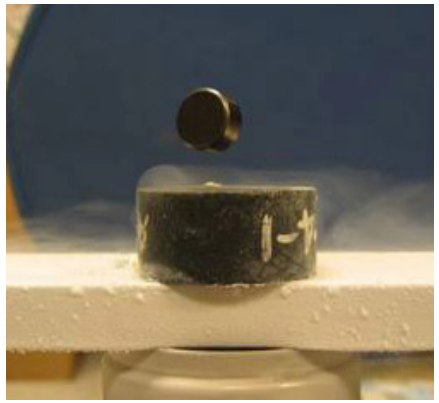
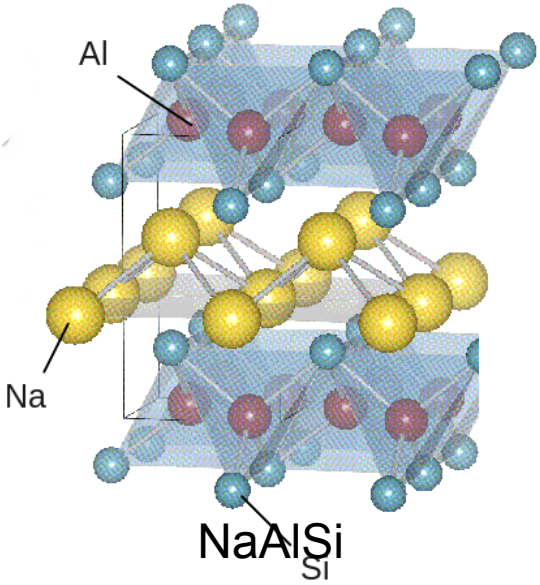
Superconductivity and two dimensionality: experimental facts, theoretical issues, novel materials

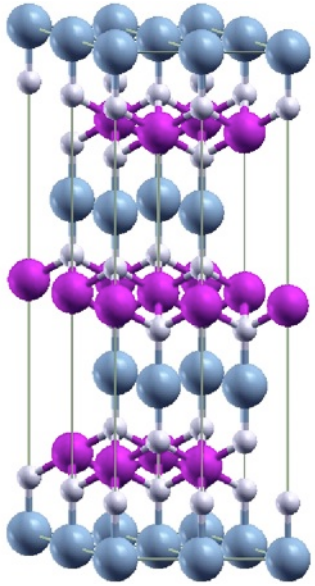
Warren E. Pickett
University of California Davis





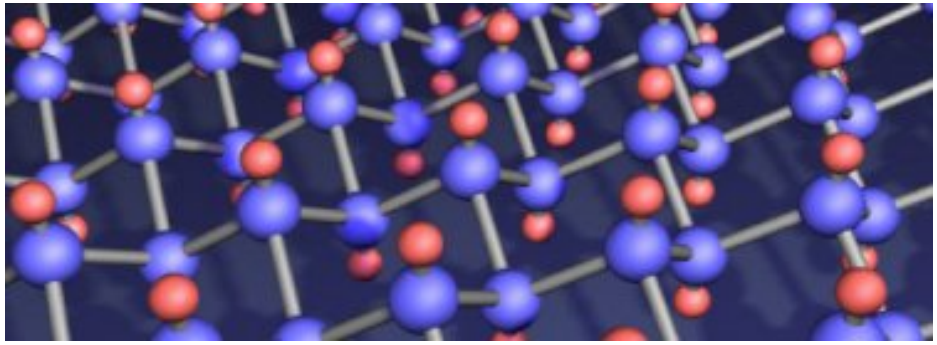
NaAlSi

Emphasis: el-ph coupling and nonmagnetic el-el coupling → higher T_c in this talk.



$CuAlO_2$

Graphane CH



Ch. 11: Superconductors, W. E. Pickett

Coming soon: Lectures on Superconductivity Theory

Ch. 10: Correlated Superconductivity, A.-M. Tremblay

Ch. 12: Electron-Phonon Coupling, R. Heid

Ch. 13: Eliashberg Theory, G. A. C. Ummarino

Educational Sites for Superconductivity

University of Cambridge *Lectures on Superconductivity*
http://www.msm.cam.ac.uk/ascg/lectures/introduction/welcome.php

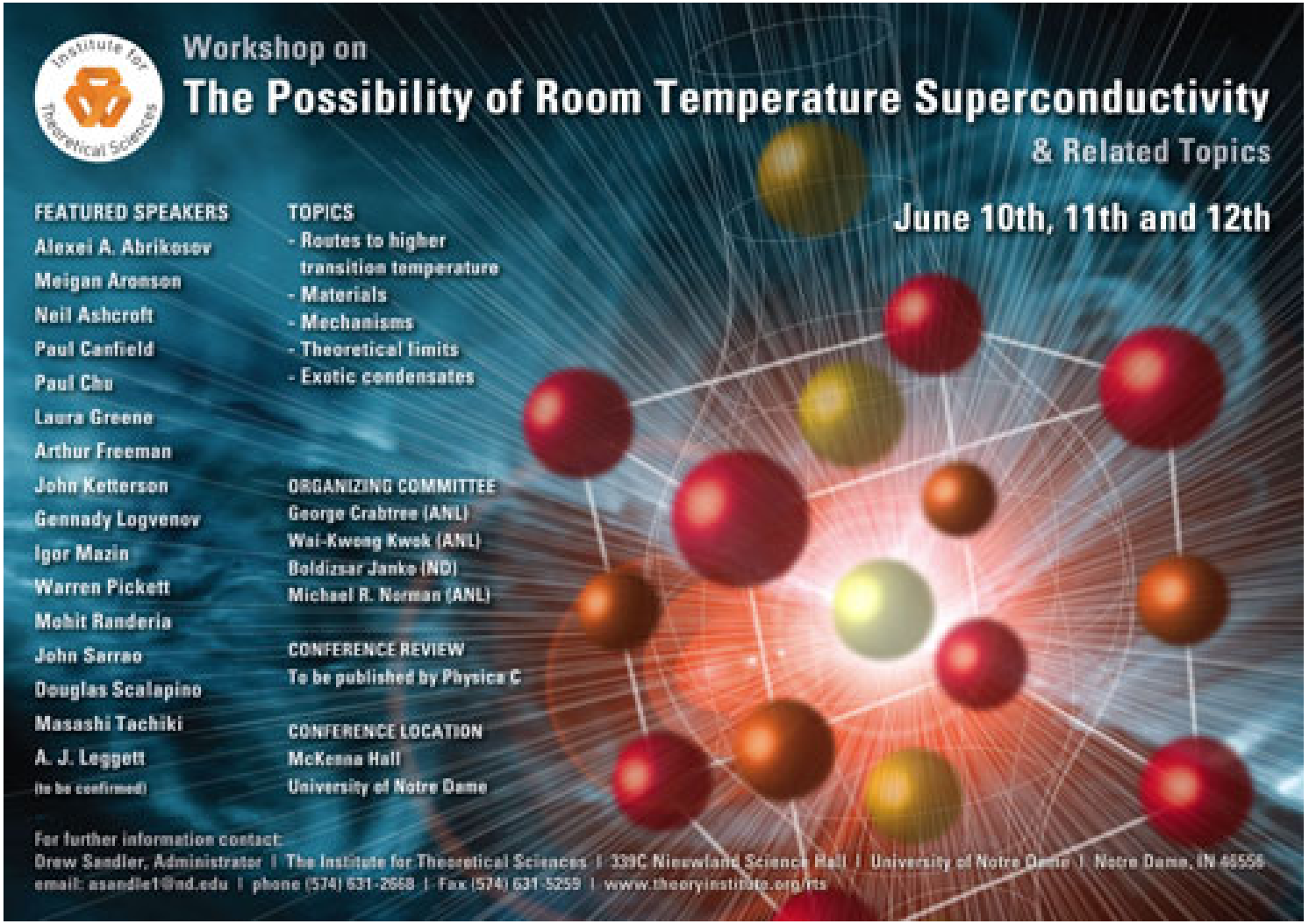
MIT Open Courseware: *Applied Superconductivity*
Very long URL, search for it.

Several others, mostly less extensive.

Also: work through the first 12-15 pages of BCS paper (Phys Rev, 1957)

And the book: *Superconductivity*, by J. R. Schrieffer (1964)

Word to the wise: regarding new, high temperature superconductors –
don't believe all (or even much) of what you find online.



