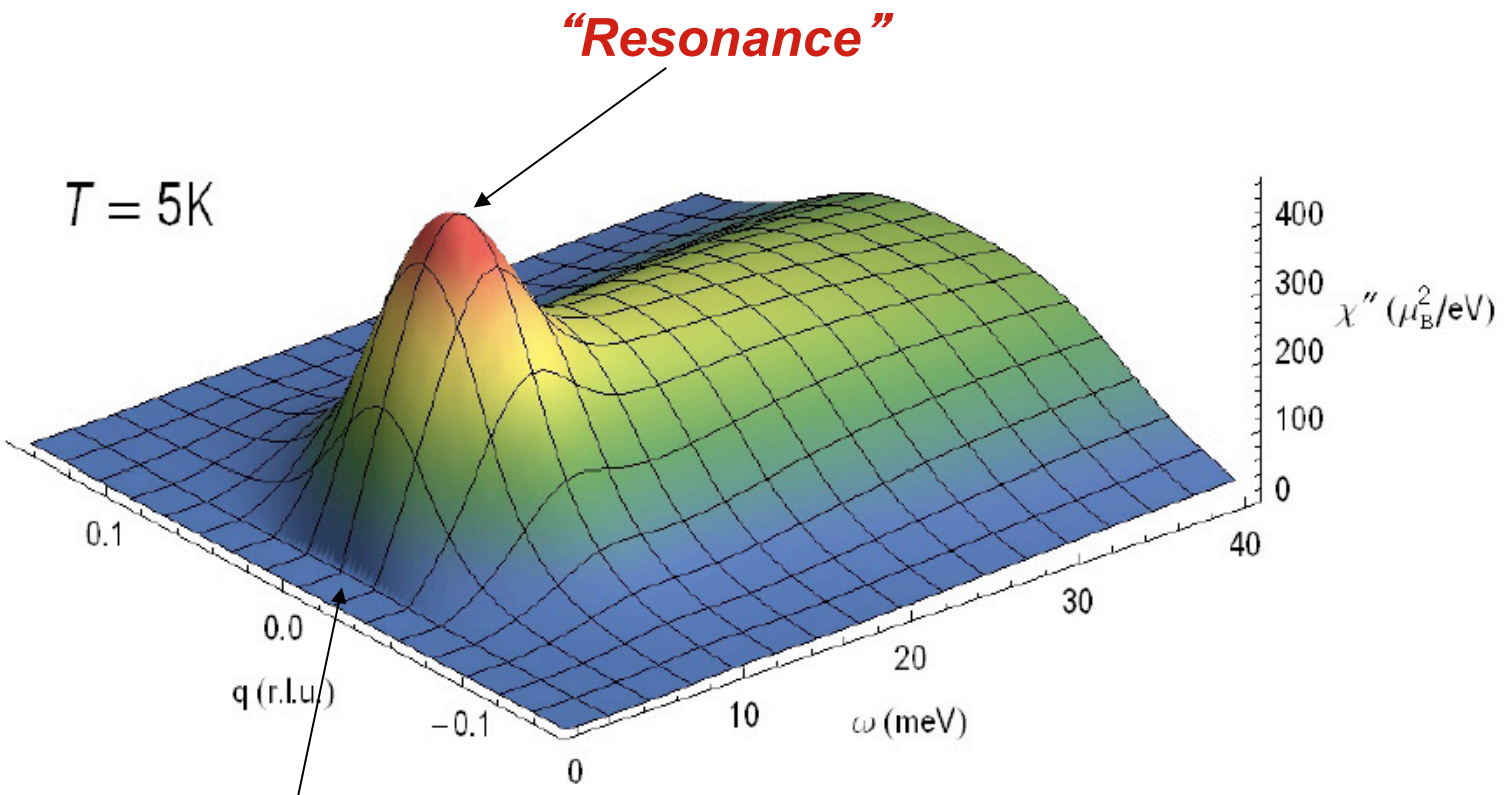
T > T_C =22K



T< T_c - note gap in spin excitations at low energies (below 2 meV)

$Ba(Fe_{0.94}Co_{0.06})_2As_2$ Crystal

D. S. Inosov et al. Nature Physics 6 (2010) 178



Loss of low energy spin excitations

$Ba(Fe_{0.94}Co_{0.06})_2As_2$ Crystal

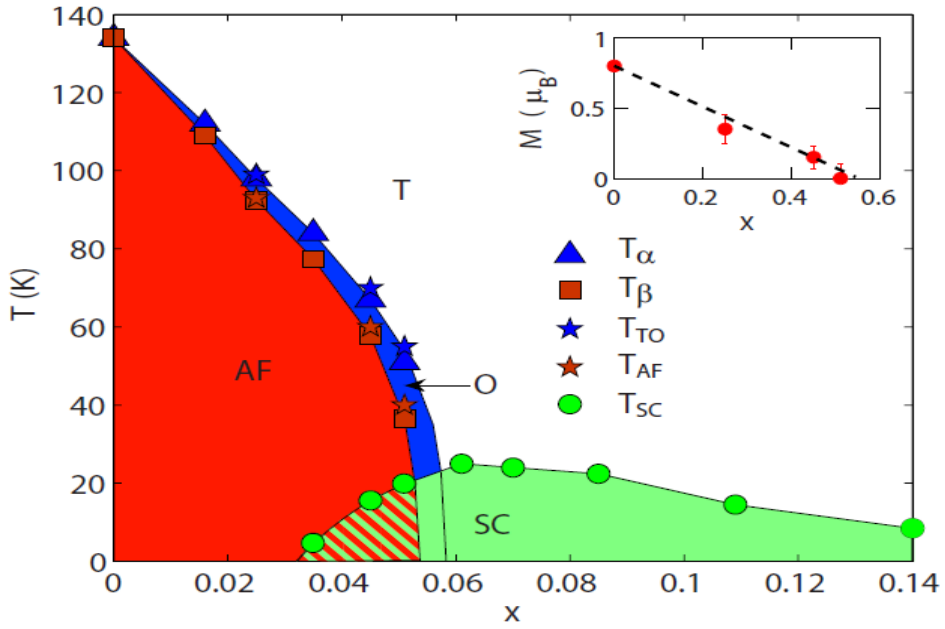
Model System for Studying Fe-based superconductors

Model system discovered by our group: $Ba(Fe_{1-x}Co_x)_2As_2$

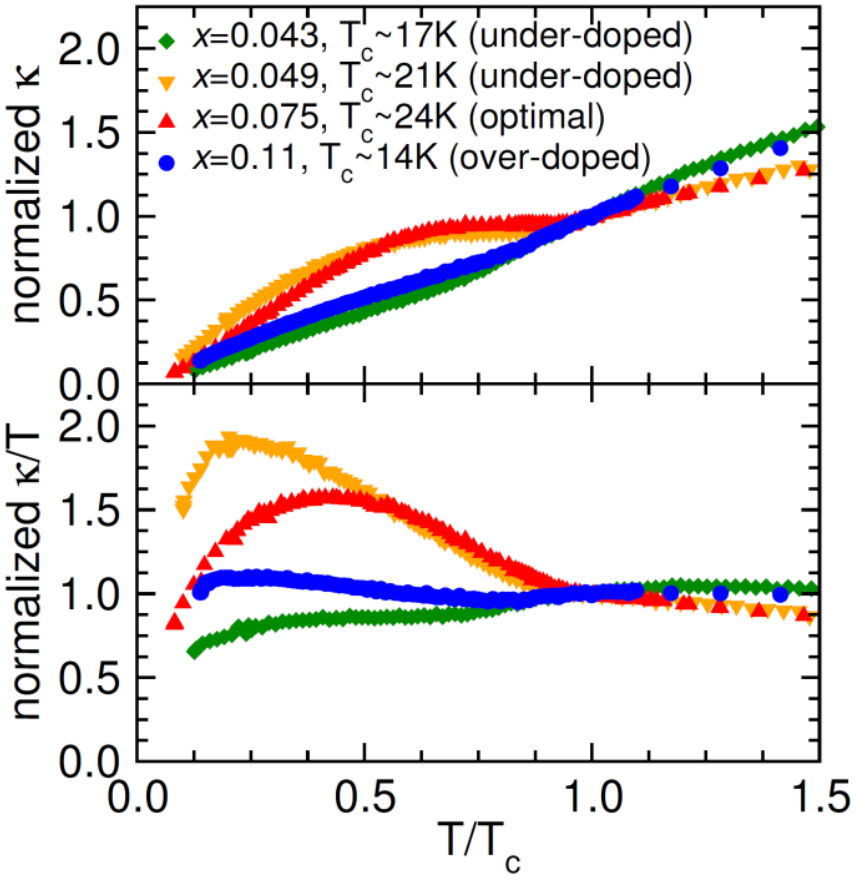
*Sefat et al. PRL **101**, 117004 (2008)

Athena Sefat

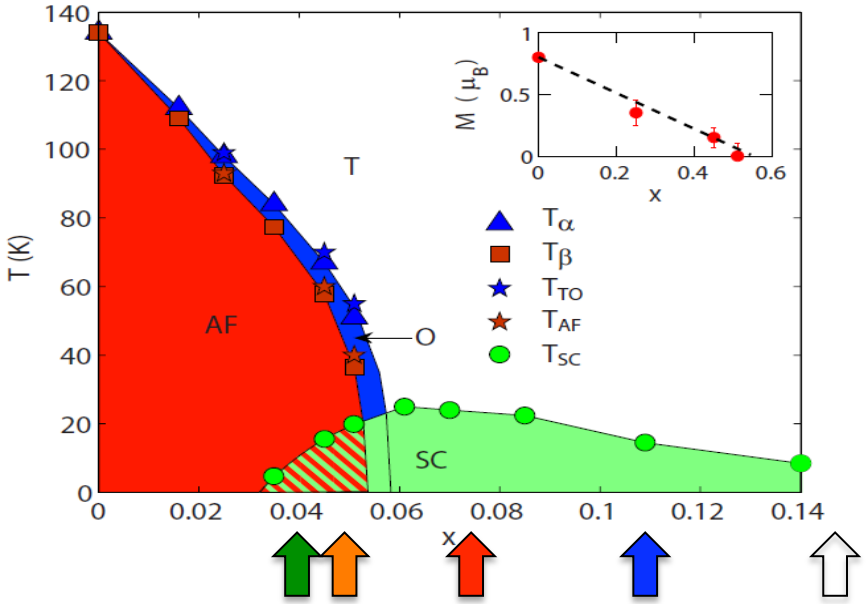
Phase Diagram $Ba(Fe_{1-x}Co_x)_2As_2$



Lester et al., PRB 79, 144523 (2009)



Phase Diagram $Ba(Fe_{1-x}Co_x)_2As_2$



May et al PRB **88** (2013) 064502

Andrew May

Superconductivity, unusual magnetism and a good thermoelectric: Mo_3Sb_7 and related alloys

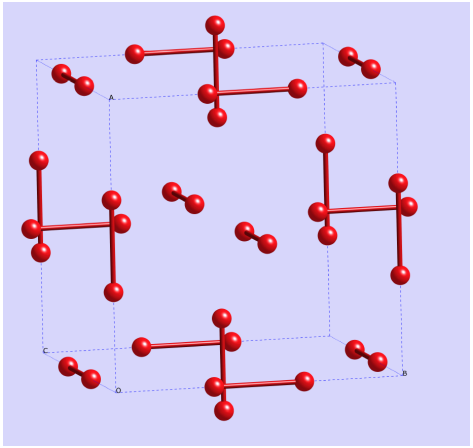
Background for Mo_3Sb_7:

1. Cubic at room temperature (Im3m space group)

2. Doped alloys show good thermoelectric performance at high temperatures (Ni, Mg, or Cu in cubic voids, or Ru for Mo or Te for Sb) – [Candalfi, 2007]- maximum ZT ≈0.9 at 1000 K

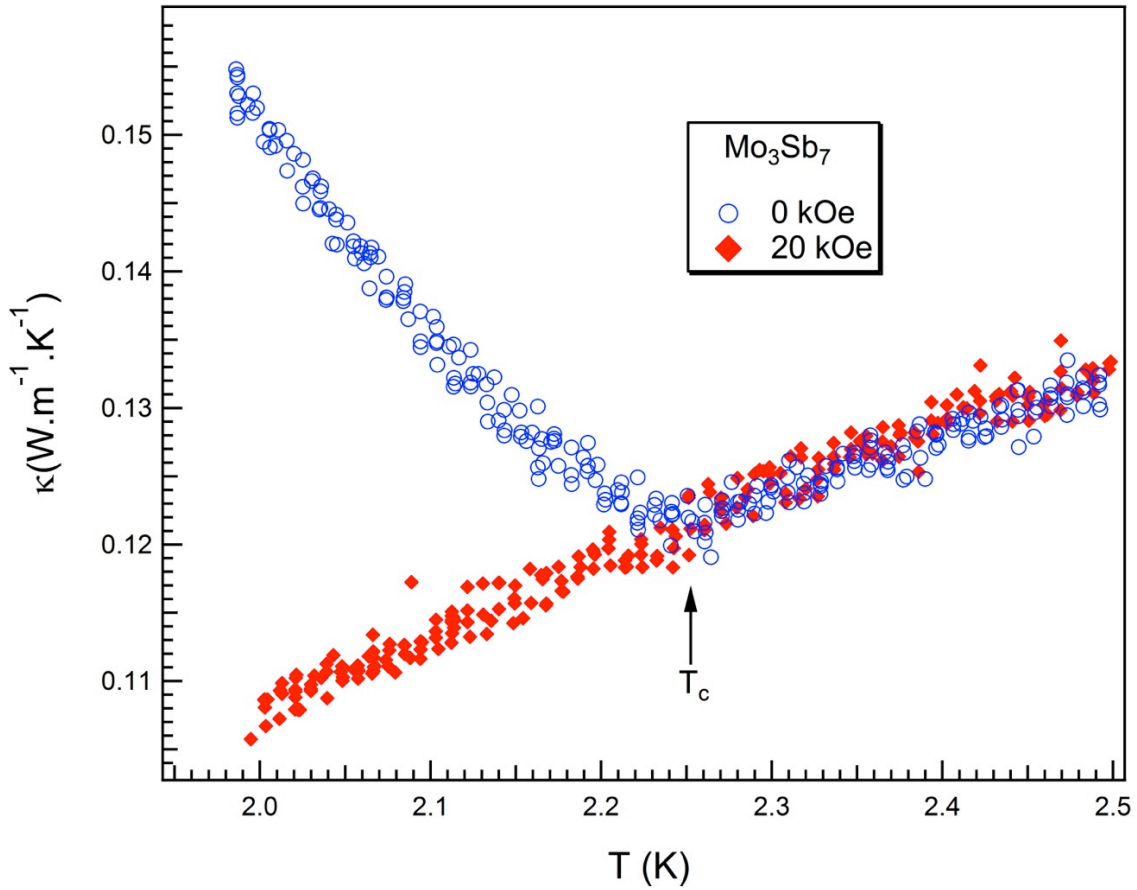
3. Magnetic susceptibility exhibits Curie-Weiss behavior above 200 K and broad maximum at 150 K. Cubic to tetragonal phase transition ≈ 50 K, also possible spin gap, formation of Mo-Mo dimers? [Tran 2008]