The Path to Room Temperature Superconductivity

Hotel Alexandra

Loen, Norway

17 - 23 June 2007

Organizers/Sponsors

Dr. Harold Weinstock, European Office of Aerospace R&D (AFOSR)
Prof. Paul C. W. Chu, Houston International Materials Forum. U. Houston
Prof. Horst Rogallo, U. Twente

All Presentations (link added 23 April 2010)

Upcoming Superconductivity Workshop
(almost certain)

"(Toward) Room Temperature Superconductivity"

Organizers: E K U Gross, A Sanna, L Boeri

June-July 2014, Leiden, The Netherlands

How to attract funding……

ASTONISH

Atomic-scale STudies Of the Nature of and conditions for Inducing Superconductivity at High-temperatures

A 2013 ERC funded research project

R. Wiesendanger, Univ. of Hamburg

In the framework of the ERC Advanced Grant "ASTONISH" (Atomic-scale STudies Of the Nature of and conditions for Inducing Superconductivity at High-temperatures), the University of Hamburg is **seeking outstanding and enthusiastic young researchers with a strong record of creativity and achievements in the area of superconductivity** in MBE grown sample systems. The project aims at a novel surface-science based approach to unconventional superconductivity, combining atomically controlled vertical growth and lateral atomic-scale manipulation tools with a unique set of atomic-resolution characterization techniques, including elastic and inelastic scanning probe spectroscopy with spin resolution at relevant energy scales…….

This announcement is currently active.

Why 2D? why low-Z? why doped insulators?

Why 2D?
- examples (following slides): many classes of good sc'ors
- phase space [N(E)] is more favorable than in 3D
- electronic and phononic structure may be distinctive

Why low-Z?
- mass is smaller → good for el-ph high T_c
- bonding is stronger → stronger el-ph coupling
- other factors?? many classes of good 2D sc'ors

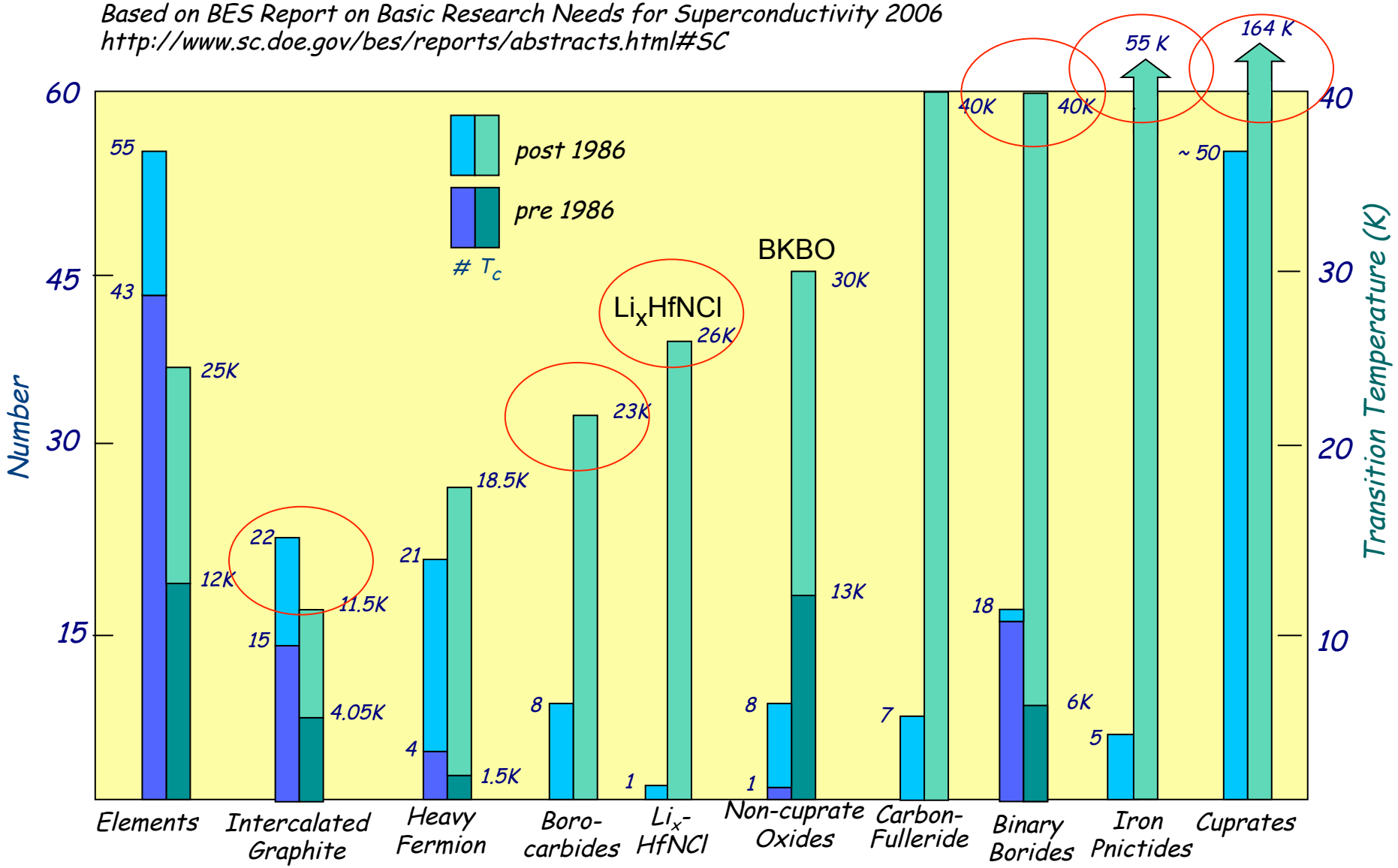
Why doped insulator? Much of the point of this talk

New Materials: Recent Superconductor Discoveries

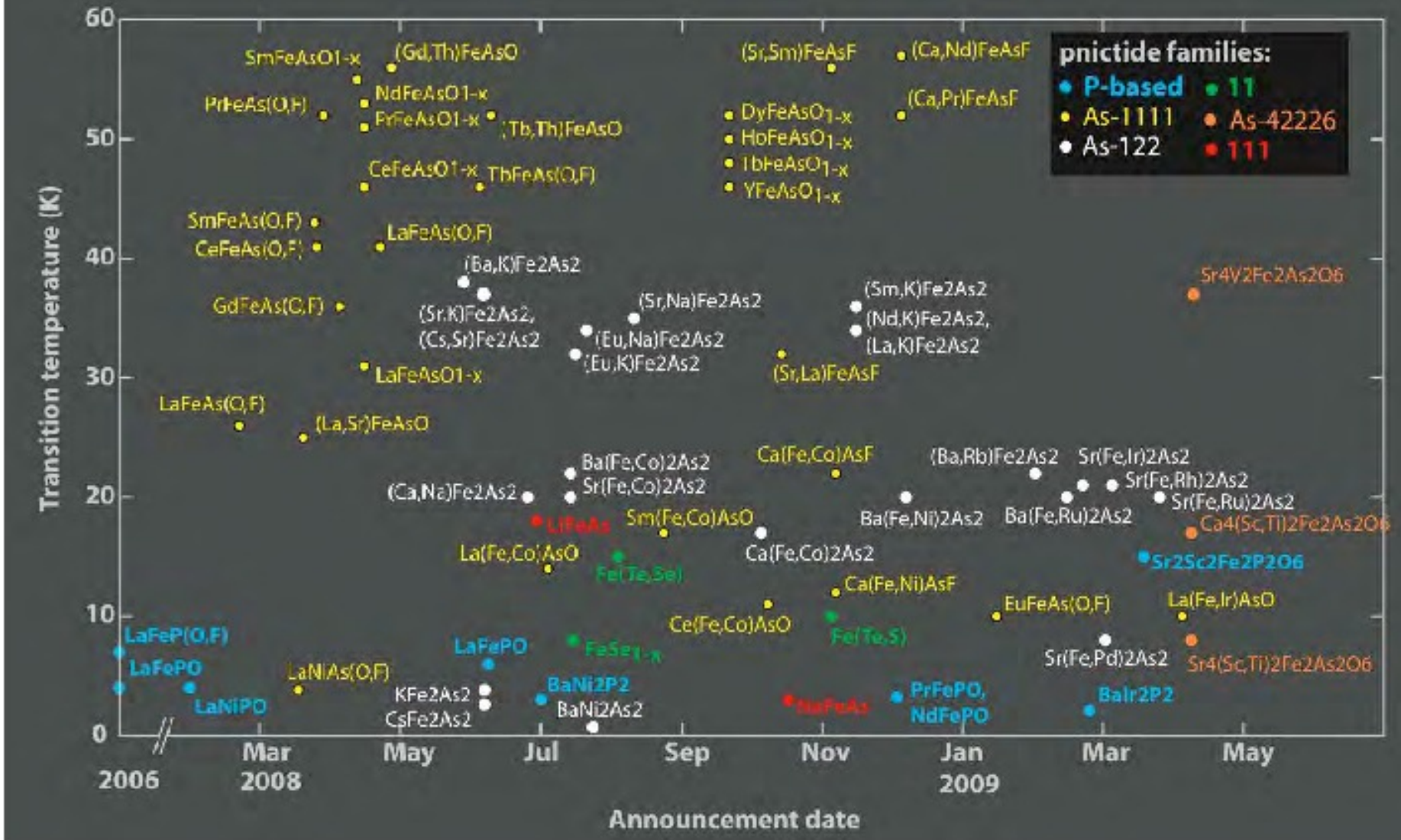
Courtesy:
G. W. Crabtree

2D materials

Based on BES Report on Basic Research Needs for Superconductivity 2006
http://www.sc.doe.gov/bes/reports/abstracts.html#SC



A partial history of the pnictide superconductors



(chemical formulas: PrFeAs(O,F) = $PrFeAsO_{1-x}F_x$, e.g.)

Think in terms of new compounds…..

Recall:

- Cuprates began with La-Ba-Cu-O with T_c=30 K
- Fe pnictides began with LaONiP with T_c= 5K

So: pay attention to new discoveries.

$Bi_4O_4S_3$ system

Mizuguchi et al., arXiv:1207.3145 was an early paper. A dozen or two papers available now.

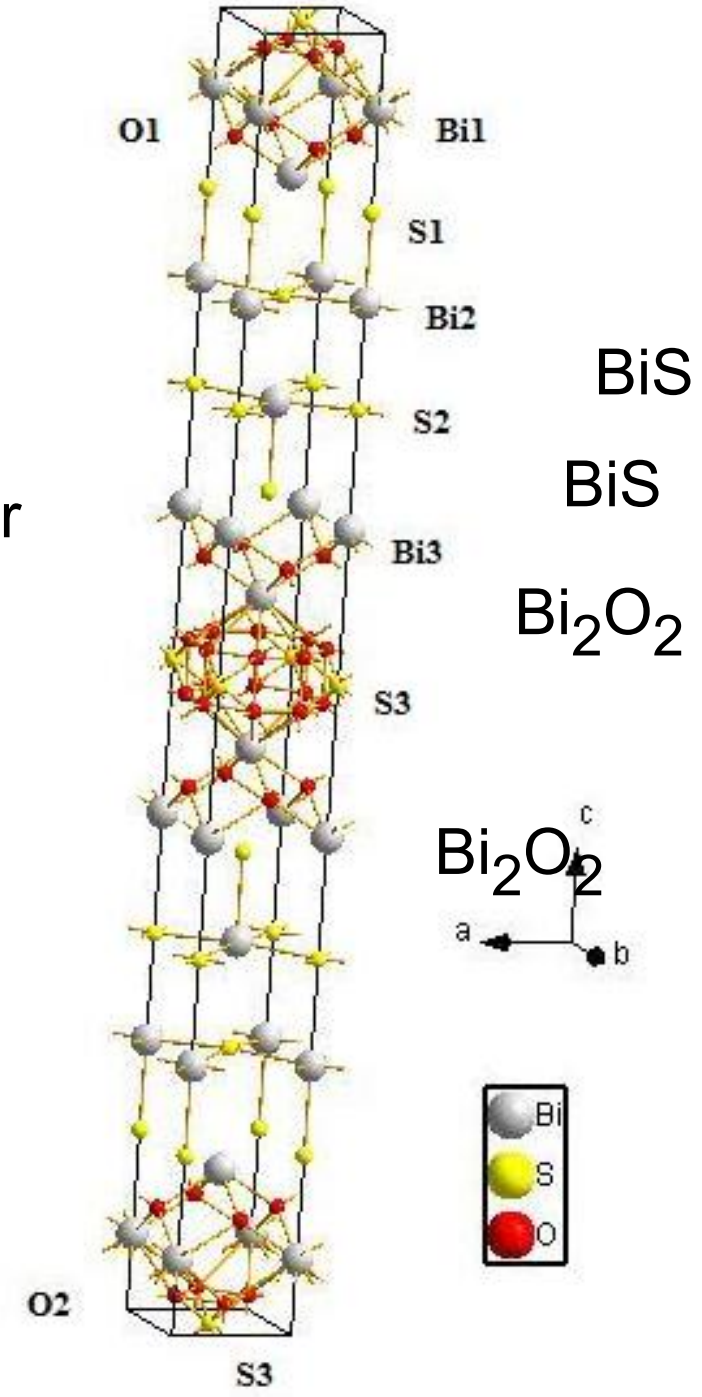
Superconducting in the Bi-S bilayer

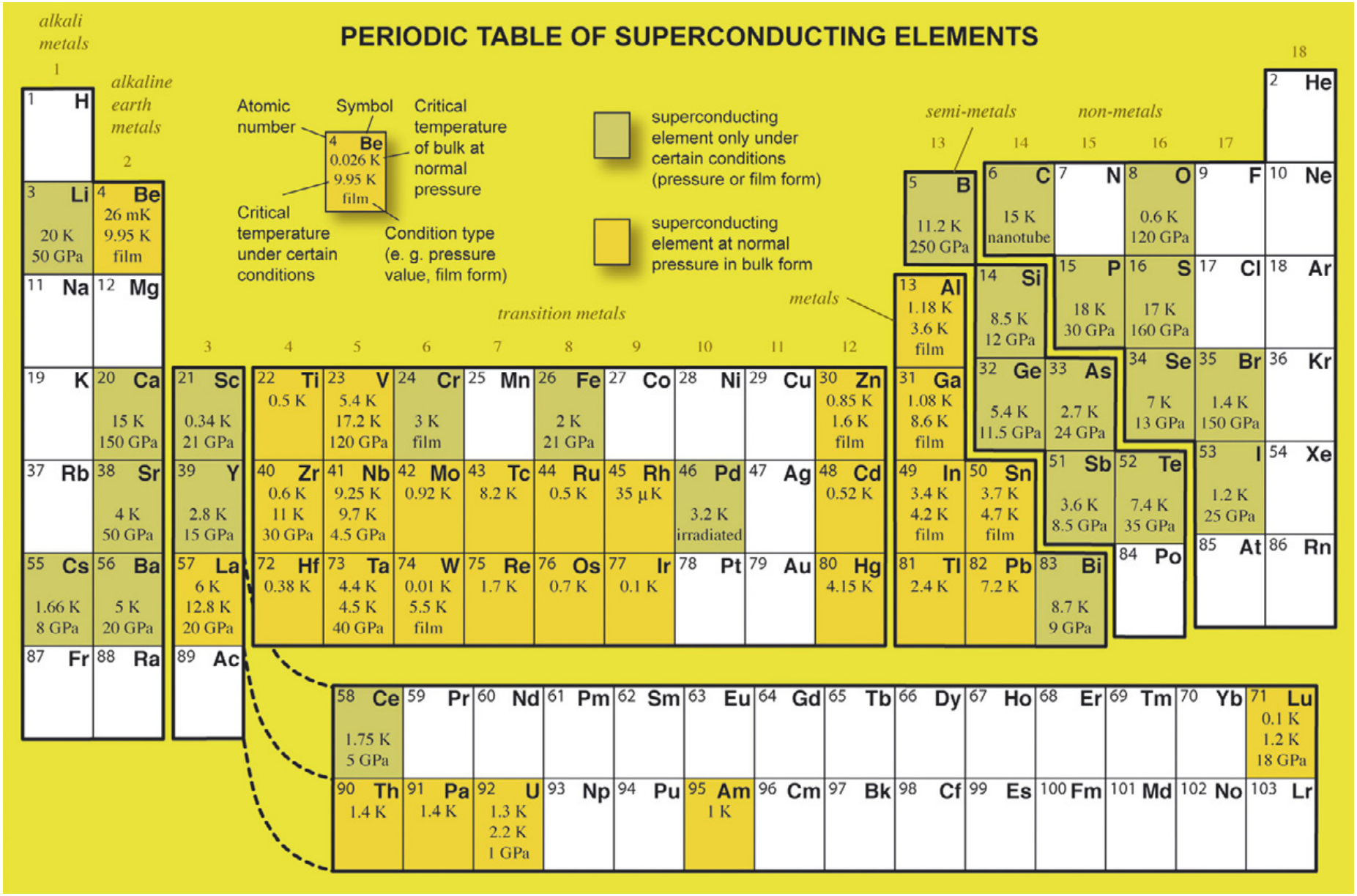
at T_c = 4.5K

Apparently, electron carriers in the Bi p_x, p_y bands

Nonstoichiometric, i.e.doped.