4. Is superconductivity at 2.3 K unconventional?



Mo_3Sb_7 crystal structure showing only Mo atoms and dimers

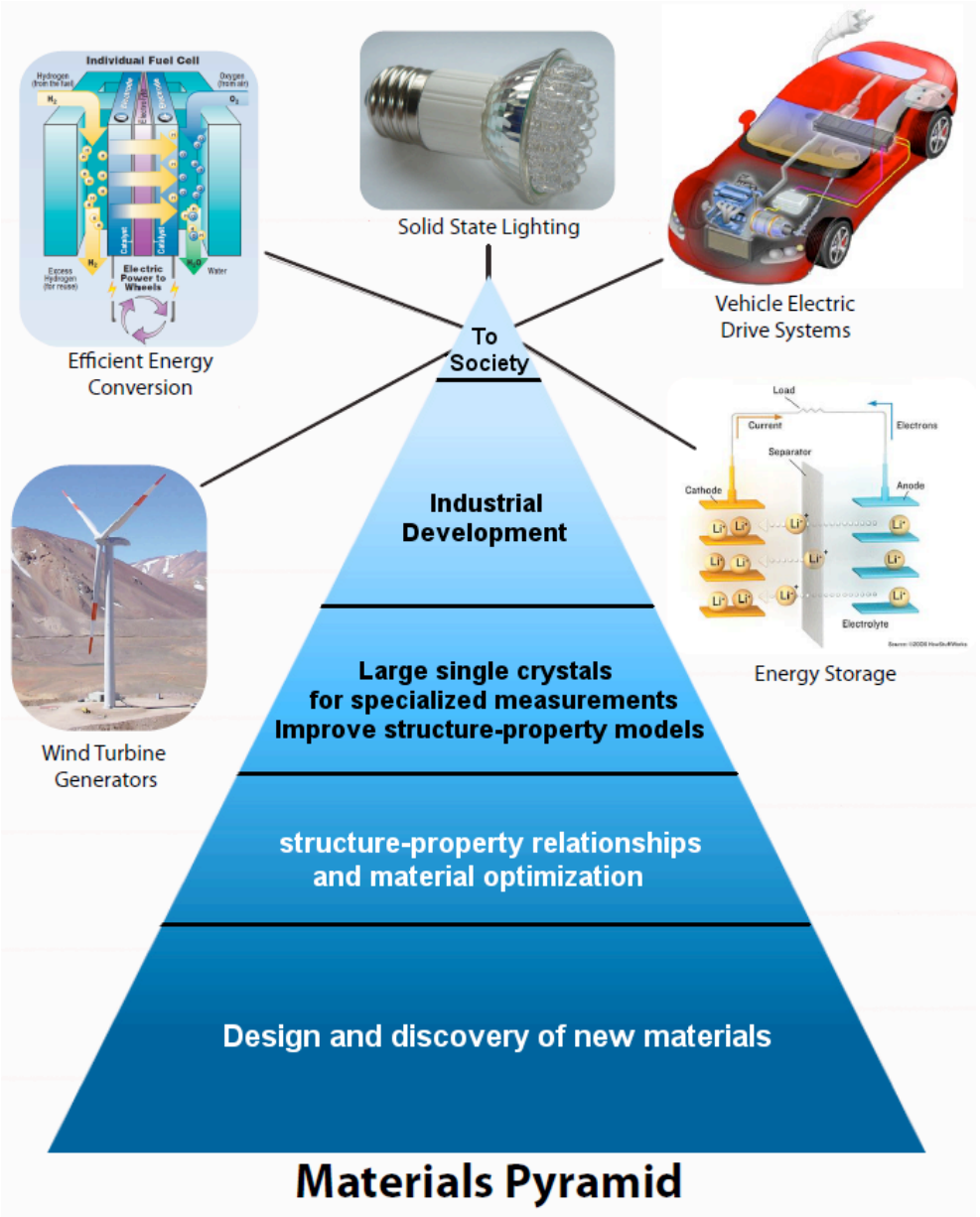
Mo_3Sb_7 : Thermal Conductivity Increases Below T_c !



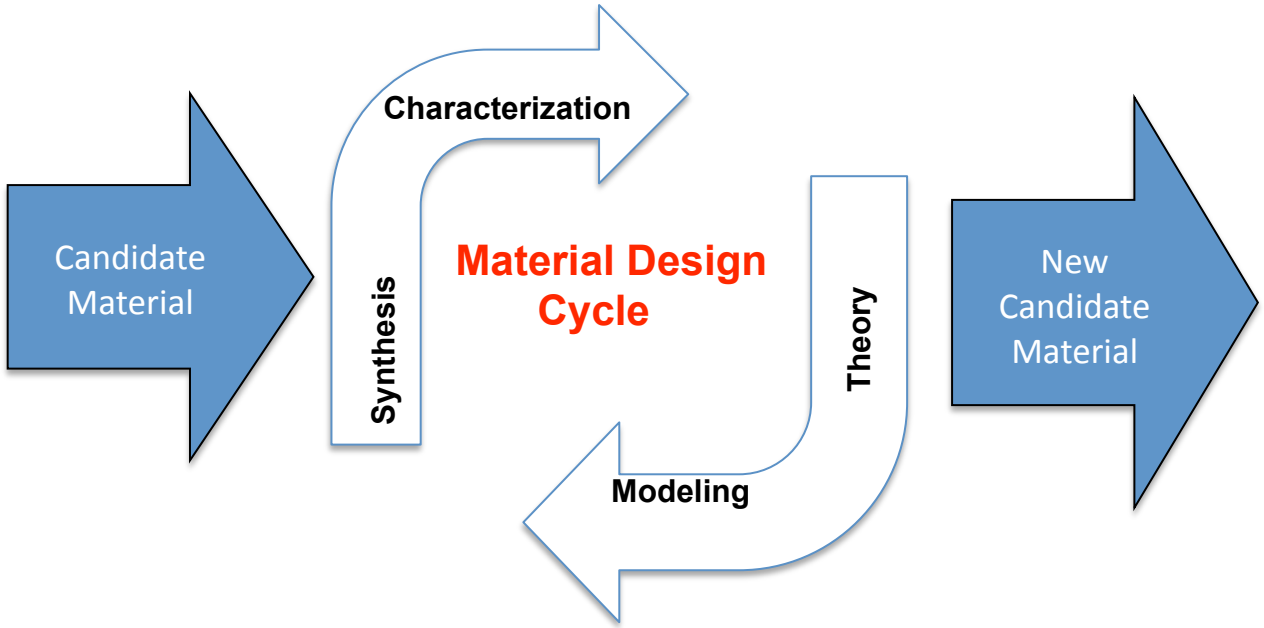
Jiaqiang Yan

Where do new materials come from?

Need
To do
Better
Than
18 Years!



In my experience, in finding a new material
theory is at best akin to a compass rather than a GPS system

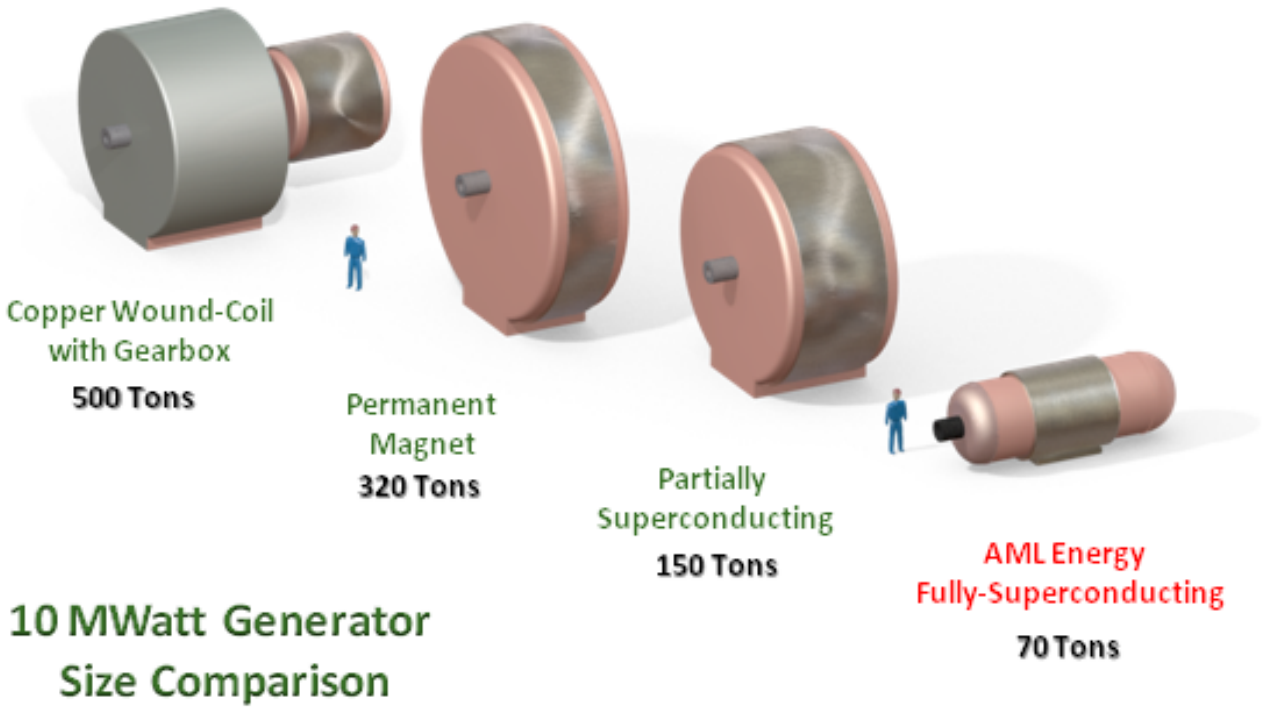


Rapid feedback between experiment and theory is still the best approach to speed the design of a new material for the foreseeable future.

Interesting Material Properties and Sample Availability Data Bases:

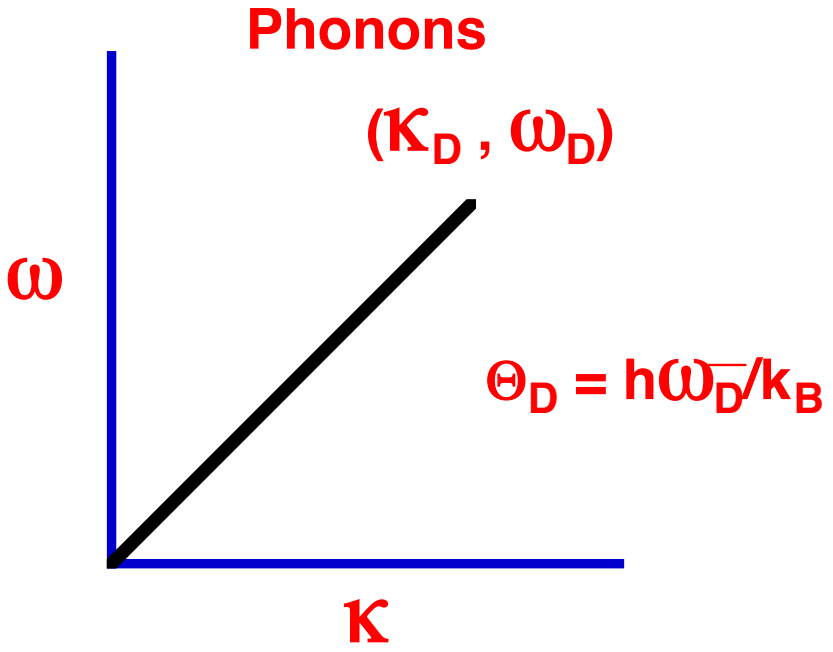
- **http://crystdb.nims.go.jp/index_en.html (AtomWorks)**
- https://materials.soe.ucsc.edu/home **(Materials Advancement Portal)**
- **https://materialsproject.org/ (Materials Project)**

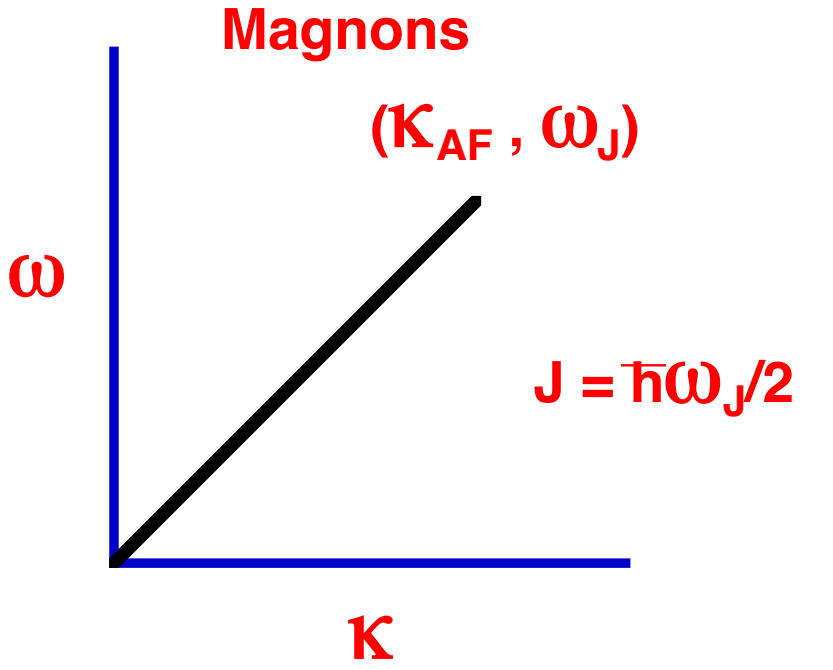
and.. new technologies



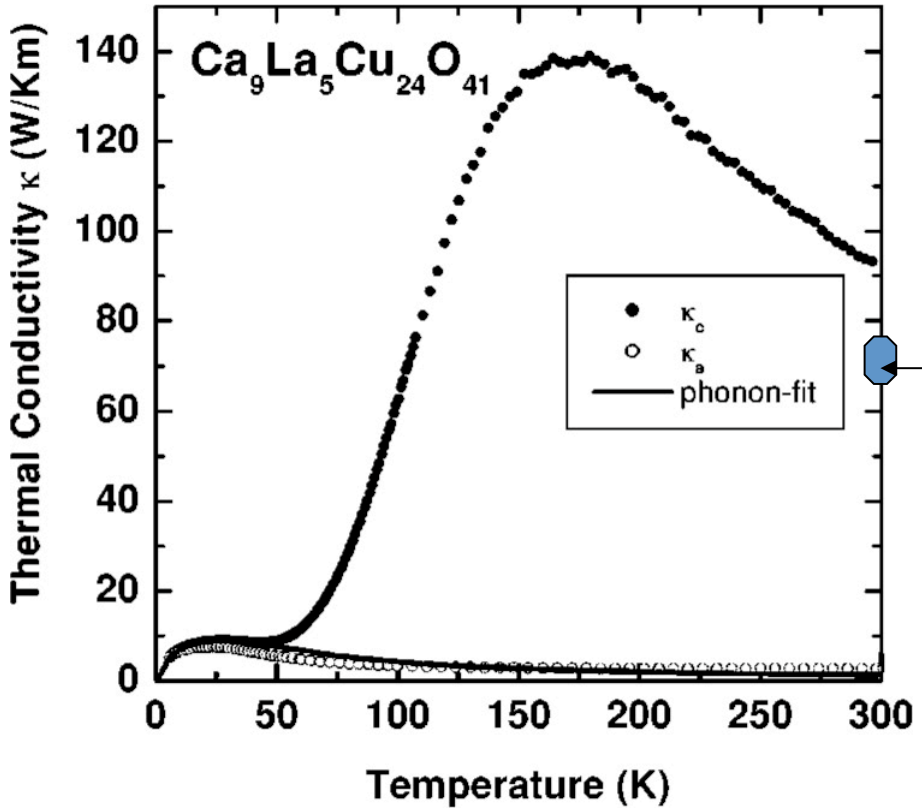
Magnons and Phonons can both Carry Heat

$$\kappa_i \approx C_i \, v_i \, d_i$$





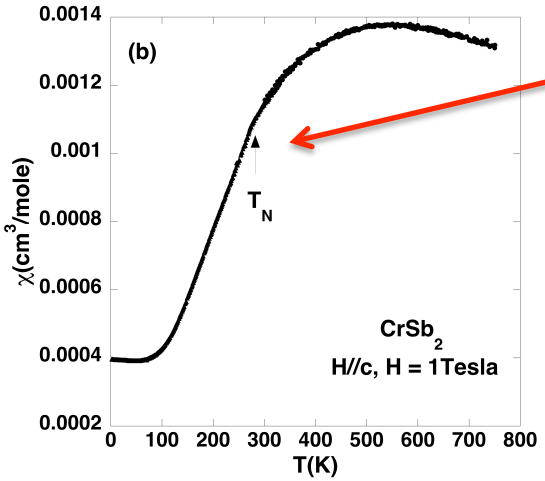
Heat Transport In Low Dimensional Magnetic Compounds
Example: Spin Ladder Compound $Ca_9La_5Cu_{24}O_{41}$
Key Observation: Huge magnon contribution to heat transport- even at room temperature!