A new platform for higher T_c?
Not yet?

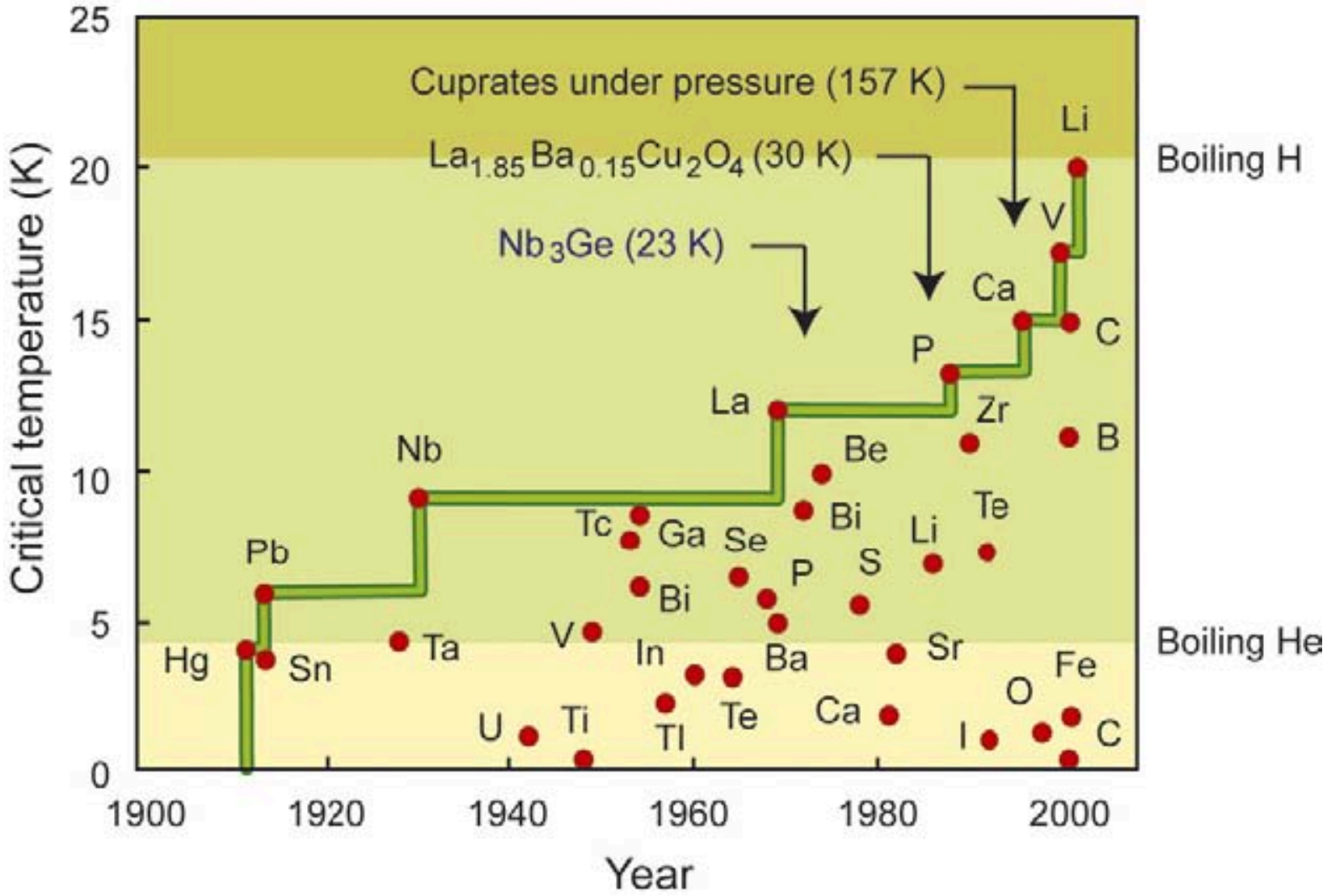




Y 20 K at 115 GPa, Ca 25 K at 161 GPa

C. Buzea *et al.,* Supercond. Sci. Technol. **18** (2005) R1–R8

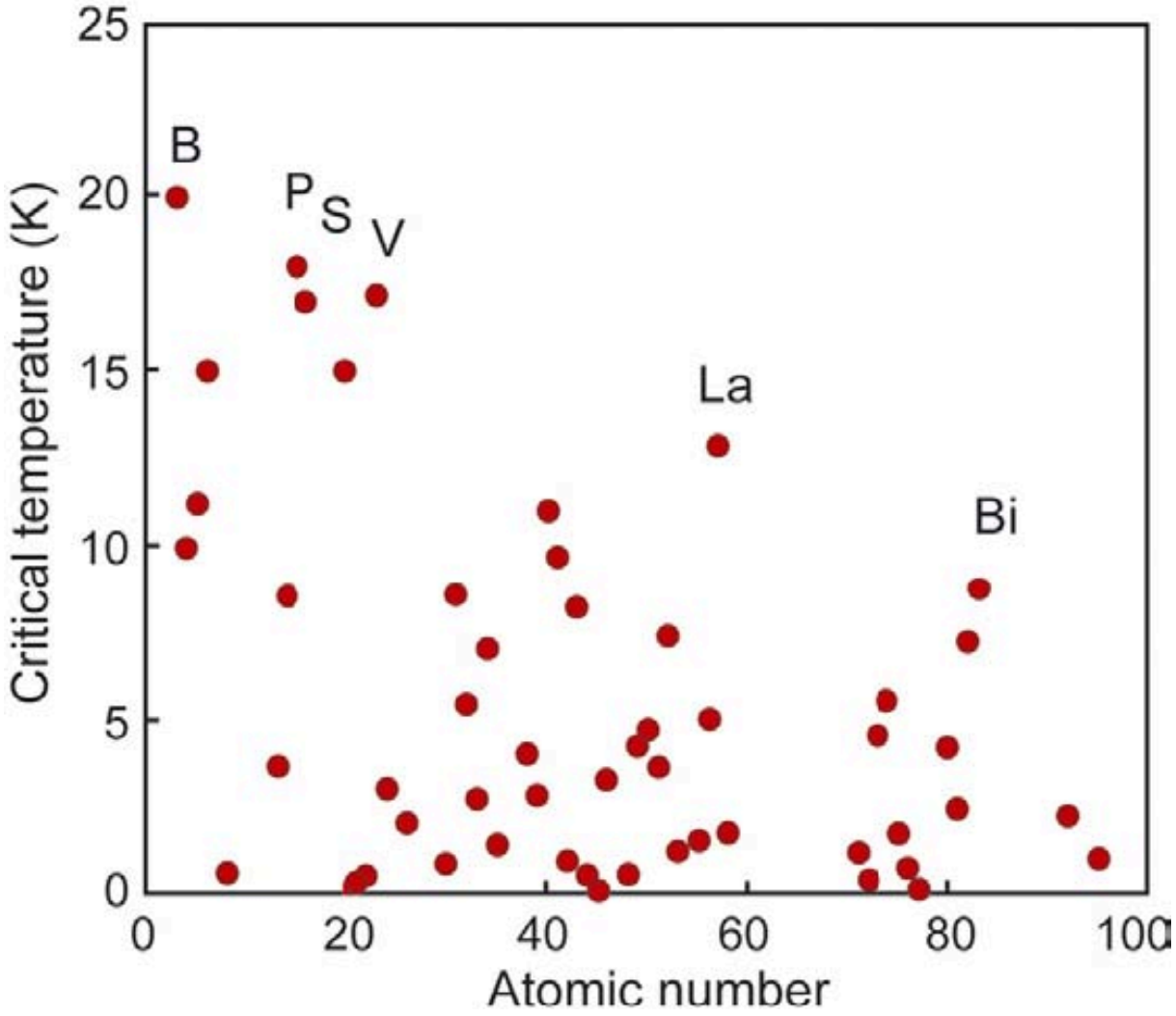
Elemental Superconductors versus Time



- Historical development of the critical temperature of simple elements

(C. Buzea *et al.,* Supercond. Sci. Technol. **18** (2005) R1–R8)

Elemental Superconductors versus Z



Highest critical temperature of simple elements plotted vs. atomic number.

[C. Buzea *et al.,* Supercond. Sci. Technol. **18** (2005) R1–R8]

(missing Li)

1972 Nobel Prize in Physics

"For their jointly developed theory of superconductivity,
usually called the BCS theory."
[This is the weak-coupling theory.]



John Bardeen, Leon Cooper, J. Robert Schrieffer

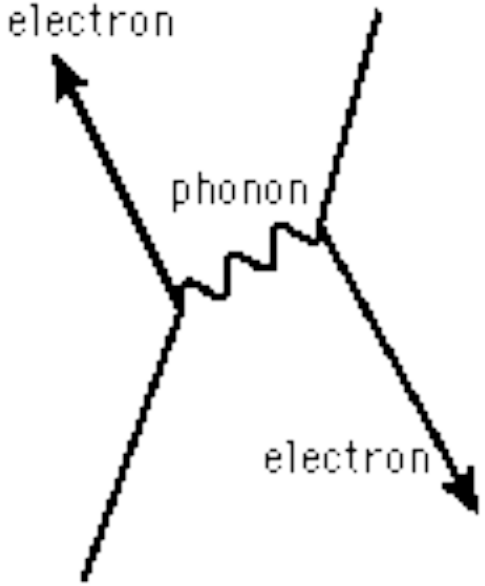
Phys. Rev. 108, 1175-1204 (1957)

The genuine article: Eliashberg theory for real materials,
including strong coupling.
Scalapino, Schrieffer, Wilkins, PR ~ 1965

Electron-Phonon Coupling

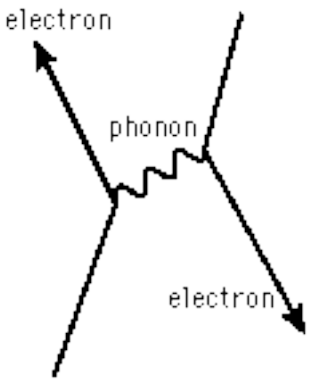
Hamiltonian for band electrons coupled to harmonic phonons:

$$H_{e-ph} = \sum_{ks} \epsilon_{ks} c^{\dagger}_{ks} c_{ks} + \sum_{q\nu} \hbar\omega_{q\nu} (b^{\dagger}_{q\nu} b_{q\nu} + \frac{1}{2}) + \sum_{ks} \sum_{q\nu} [M^{\nu}_{k,q} c^{\dagger}_{k+q,s} c_{k,s} b_{q\nu} + h.c.]$$



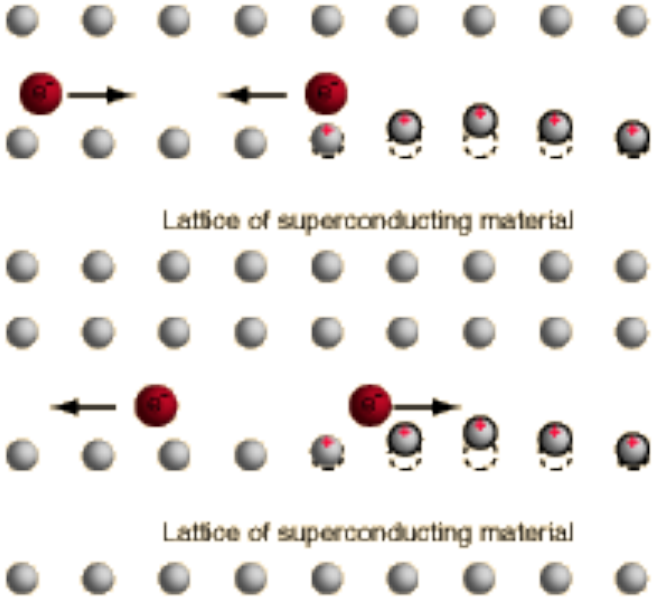
Matrix element: mplitude for scattering from the one-electron state $|\boldsymbol{k}j\rangle$ to the state $|\boldsymbol{k}+\mathbf{Q}\ j'\rangle$ via the phonon $\mathbf{Q}\nu$

$$M^{\vec{Q}\nu}_{\vec{k}+\vec{Q}j',\vec{k}j} = \left\langle \vec{k}+\vec{Q}j' \left| \delta^{\vec{Q}\nu} V_{eff} \right| \vec{k}j \right\rangle$$



The scattering diagram

The physical picture (a crude version)



An electron moving through the lattice disturbs the positions of the ions (electron-phonon interaction), a later electron experiences the deformation, with a net attractive interaction.

$v_{ph}/v_{el} << 1$ is the expansion parameter in perturbation theory

1st three: Bernd Matthias's rules for finding high T_c superconductors (~1970).
Last four: extended to ~1980 understanding.

1. Must have d electrons (not just s-p, nor f)
2. High symmetry is good, cubic is best
3. Need a peak in density of states at Fermi level
4. Must spread the coupling over all phonons
5. Coulomb interaction must be docile
6. Stay away from oxides
7. Stay away from magnetism

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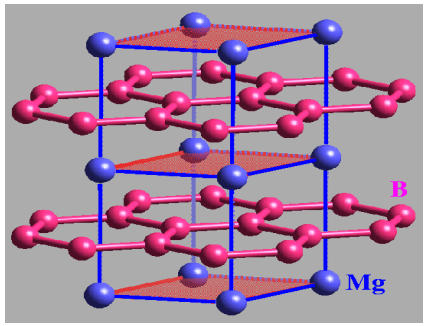
6. Stay away from oxides
7. Stay away from magnetism
8. Stay away from theorists!

Bernd Matthias's rules for finding high Tc superconductors (~1970). Extended to ~1980 understanding.

1. Must have d electrons (not just s-p, nor f) X MgB_2
2. High symmetry is good, cubic is best X Best are 2D!
3. Need a peak in density of states at Fermi level X MgB_2, …
4. Must spread the coupling over all phonons X MgB_2
5. Coulomb interaction must be docile X Cuprates, FeSCs
6. Stay away from oxides X Cuprates, BKBO
7. Stay away from magnetism X Cuprates, FeSCs, HFs
8. Stay away from rules for finding higher T_c!

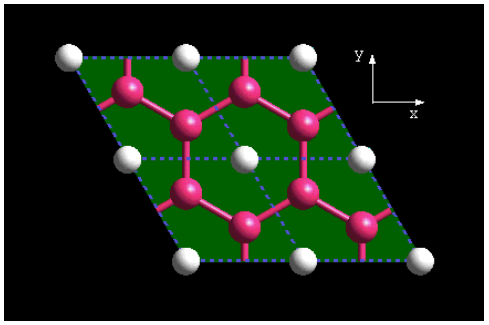
Akimitsu's Discovery (2001): T_c=40K in MgB_2



1. MgB_2: covalent bonds driven metallic by chemistry
2. Deformation potential *D*=13 eV/A

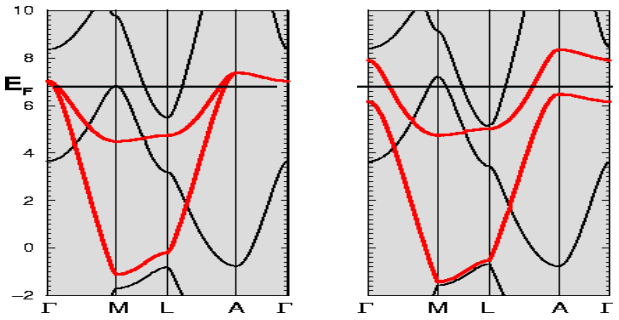
   (amazingly large for a metal)
3. 2D (cylinder) Fermi surfaces focus coupling strength
4. Yet structure remains stable: intrinsic covalency and very strong bonds

MgB_2 is naturally "hole-doped."