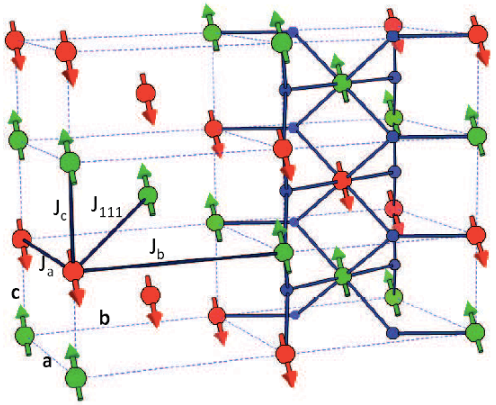
C. Hess et al., Phys. Rev B. 64 (2001) 184305

Pt Kappa

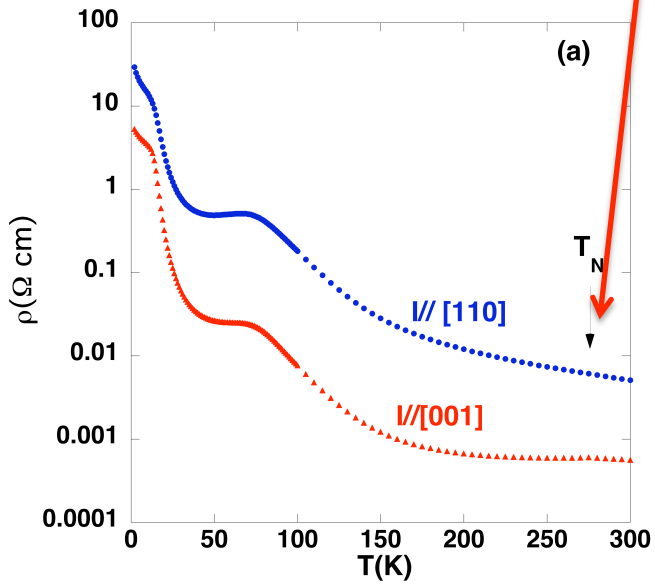
$CrSb_2$ Magnetic and Electrical Properties

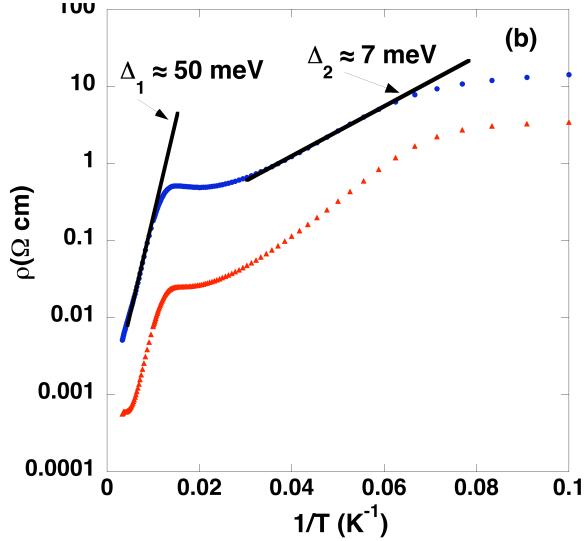


Weak anomaly at T_N in magnetic susceptibility and resistivity data suggests low-dimensional magnetism



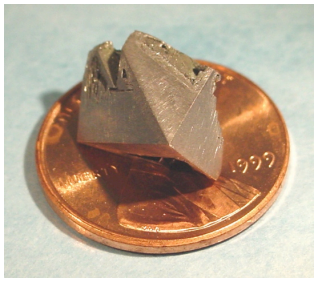
Magnetic Structure
$CrSb_2$ – $2\mu_B$ per Cr



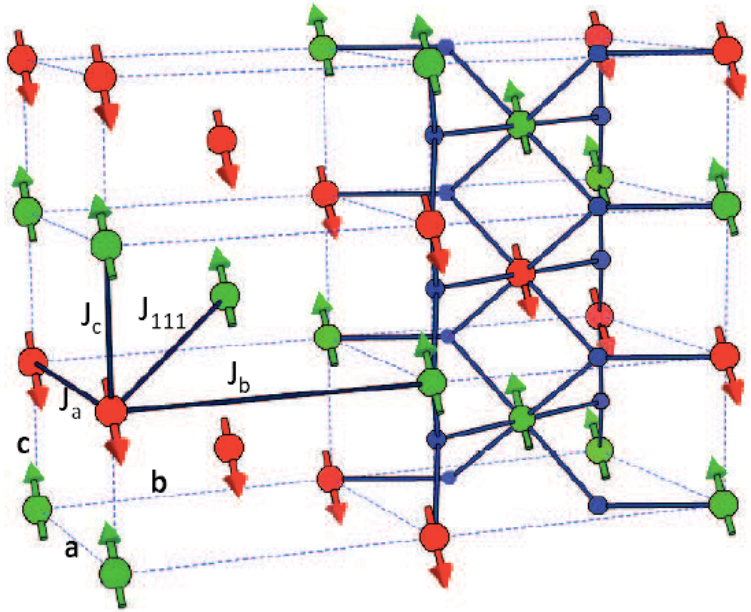


Resistivity data suggests two gaps: valence band-conduction band gap ≈ 100 meV and a donor level 14-16 meV below conduction band edge.

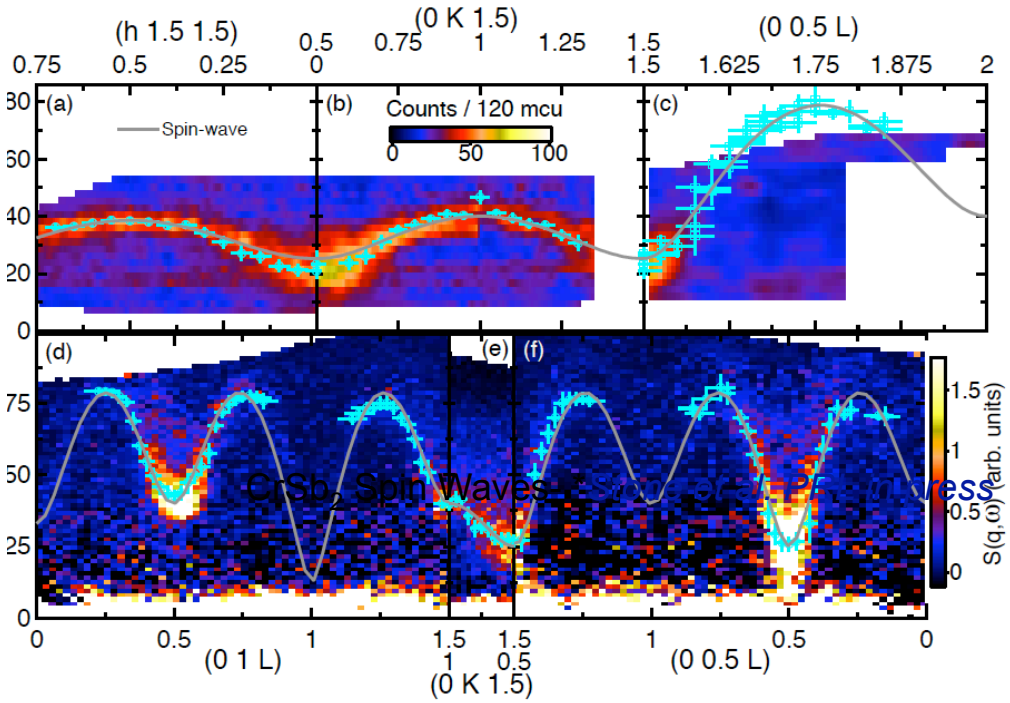
$CrSb_2$: Elastic and Inelastic Neutron Scattering



Quasi 1-d Antiferromagnetic Semiconductor: $CrSb_2$
Orders Magnetically at 273 K

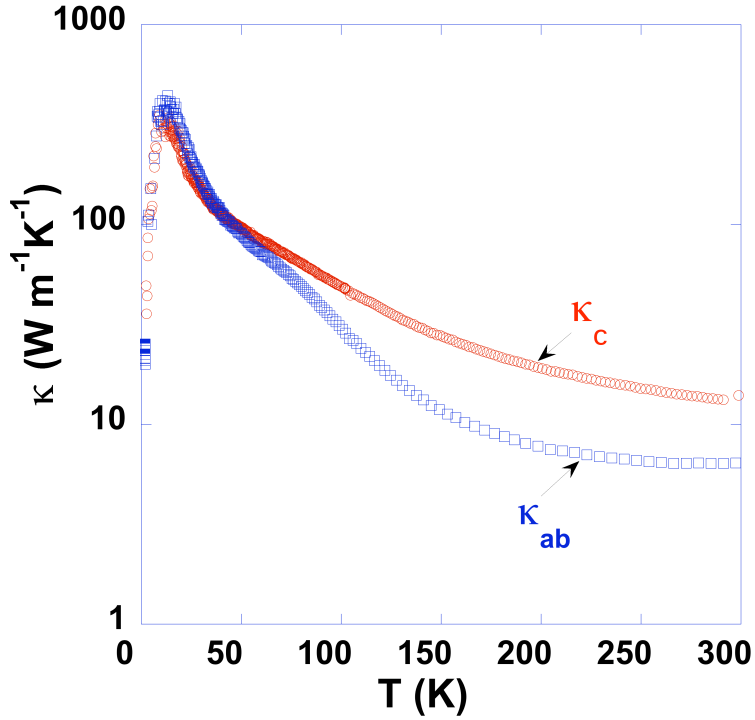


J_c = 35 meV
$J_a \approx J_b \approx J_{111} \approx$ 1 meV



Stone et al. PRL 108 (2012) 054515

Thermal Conductivity Data from $CrSb_2$

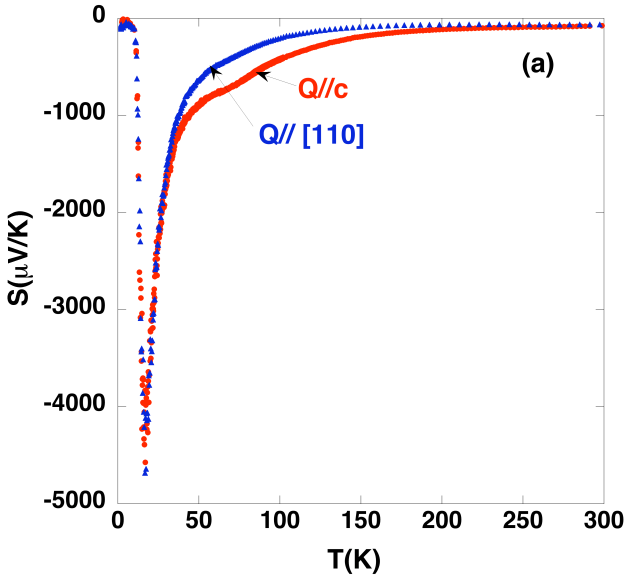


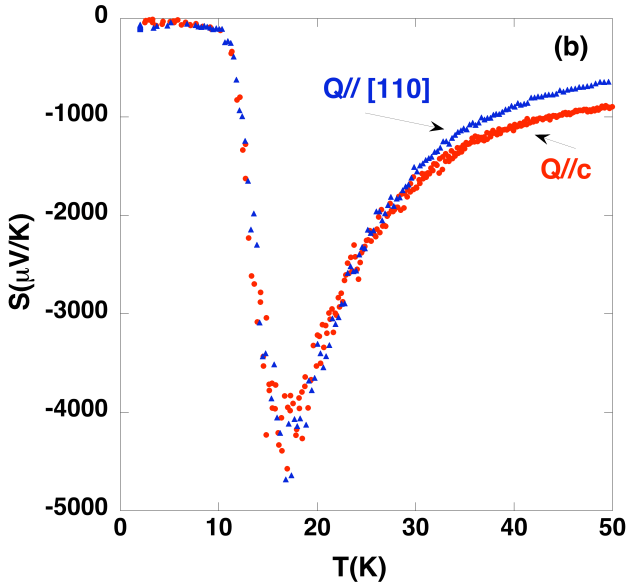
Below 50 K , κ similar in both directions- consistent with gap for magnetic excitations measured using neutron scattering (≈ 25 meV)

Deviation above 50 K consistent with either magnon heat conduction along c or increased scattering of phonons by magnons

Stone et al. PRL 108 (2012) 054515

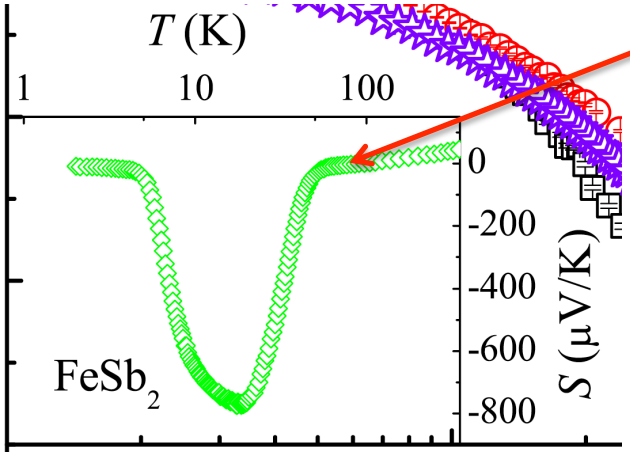
Seebeck Data from $CrSb_2$



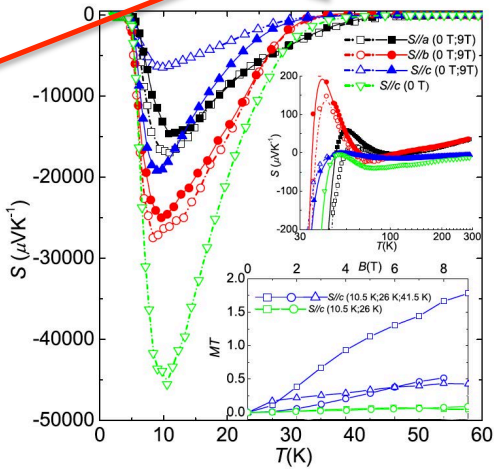


Sales et al- in press

Large Seebeck Coefficient ≈ -4500 μV/K at 18 K
unusual asymmetric shape – very similar to $FeSb_2$