J. M. An and WEP, Phys. Rev. Lett. (2001)
J. Kortus et al., Phys. Rev. Lett. (2001)
Y. Kong et al., Phys. Rev. B (2001)
K.-P. Bohnen et al., Phys. Rev. Lett. (2001)
……..more…….

Highly focused EPI



T. Yildirim (NIST)

Y. KONG, O. V. DOLGOV, O. JEPSEN, AND O. K. ANDERSEN PHYSICAL REVIEW B 64 020501(R)

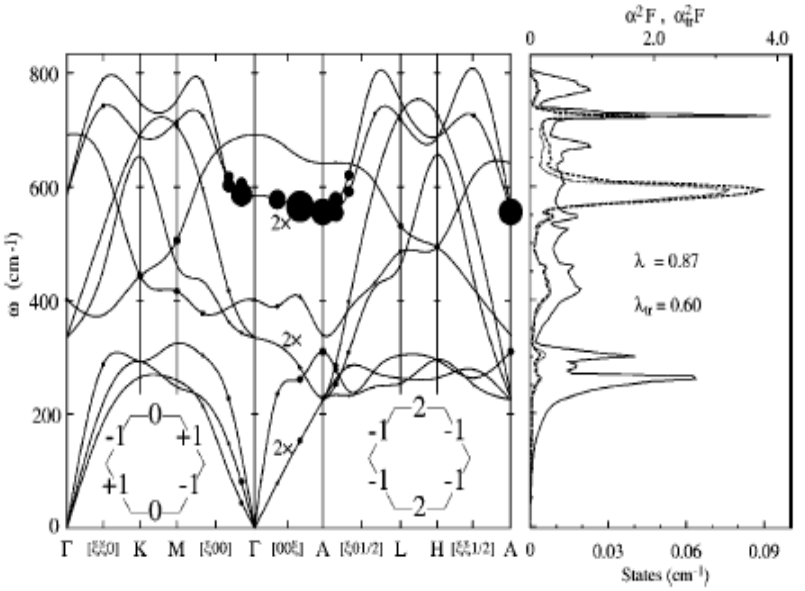


FIG. 1. Left: Calculated phonon dispersion curves in MgB_2. The area of each circle is proportional to the mode λ. The insets at the bottom show the two Γ*A* *E* eigenvectors (not normalized), which apply to the holes at the top of the σ bands (bond-orbital coefficients) as well as to the optical bond-stretching phonons (relative change of bond lengths). Right: $F(\omega)$ (full curve and bottom scale), $\alpha^2(\omega)F(\omega)$ (broken), and $\alpha^2_{tr}(\omega)F(\omega)$ (dotted). See text.

Electron-Phonon Coupling: General Results for $\lambda_{Q\nu}$ and $\gamma_{Q\nu}$

P. B. Allen, PR B6, 2577 (1972)

$$\lambda = \frac{1}{N_\nu}\sum_{Q,\nu=1}^{N_\nu}\lambda_{\vec{Q},\nu} = 2\int\frac{\alpha^2F(\omega)}{\omega}d\omega$$

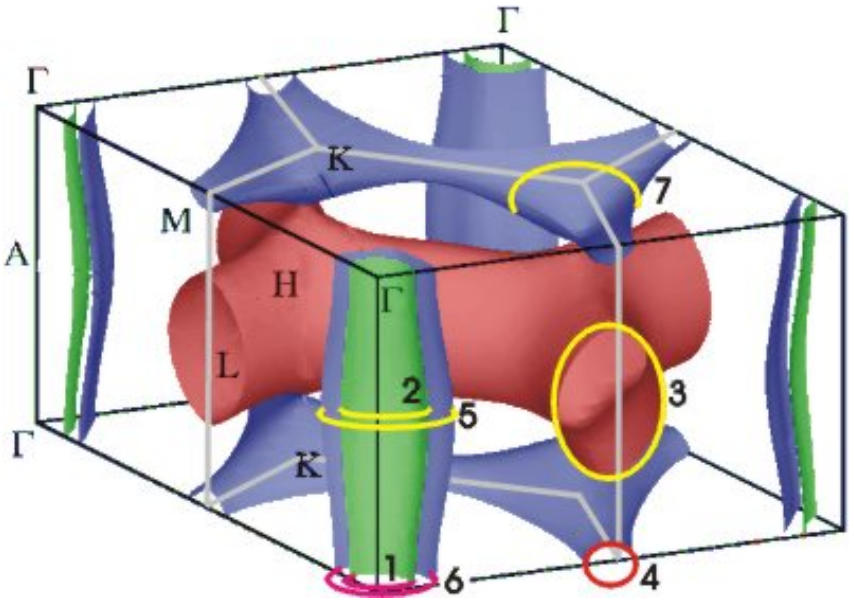
$$\alpha^2F(\omega) = \frac{2}{\pi N(0)\omega}\sum_{Q\nu}\gamma_{Q\nu}\delta(\omega_{Q\nu}-\omega)$$

$$\omega_{Q\nu}^2 = \Omega_{Q\nu}^2 + 2\Omega_{Q\nu}^2 Re\ \Pi(Q,\omega_{Q\nu})$$

$$\gamma_{Q\nu} = \frac{\Omega_{q\nu}}{\omega_{Q\nu}} Im\ \Pi(Q,\omega_{Q\nu})$$

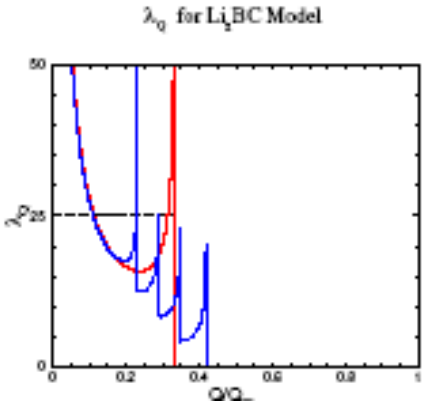
$$= \pi\sum_k |M_{k,k+Q}|^2\delta(\varepsilon_k)\delta(\varepsilon_{k+Q})$$

$$\lambda = \frac{1}{N_\nu}\sum_{Q\nu}\lambda_{Q\nu} = \frac{4}{\pi N(0)}\sum_{Q\nu}\frac{\gamma_{Q\nu}}{\omega_{Q\nu}^2}$$



$$\lambda_{\vec{Q},\nu} = 4\frac{2}{\omega_{\vec{Q},\nu}}\sum_k |M_{k,k+Q}|^2\delta(\varepsilon_k)\delta(\varepsilon_{k+Q})$$

$$= 4\frac{4\pi V_c|M|^2}{\omega_{\vec{Q},\nu}ck_F^2}\frac{1}{x\sqrt{1-x^2}}, x\equiv\frac{Q}{2k_F}$$

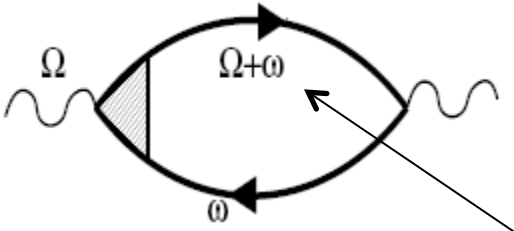


3% of phonons have $\lambda \sim 25$!

Rest of phonons have $\lambda \sim 0.3$

Phonon Renormalization (Self Energy)

simple and distinctive phase space in 2D



Extreme Electron-Phonon Coupling:
Kohn Anomalies

$$\omega_{Q\nu}^2 = \Omega_{Q\nu}^2 + 2\Omega_{Q\nu}^2 \Pi(Q, \omega_{Q\nu})$$

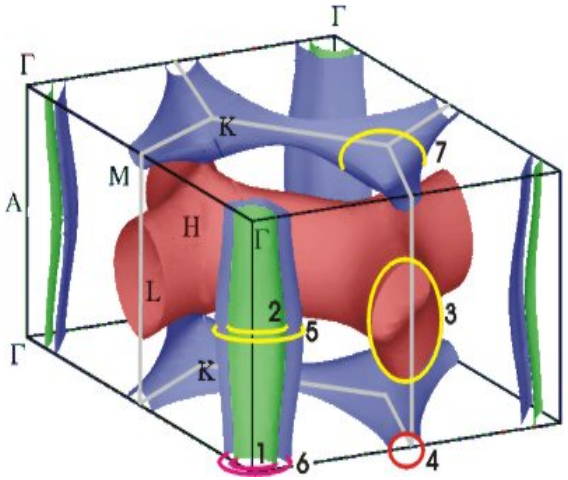
$$\Pi(Q,\omega) = -2\sum_k |M_{k,k+Q}|^2 \frac{f_k - f_{k+Q}}{\varepsilon_{k+Q} - \varepsilon_k - \omega - i\delta}$$

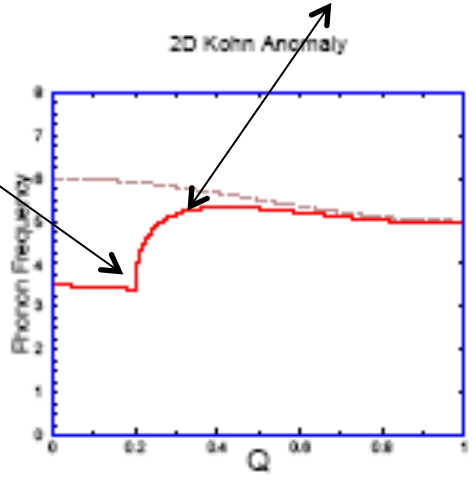
2D dispersion, slowly varying matrix elements give

$$\Pi_\nu(Q,\omega) = -2|M_\nu|^2 \chi_L^{2D}(Q,\omega)$$

Cylinder Fermi surface leads to sharp Kohn anomaly

Large matrix elements lead to strong renormalization for $Q<2k_F$





Phonon softening in MgB_2

Extreme Electron-Phonon Coupling: Kohn Anomalies

$$\omega_{Q\nu}^2 = \Omega_{Q\nu}^2 + 2\Omega_{Q\nu}^2 \Pi(Q, \omega_{Q\nu})$$

$$\Pi(Q,\omega) = -2\sum_k |M_{k,k+Q}|^2 \frac{f_k - f_{k+Q}}{\varepsilon_{k+Q} - \varepsilon_k - \omega - i\delta}$$

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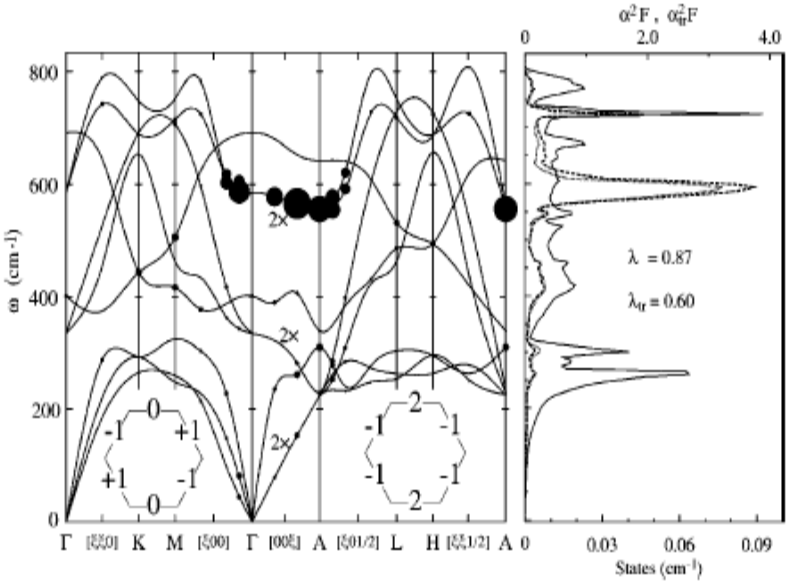

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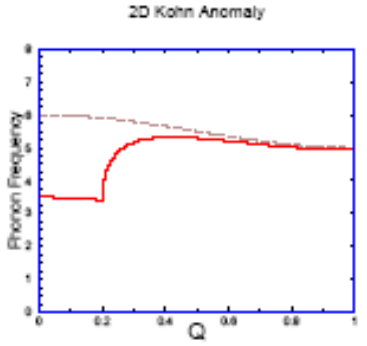


(No) theoretical limit on T_c. BCS: $T_c \sim e^{-1/\lambda}$

$$T_c = \frac{\langle\omega\rangle}{1.20} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

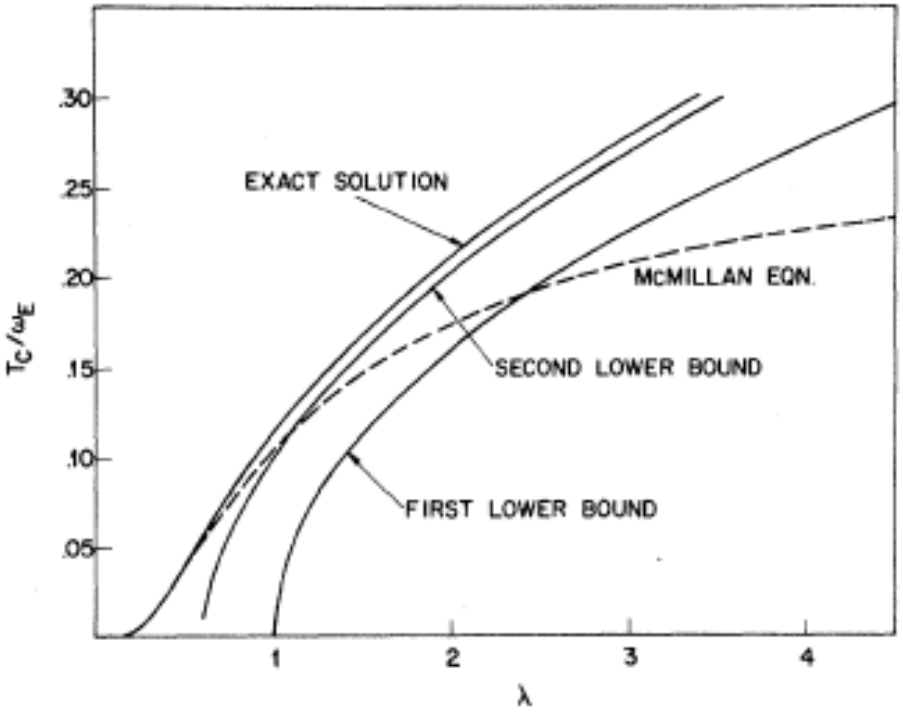
McMillan equation for T_c saturates for $\lambda > 1$

$$T_c = \frac{f_1 f_2 \omega_{\log}}{1.20} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right)$$

Allen-Dynes equation for T_c (1975)

$$f_1 = [1 + (\lambda/\Lambda_1)^{3/2}]^{1/3}, \qquad \Lambda_1 = 2.46(1 + 3.8\mu^*),$$

$$f_2 = 1 + \frac{(\bar{\omega}_2/\omega_{\log} - 1)\lambda^2}{\lambda^2 + \Lambda_2^2}, \qquad \Lambda_2 = 1.82(1 + 6.3\mu^*)(\bar{\omega}_2/\omega_{\log})$$



From full "Eliashberg theory" in the strong coupling regime

$\lambda >> 1$, $T_c \rightarrow \lambda^{1/2}$

Extremely encouraging news for those interested in high T_c!