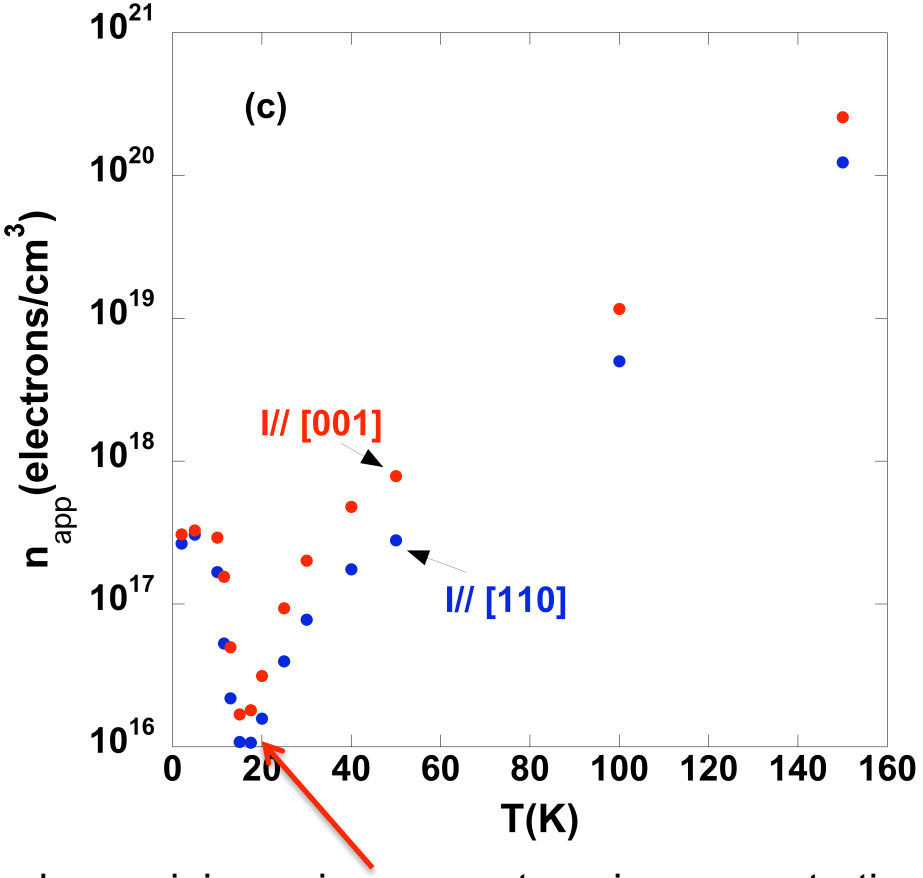


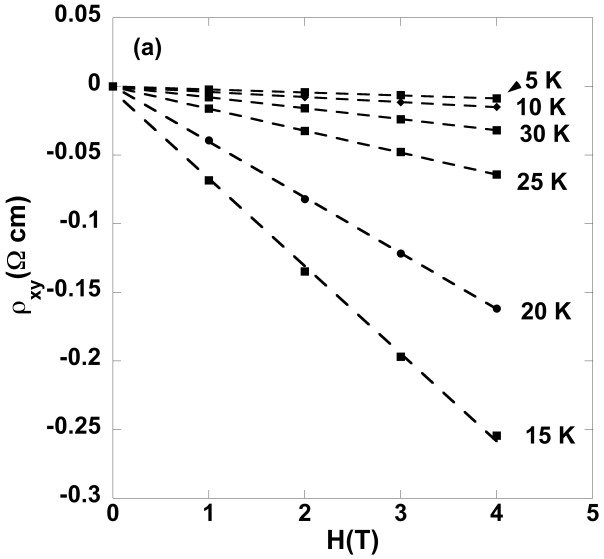
Wang et al. JAP 112 (2012) 013703

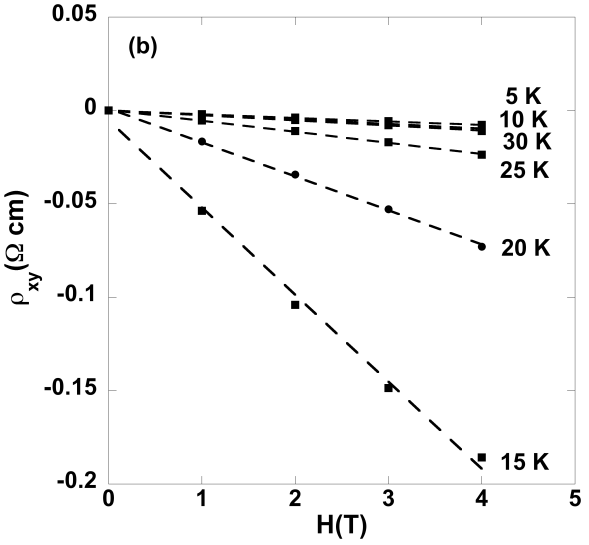


Bentien et al. EPL 80 (2007) 17008

Hall Data from $CrSb_2$

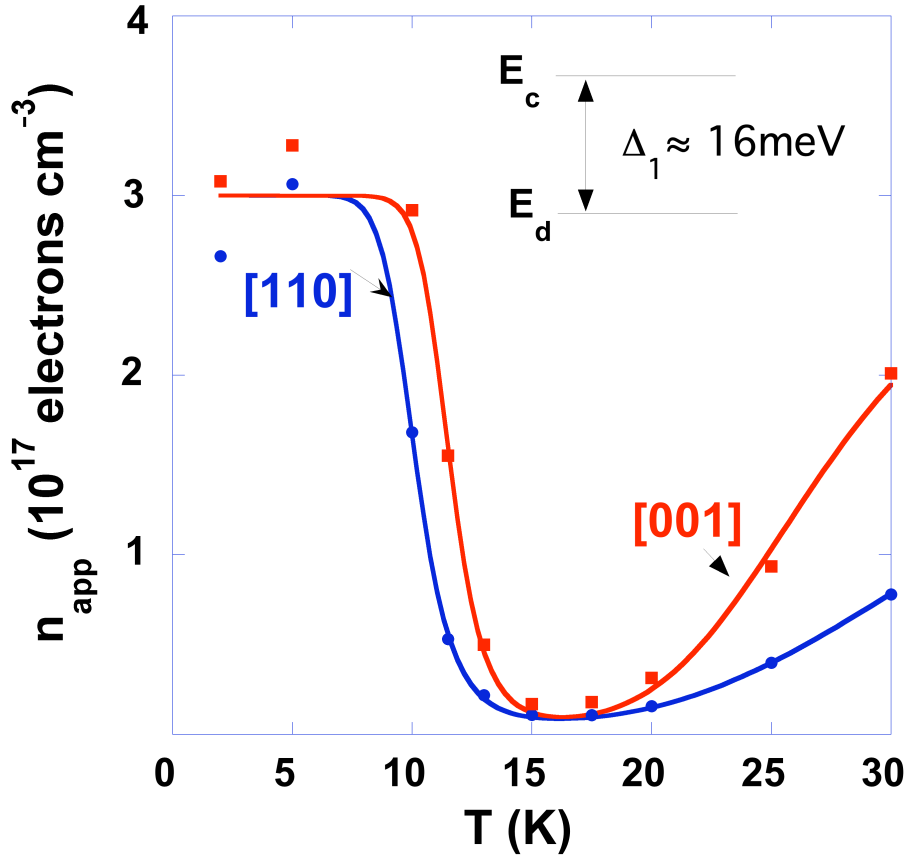






Note sharp minimum in apparent carrier concentration.
Similarity of Hall and Seebeck data below 30 K.
A sharp minimum also can occur in doped Ge crystals

Simple Explanation of Hall Data from $CrSb_2$



$$N_{con} = 3 \times 10^{17} \frac{G\exp(-\Delta/k_B T)}{1 + G\exp(-\Delta/k_B T)}$$

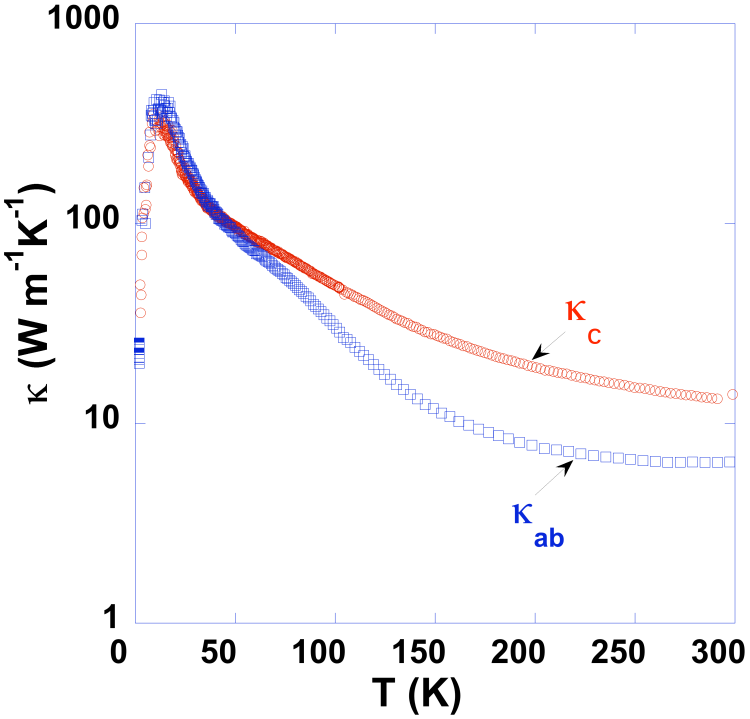
$$n_{app} = \frac{(N_{imp} + N_{con} b)^2}{N_{imp} + N_{con} b^2}$$

b ≈ 130

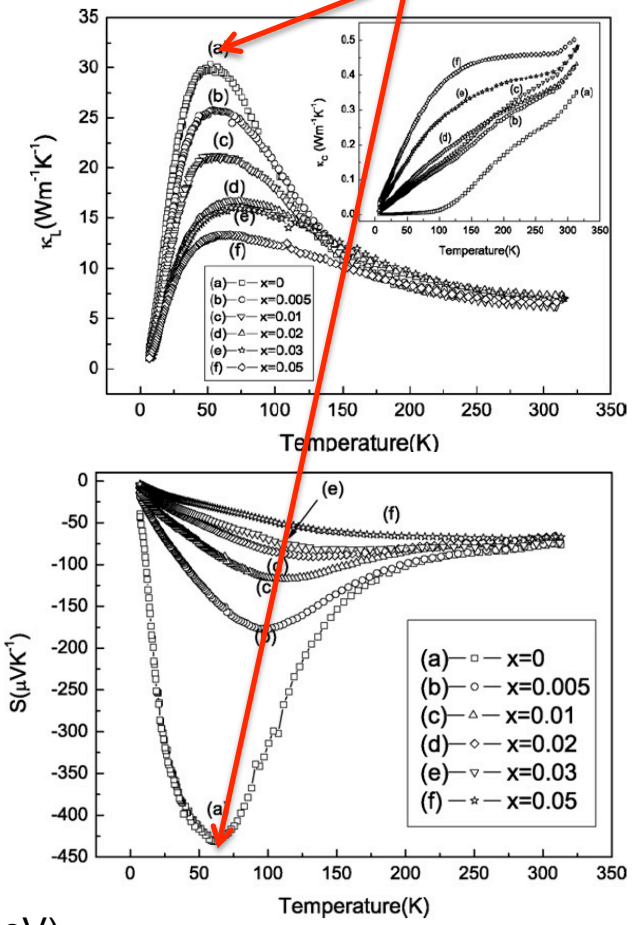
G ≈ 100

Note sharp minimum in apparent carrier concentration.
Similarity of Hall and Seebeck data below 30 K.
A sharp minimum also can occur in doped Ge crystals, and $FeSb_2$

Thermal Conductivity Data from $CrSb_2$



Polycrystalline $CrSb_2$

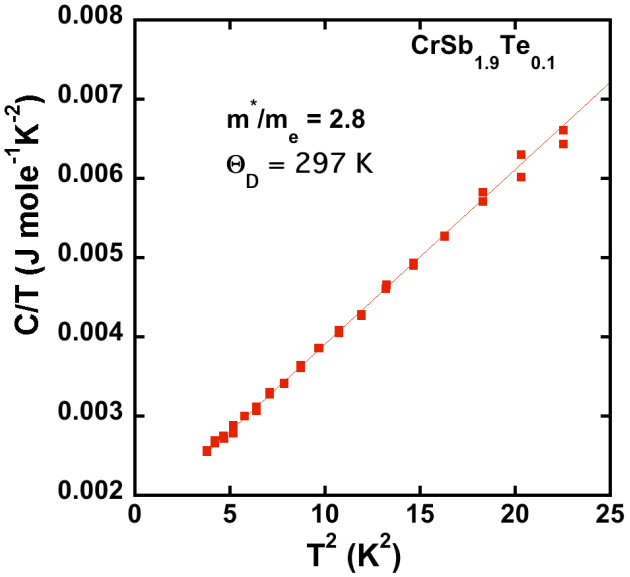


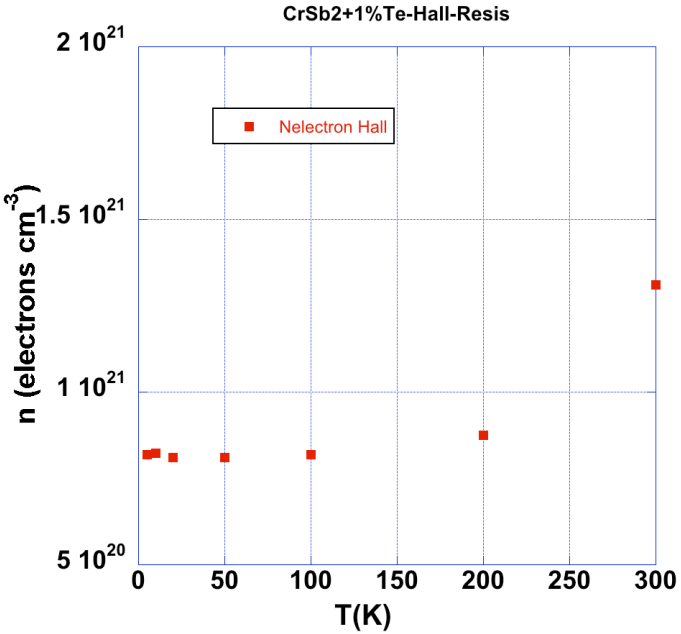
Below 50 K , κ similar in both directions- consistent with gap for magnetic excitations measured using neutron scattering (≈ 25 meV)

Deviation above 50 K consistent with either magnon heat conduction along c or increased scattering of phonons by magnons

Note: Large value of κ at 18 K consistent with phonon-drag mechanism as likely origin of large peak in Seebeck data For polycrystalline $CrSb_2$- both κ and S are 10 times smaller

No Evidence of Significant Mass Enhancement for Carriers in $CrSb_2$

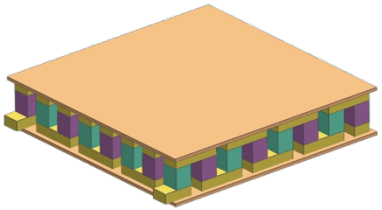


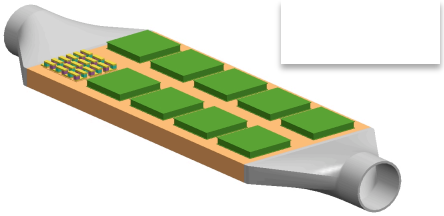


Relevance of Research to DOE Energy Mission:

Superconducting generators for large (> 10 MW wind turbines)

Magnets for electric motors





Thermoelectric materials for waste heat recovery- for cars to improve gas mileage

Note: All these energy applications require “bulk” quantities of material

Thermoelectric Properties of FeSi and Related Alloys: Evidence of strong electron-phonon interactions

***Brian Sales**, Olivier Delaire, Michael McGuire and Andrew May*

Oak Ridge National Laboratory, Oak Ridge TN

Focus Session: Thermoelectric Materials

Session T20.00011

March Meeting 2011

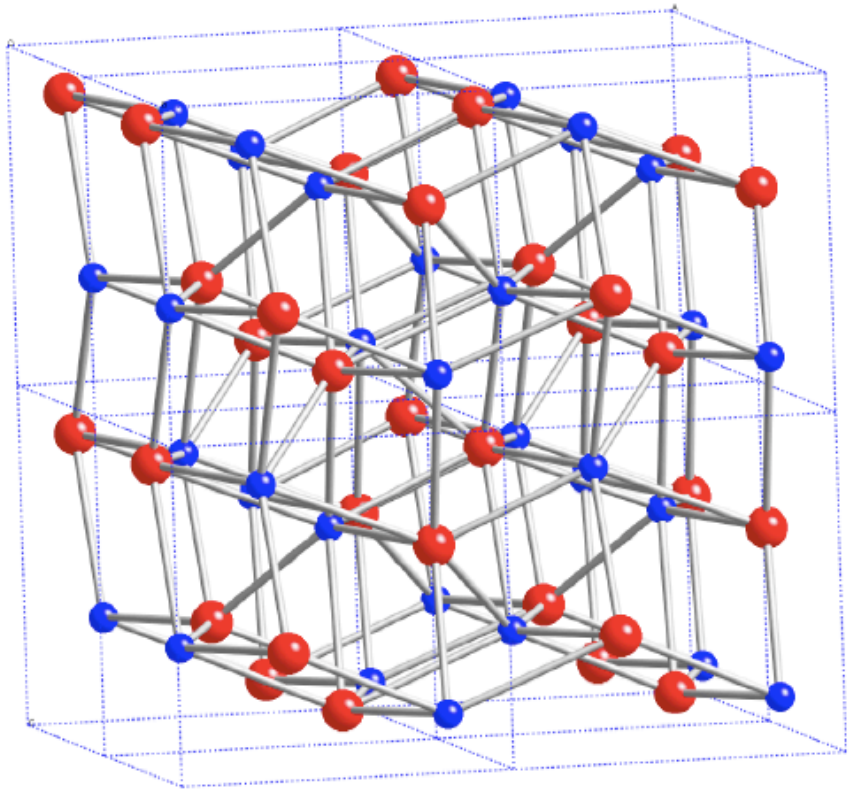
Dallas, Texas

Research supported by the Materials Sciences and Technology Division, Basic Energy Sciences, U.S. Department of Energy

Unusual Crystal Structure of Cubic FeSi

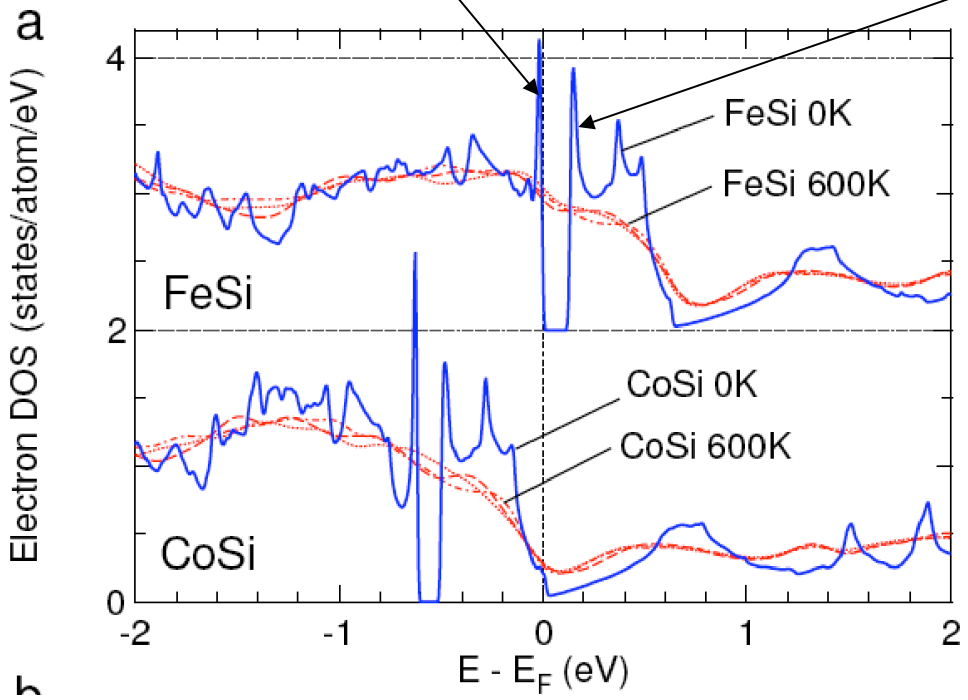
- ***No inversion symmetry***
- ***Fe is coordinated by 7 Si: 2.294 Å, 2.341 Å (x3), 2.515 Å (x3)***
- ***Si coordinated by 7 Fe***
- ***Fe-Fe nnn 2.753 Å***
- ***Fe-Fe nn distance in bcc Fe metal: 2.482 Å***

FeSi

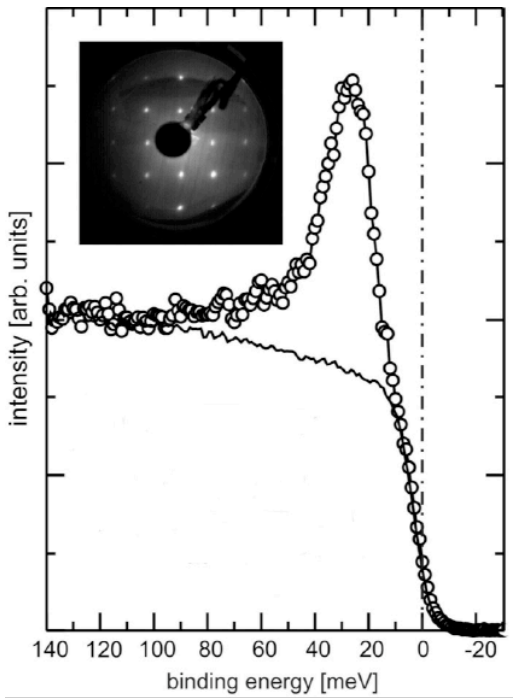


FeSi is a narrow gap semiconductor ($E_g \approx 0.1$ eV)
Possible material for low temperature (80 K) solid-state refrigeration?

Sharp peaks in the electronic density of states at both the conduction band and valence band edges



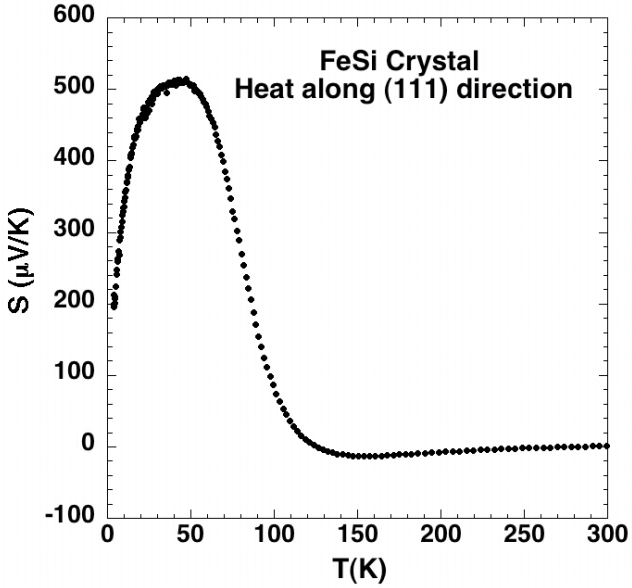
Delaire et al.PNAS (2011)

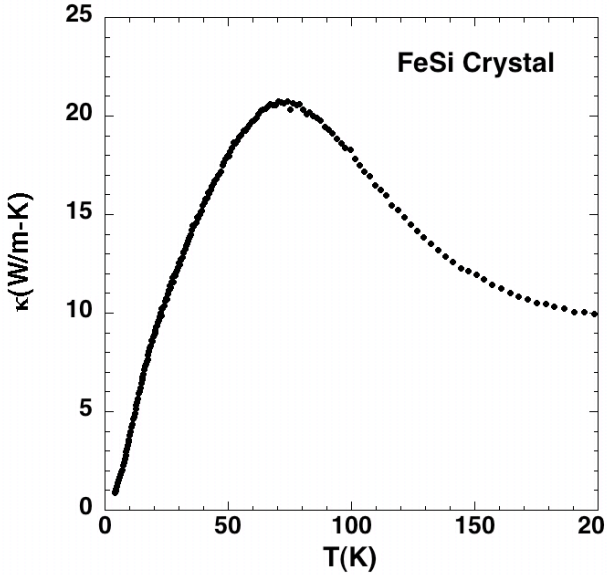


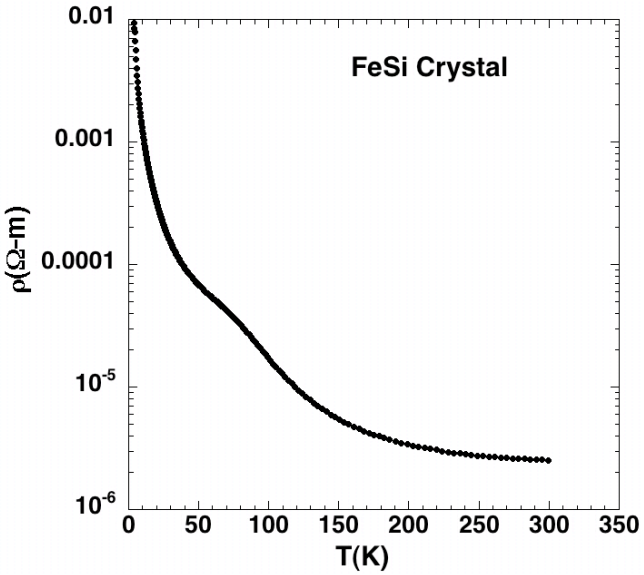
Klein et al. PRL 101 (2008) 046406

Note: for this material and related monosilicides DFT seems to get the gap and the sharp peaks in the DOS pretty close to experiment

Transport Properties of FeSi (single crystal)

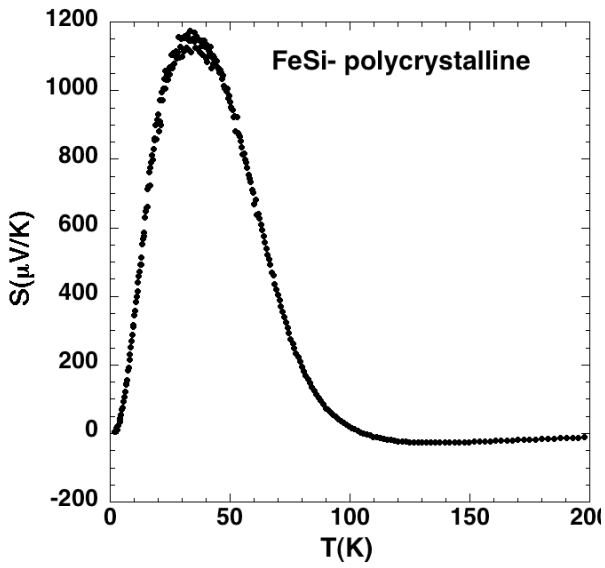


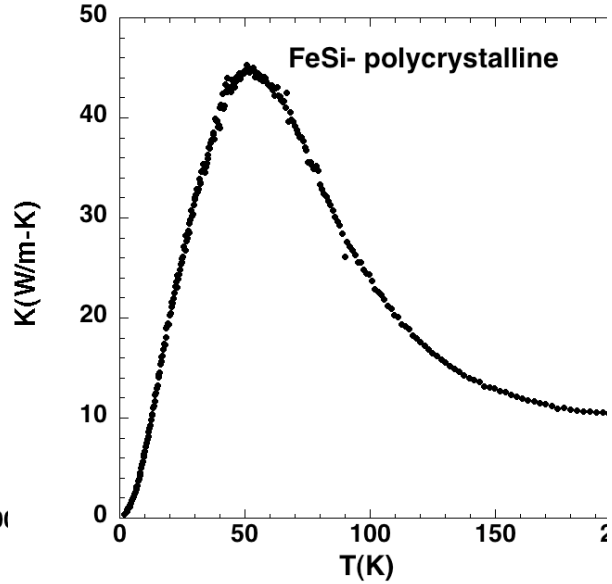


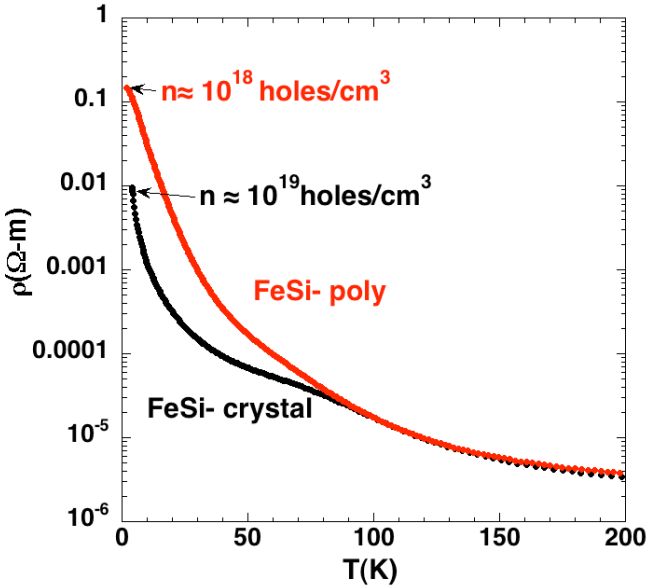


Debye Temperature ≈ 460 K
Sound velocity ≈ 3500 m/sec

Transport properties of FeSi Polycrystalline sample with lower extrinsic carrier concentration







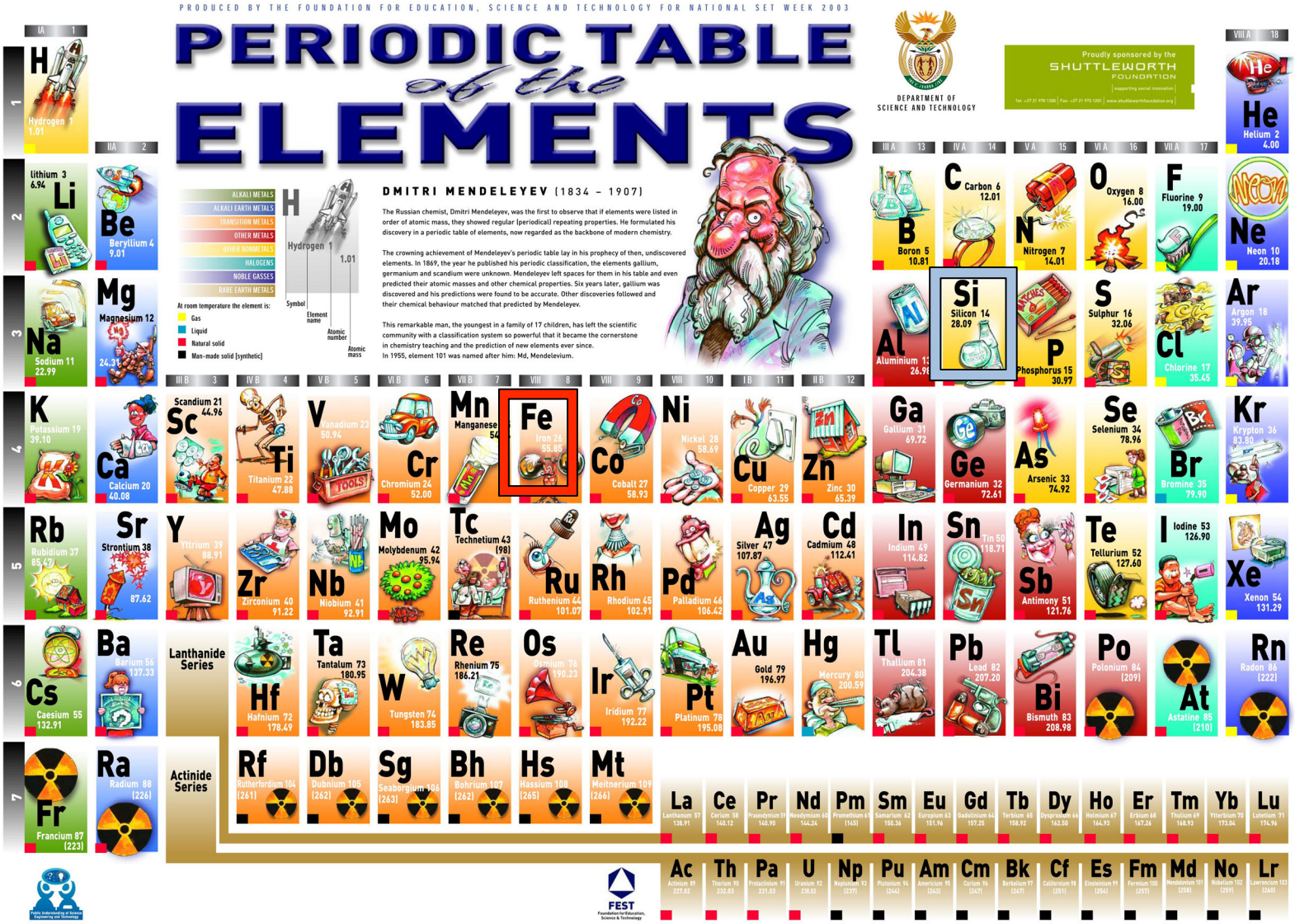
At 50K 99% of heat carried by phonons (WF)
yet change in carrier concentration produces
factor of 2 change in Kappa -electron-phonon scattering

Thermoelectric properties not very good (ZT≈0.013 at 70 K)
Need to Dope it !

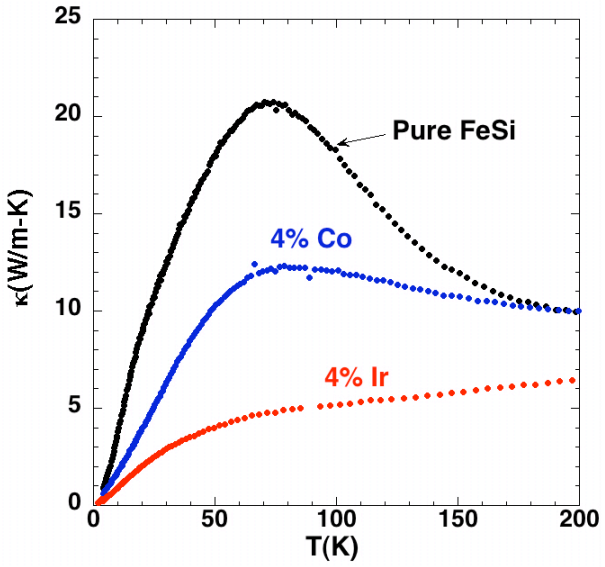
How to “dope” a semiconductor ?

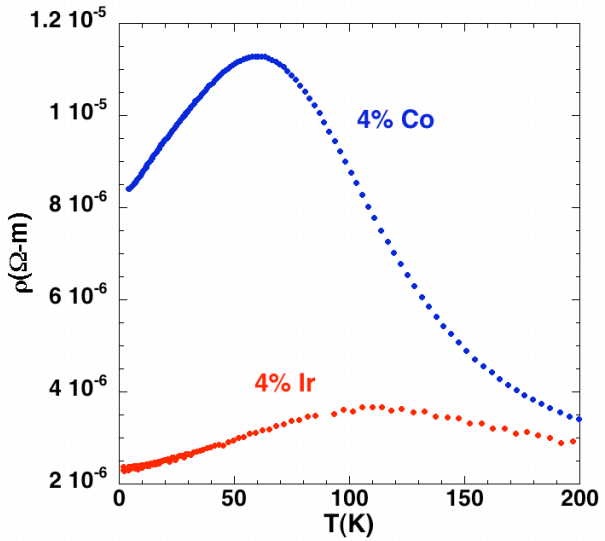
Very difficult to theoretically predict

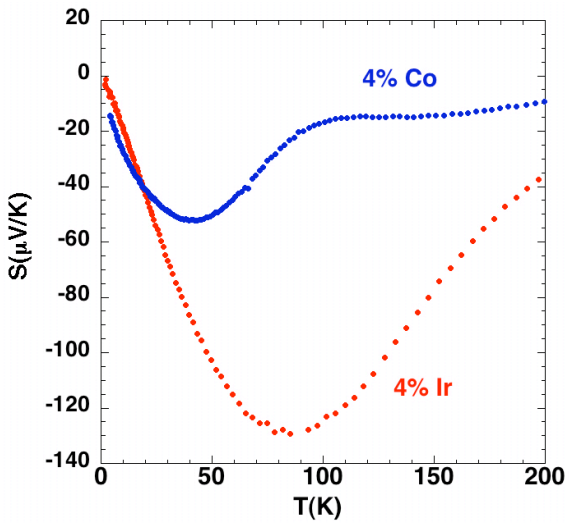
A. Zunger, APL 83 (2003) 57



Co vs Ir doping







Greater decrease in kappa with Ir doping explainable by point defect scattering formula derived by Klemens (1955)

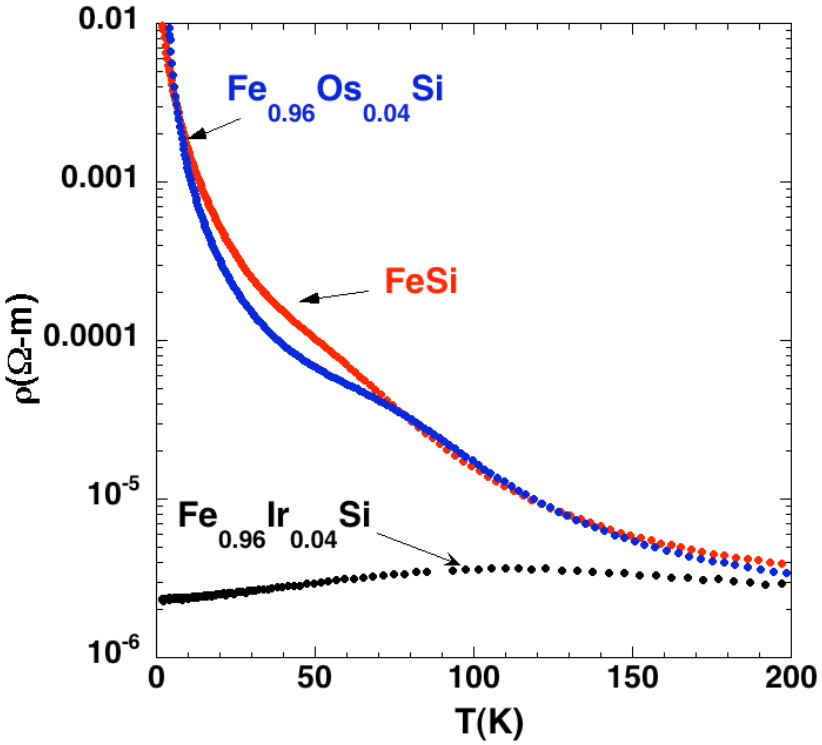
Goes like $(1-M_{dopant}/M_{av})^2$

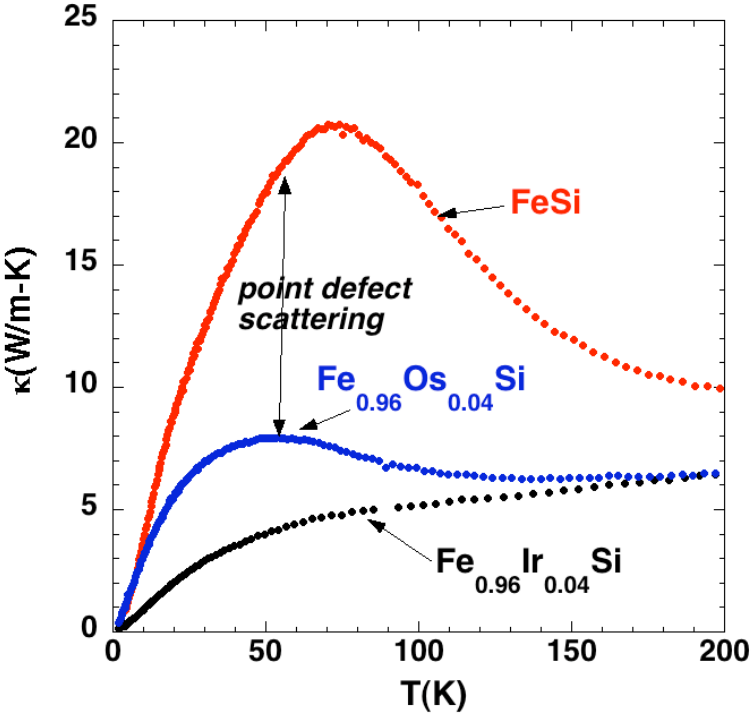
Thermoelectric values of all three properties better with Ir doping, but ZT_{MAX}= 0.08 at 90 K

Os (isoelectronic with Fe) vs Ir doping

Os doping- not much change in carrier concentration (relative to FeSi single crystal)

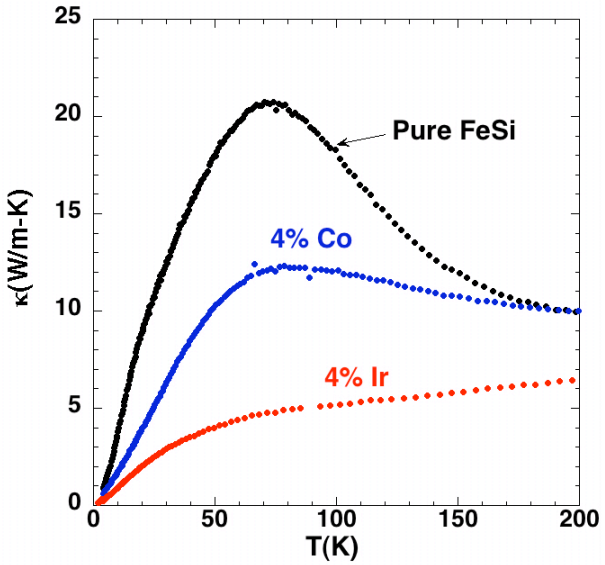
Ir and Os have similar masses :similar point defect scattering

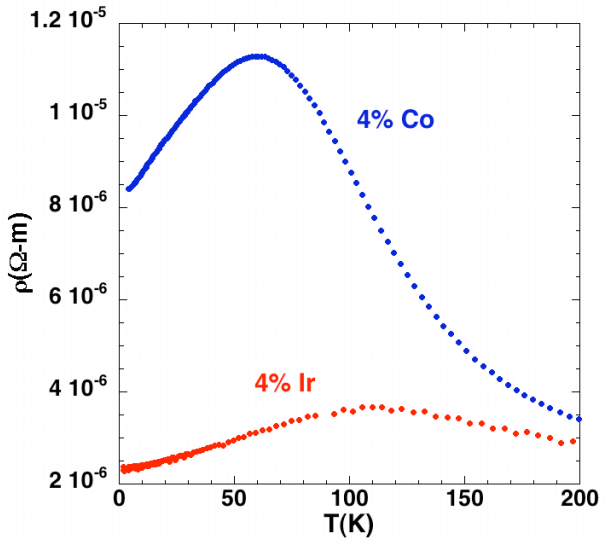


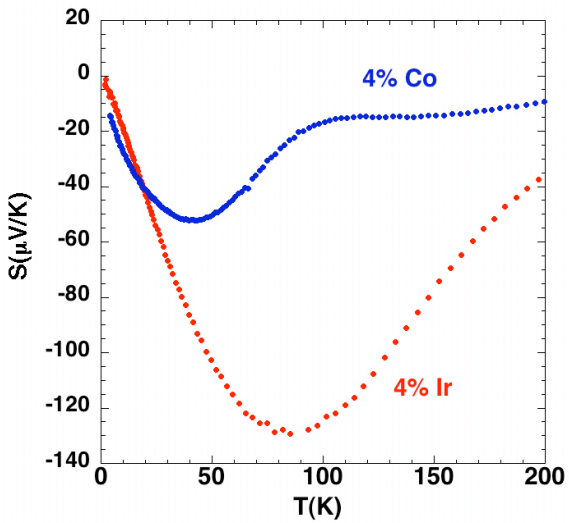


Note common approximation of independent $\kappa_{Lattice}$:
$\kappa = \kappa_{electronic} + \kappa_{Lattice}$ not
valid with strong electron-phonon scattering

Co vs Ir doping







Greater decrease in kappa with Ir doping explainable by point defect scattering formula derived by Klemens (1955)

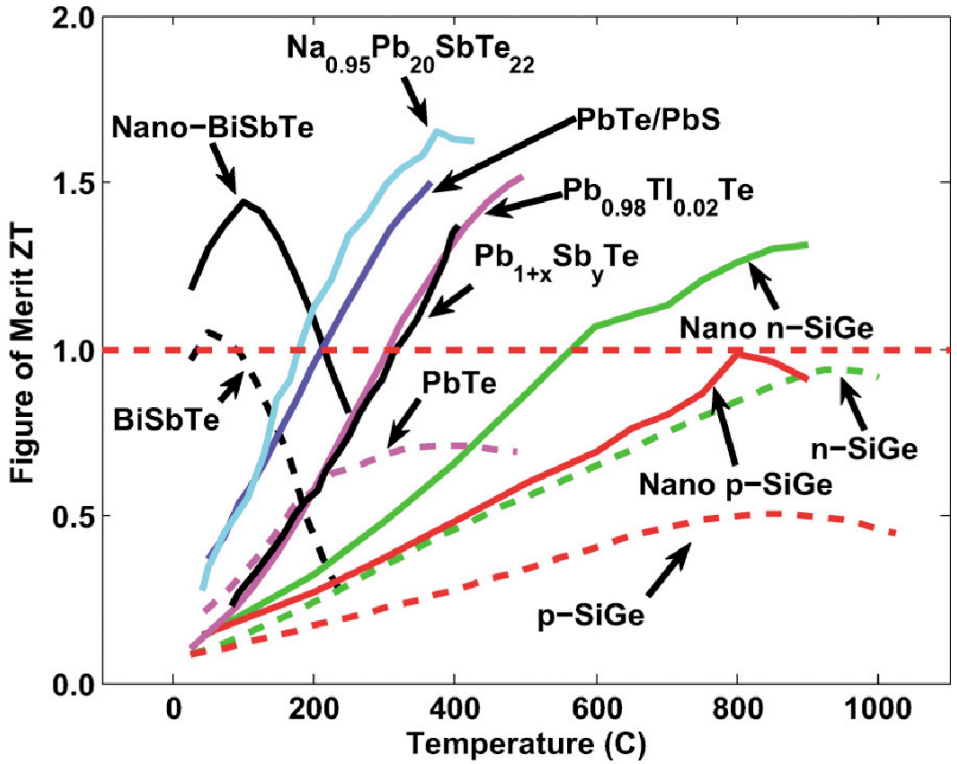
Goes like $(1-M_{dopant}/M_{av})^2$

Thermoelectric values of all three properties better with Ir doping, but ZT_{MAX}= 0.08 at 90 K

What about nanostructuring FeSi alloys?

Nanostructuring to lower Lattice Thermal Conductivity without comparable lowering of electrical conductivity: Net increase in ZT

Key Idea :
mean free path electrons << grain size << mean free path phonons



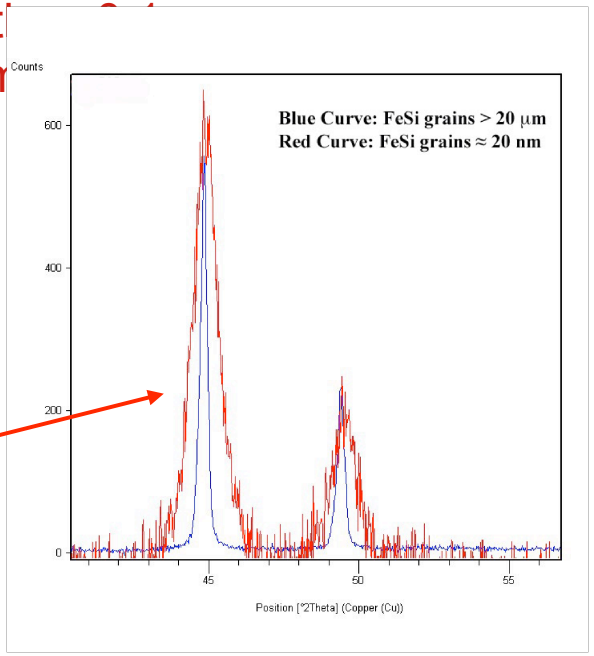
Examples of bulk systems where nanostructuring has improved ZT (Minnich et al. Energy&Env. Sci 2 (2009) 466)

Does "Nanostructuring" $Fe_{0.96}Ir_{0.04}Si$ Increase ZT?

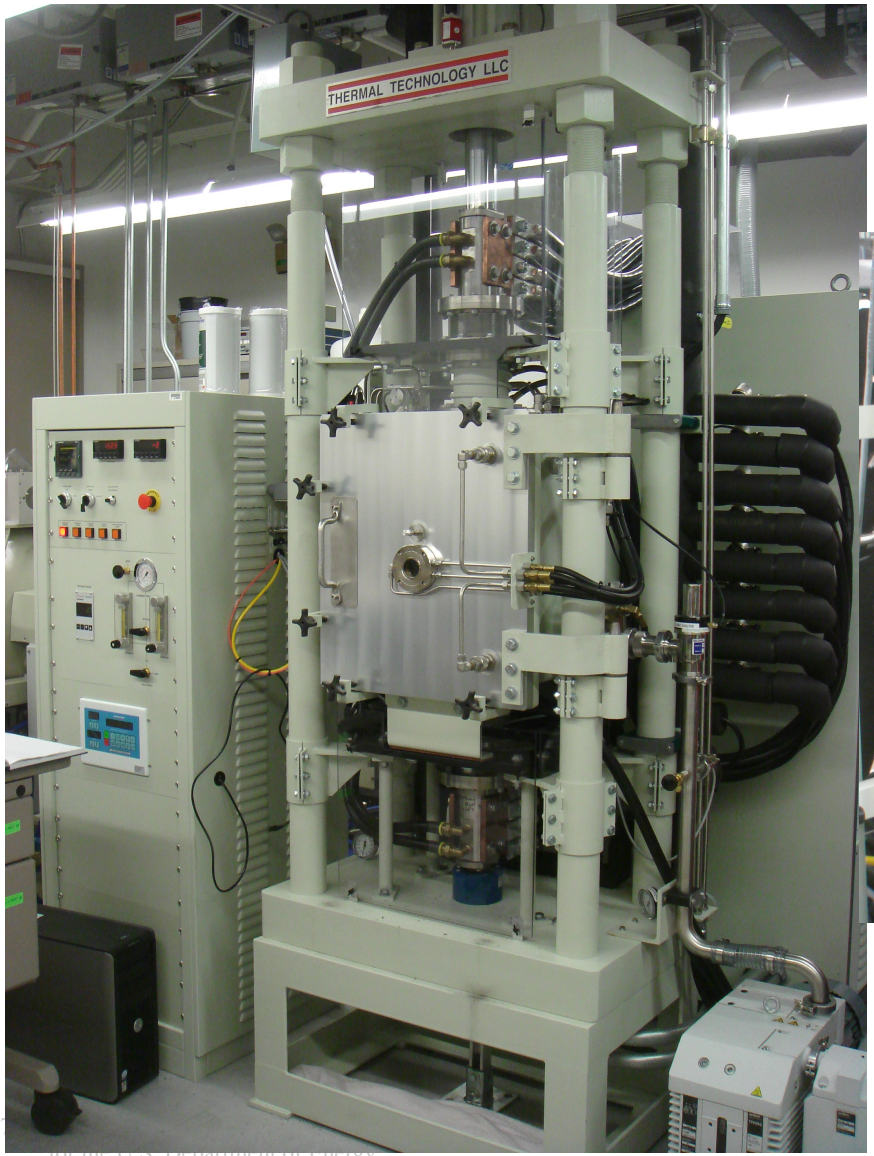
Samples of $Fe_{0.96}Ir_{0.04}Si$ Prepared 3 different ways:

1. Arc-melt elements together, slow cooling mm size grains
2. Arc-melt elements/ coarse ball mill 1h/Spark Plasma Sintering (SPS) near theoretical density mainly 20-100 micron size grains, some smaller
3. Arc-melt elements/coarse ball mill 1h/ planetary mill 40 h SPS to theoretical density mainly less t… micron som…

Broadening of X-ray peaks from plan milled powder suggest grains ≈ 20 nm



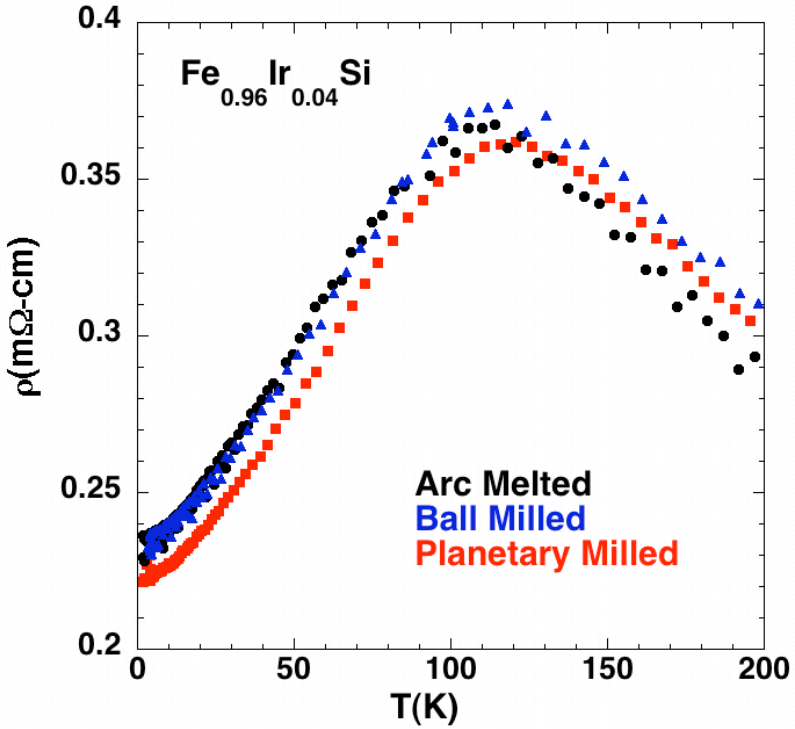
ORNL Spark-Plasma Sintering System:

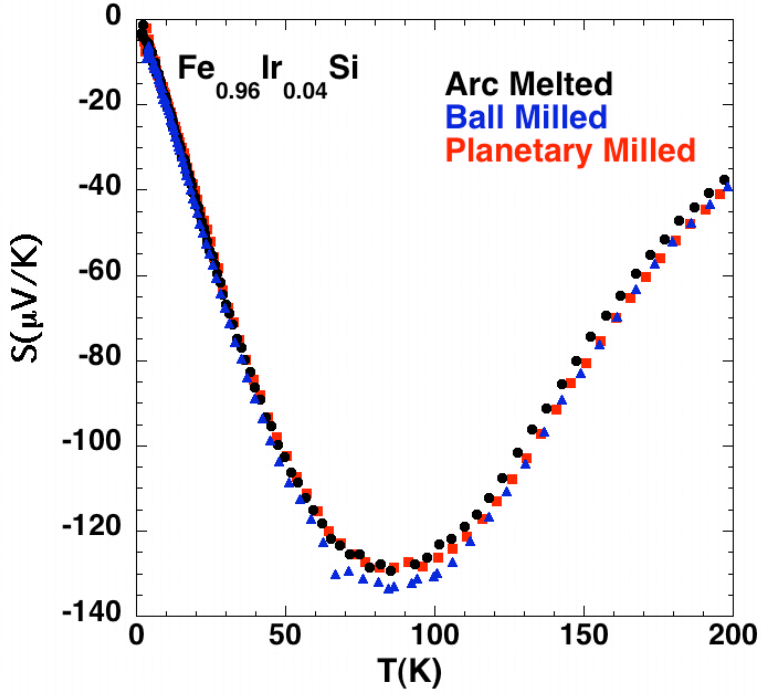


≈ 1000 Amps

≈ 800 kg (3/4” sample)

"Nanostructuring" $Fe_{0.96}Ir_{0.04}Si$- Transport Properties

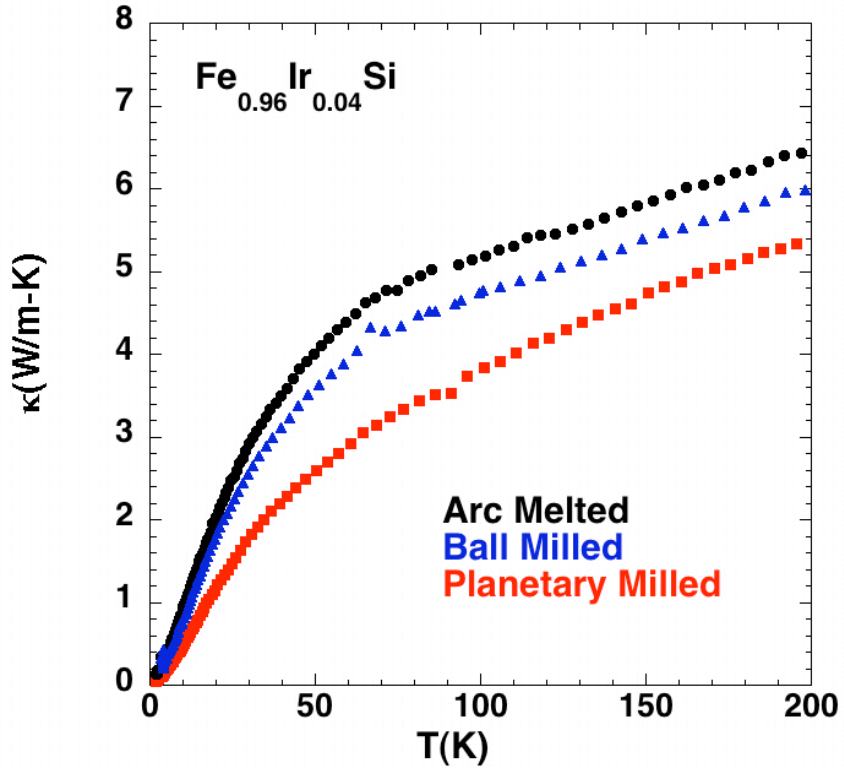


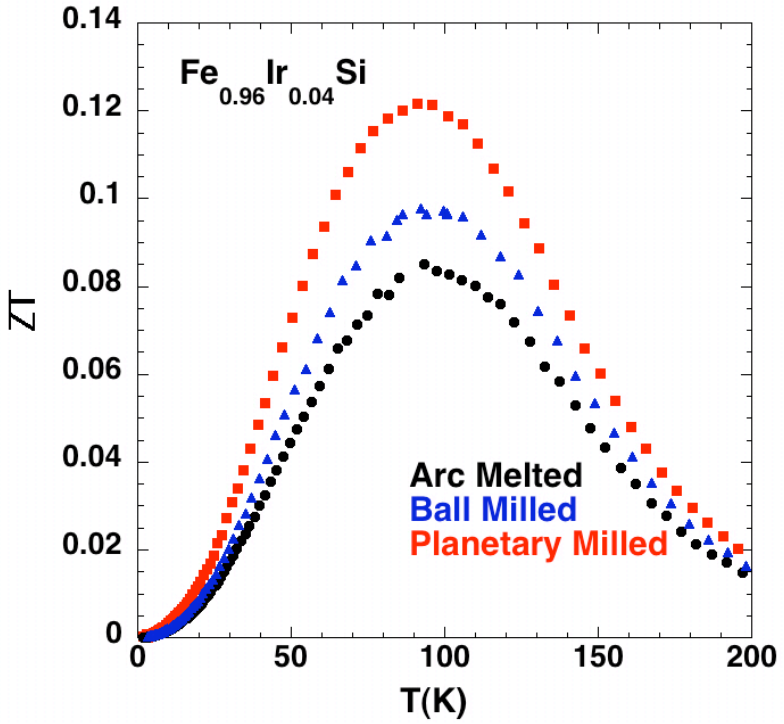


Resistivity and Seebeck Not Effected by Grain Size

BUT

“Nanostructuring”- 50% increase in ZT max due to decrease in thermal conductivity





Should Nanostructuring $Fe_{0.96}Ir_{0.04}Si$ Work ?

Electron mean free path:

$d_{electron} = 1.5\pi h/(e^2 k_F^2 \rho) \approx$ 3nm

At 90 K (8meV) mainly acoustic phonons excited from

$\kappa = 1/3 C_v v_s d$

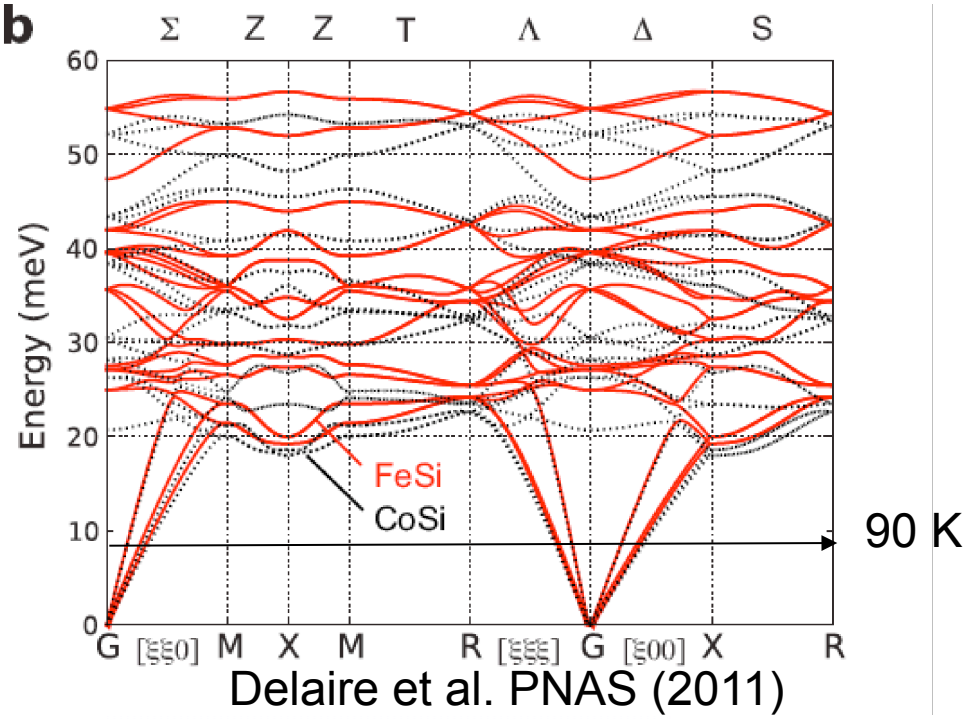
$d_{phonon} \approx$ 4nm

Not very Encouraging!

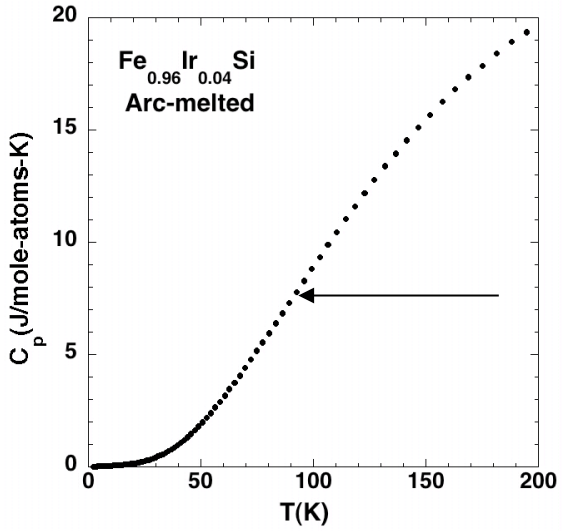
(analysis too simple!)

Phonon wavelength not considered

Which phonons are carrying heat?



Delaire et al. PNAS (2011)



Summary and Conclusions

1. Correlations don't seem to be that important in FeSi- DFT does a pretty good job. Many of other "anomalies" concerning material related to thermal disorder, small gap and effects of coupling between electrons and phonons – Discussed in next talk

2. Doping a semiconductor- need theory of which dopants will work the best

3. Illustrated why common approximation of independent $\kappa_{Lattice}$: $\kappa = \kappa_{electronic} + \kappa_{Lattice}$ clearly not valid with strong electron-phonon scattering

4. ZT of $Fe_{0.96}Ir_{0.04}Si$ enhanced by 50% by starting with small grains- need to increase further by a factor of 6 to be useful

5. To effectively use nanostructuring, there has to be a better fundamental understanding of which phonons (wavelength and energy) carry heat and how much.- theory

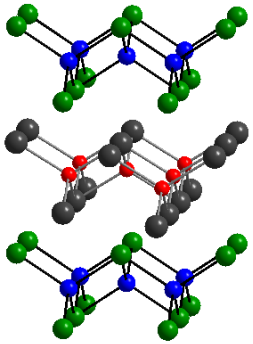
Collaborators and Contributors to this Work

Michael McGuire
Hsin Wang
Jane Howe
Olivier Delaire
David Singh
David Parker
David Mandrus
Hu Longmire
Andrew May
Jie Ma

Thank You !

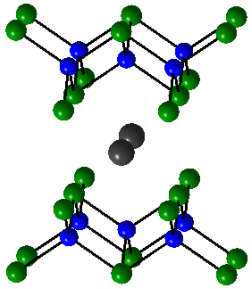
Square nets of tetrahedrally coordinated iron

LaFeAsO



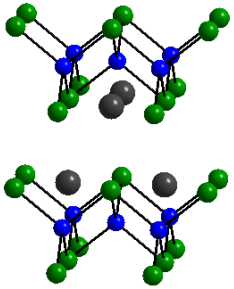
d(Fe-Fe) = 2.85 Å

$BaFe_2As_2$



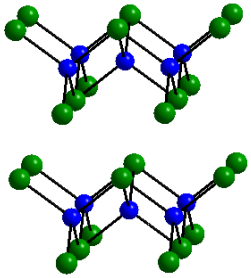
2.80 Å

LiFeAs

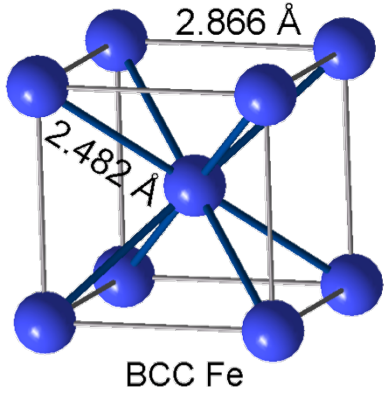


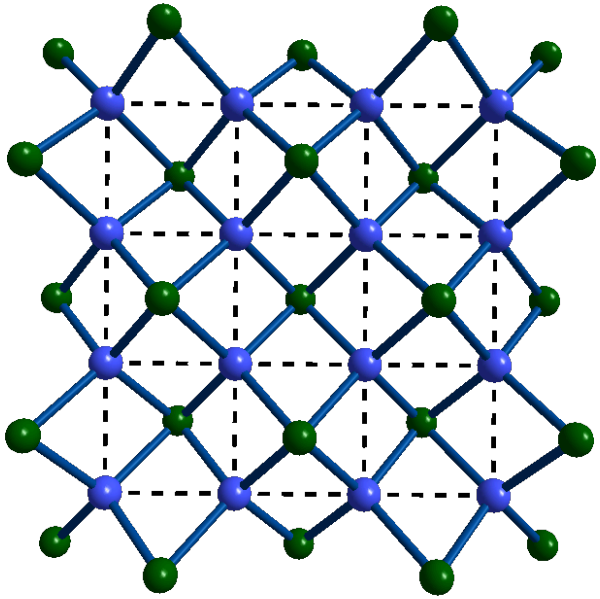
2.67 Å

FeSe



2.67 Å





FeAs / FeSe layer

Department of Materials
Science and Engineering ,

Effects of electronic structure on phonons (Main thrust of Olivier Delaire's research at ORNL)

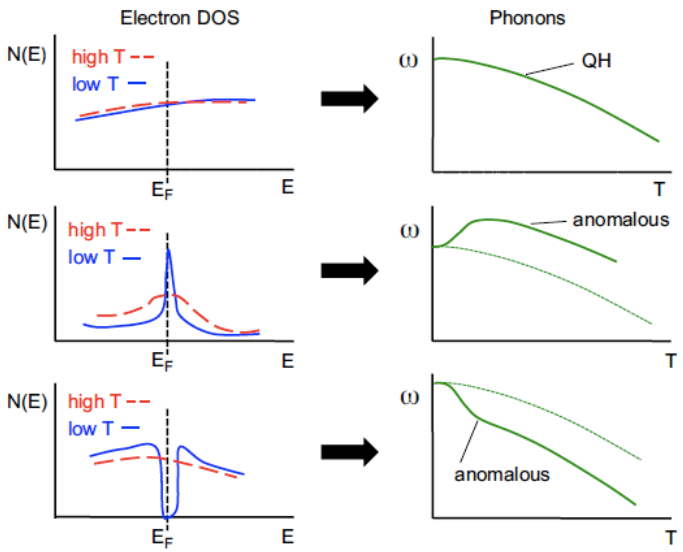
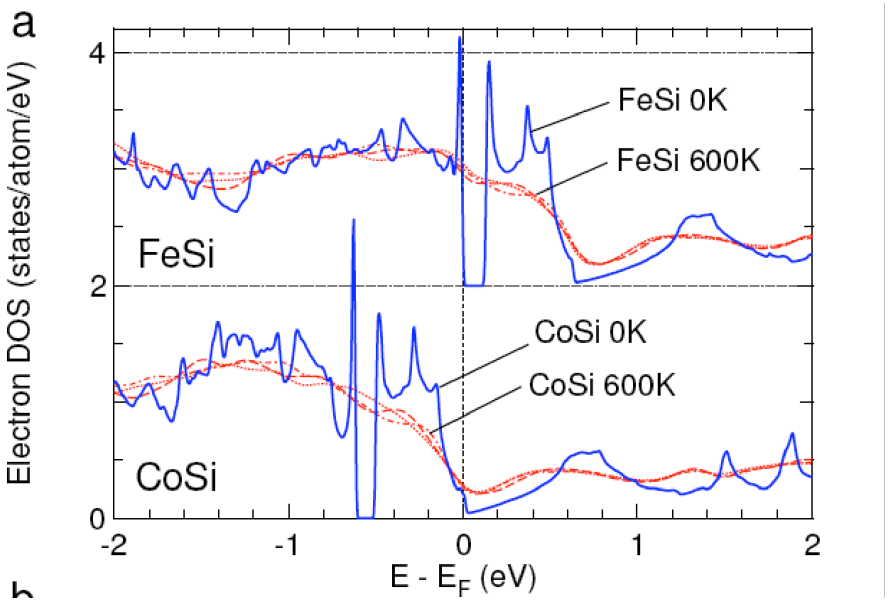
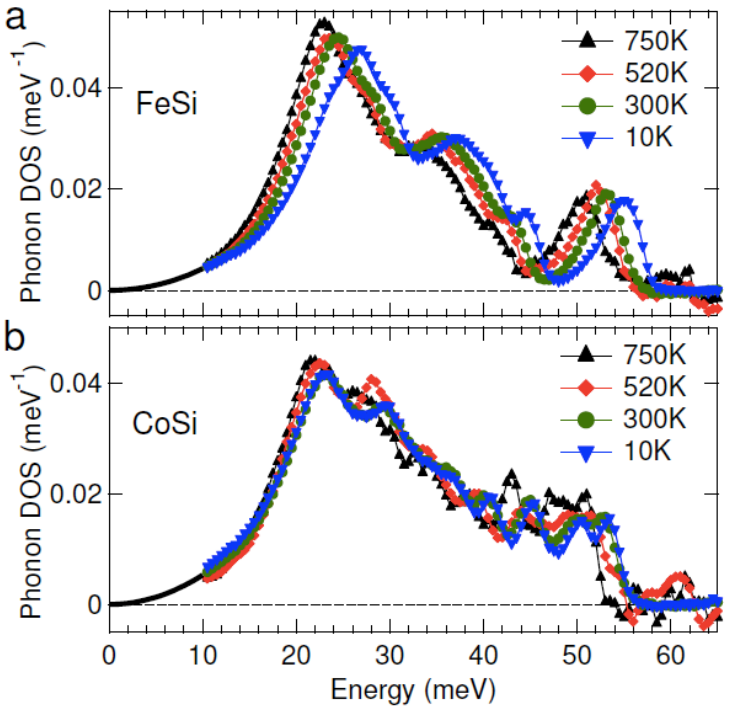


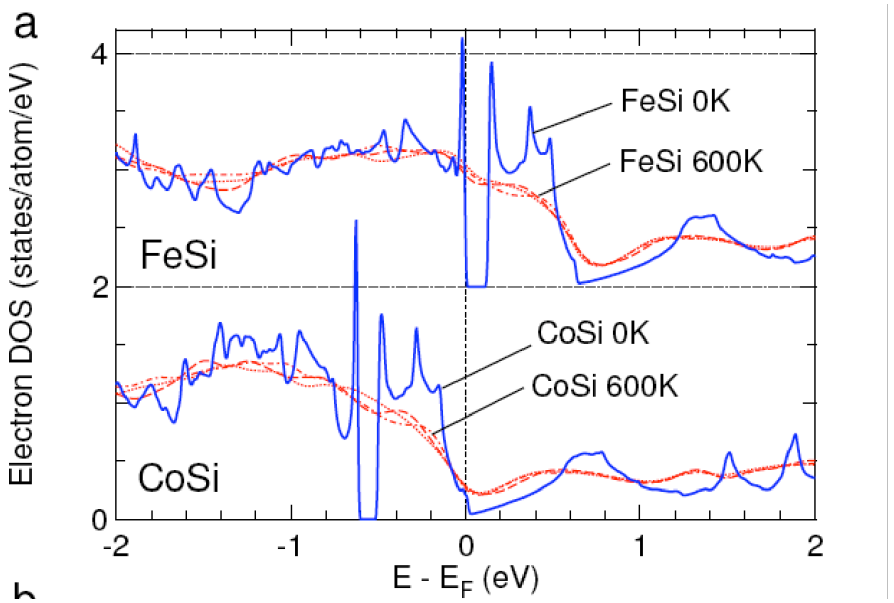
FIG. 1: Trends in the temperature dependence of phonon energies for different electronic densities of states (DOS). The Fermi energy is denoted by E_F, and $\langle\omega\rangle$ represents an average phonon energy, as function of temperature T.



First principles electronic structure Calculations for FeSi and CoSi

Phonon DOS from Inelastic Neutron Scattering
Delaire et al. submitted PRL

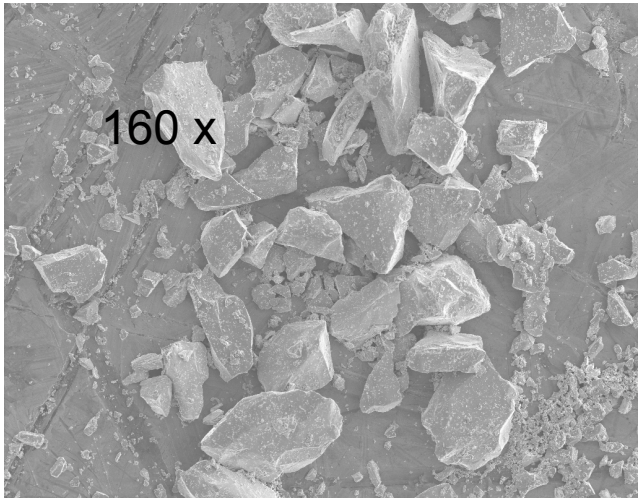




Conclusions: Thermal disorder plus strong coupling between electrons and phonons in FeSi leads to anomalous softening of phonons with temperature. At the same time the renormalization of the electronic structure induces a semiconductor-to-metal transition with increasing temperature. Net Result: T=0 gap of FeSi (0.15 eV) closes at a relatively low temperature ≈ 200-300 K.

Ball Mill vs Planetary Mill: $Fe_{0.96}Ir_{0.04}Si$

Ball Mill 2h/ Ar gas



Plan Mill 40 h/ He gas