Strong Coupling: Good News, Bad News

Good news: T_c is unbounded in Eliashberg theory

Bad news: real materials are complicated

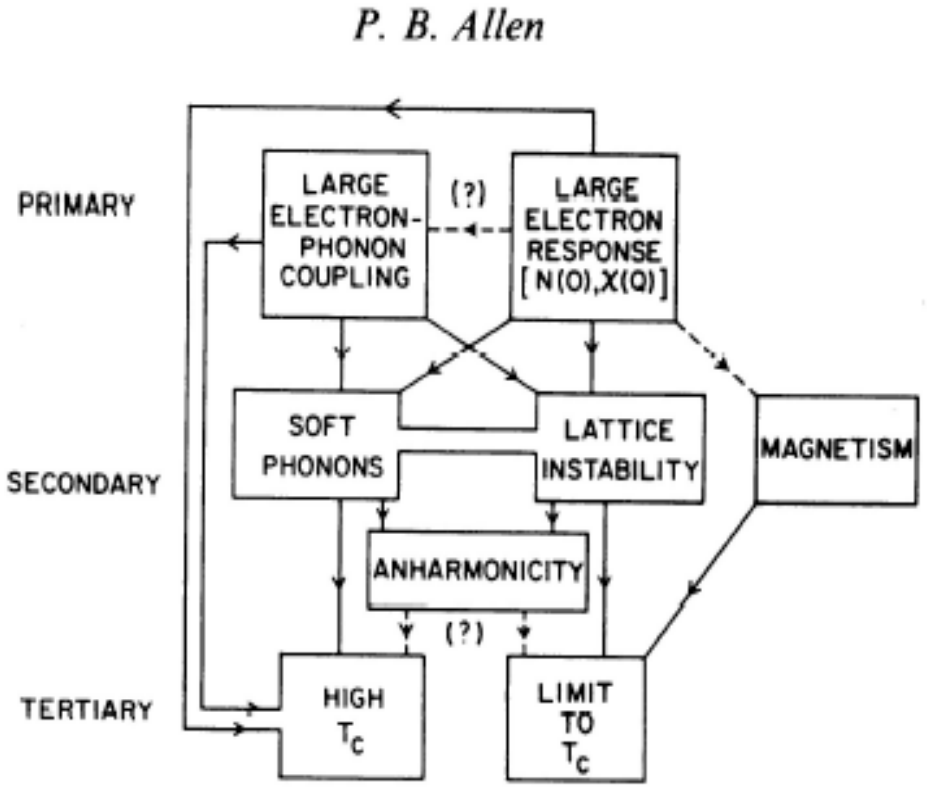
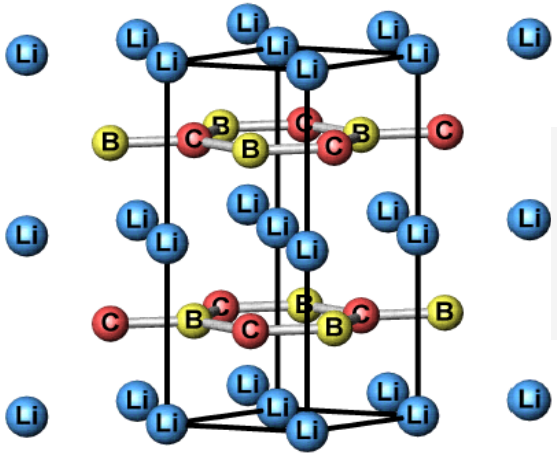


Fig. 3. Causative relations are indicated by arrows. High T_c is partly a direct consequence of the primary factors, and partly indirect through the phonon dispersion. Dashed lines with arrows represent less certain relationships.

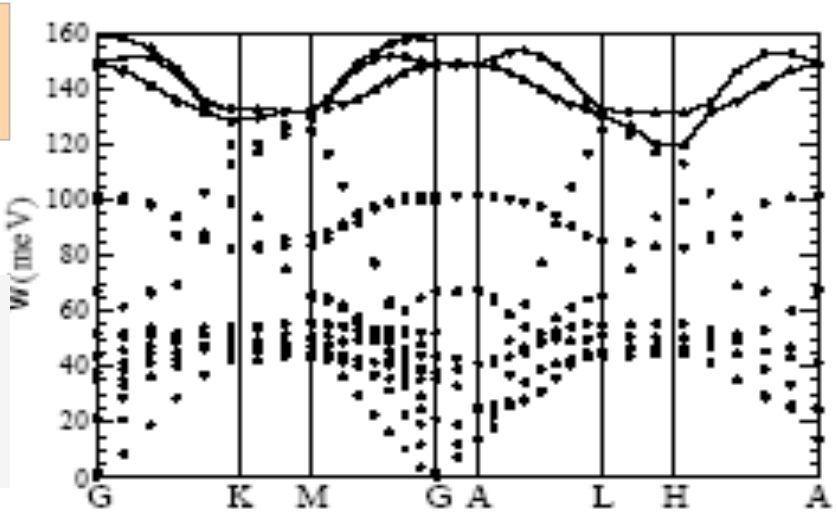
Electron-Phonon Coupling Strength Calculated for $Li_{1-x}BC$

Rosner, Kitiagorodsky, WEP, Phys. Rev. Lett. (2002)

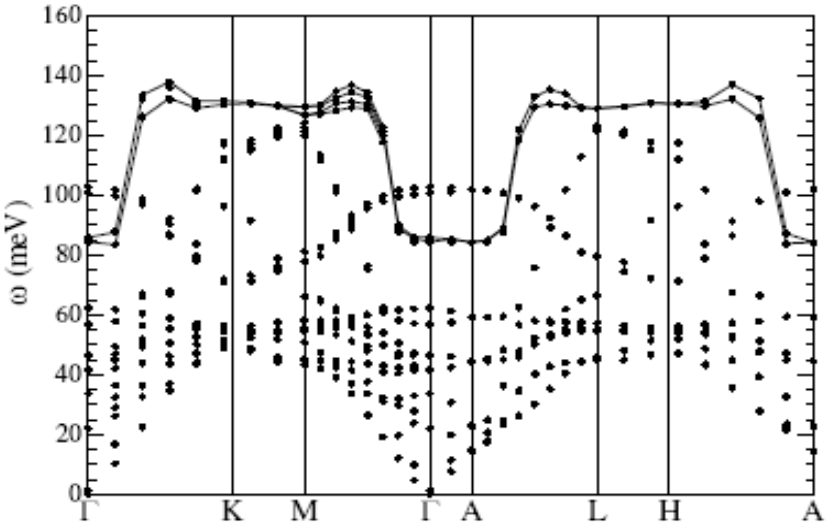
Semiconductor x=0
Simple vibrational spectrum



$T_c \sim 75$ K
using same theory as for MgB_2



Metal for x=0.25
Extreme Kohn anomalies



Not so simple experimentally!
Li is very active chemically in LiBC.
Hole doping → phase separation.

The "complete understanding" of el-ph mechanism allows a rational search and/or design of new/better examples.

It is the materials that are complex and devious.

Why 2D? why low-Z? why doped insulators?

Why 2D?

- examples (following slides): many classes of good sc'ors
- phase space [N(E)] is more favorable than in 3D
- electronic and phononic structure may be distinctive

Why low-Z?

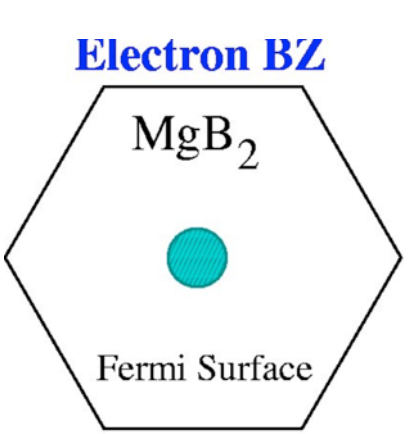
- mass is smaller → good for high T_c (isotope effect)
- bonding is stronger → stronger el-ph coupling
- other factors?? many classes of good 2D sc'ors

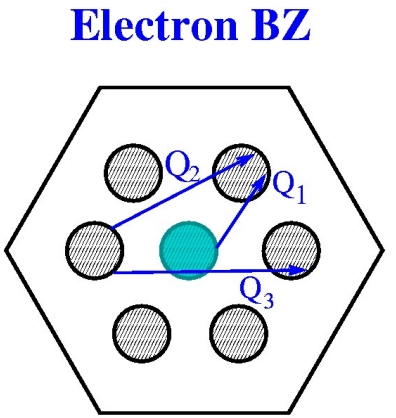
Why doped insulator? Much of the point of this talk

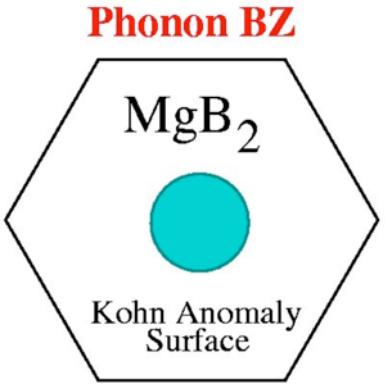
Rational Design/Search for new hTS

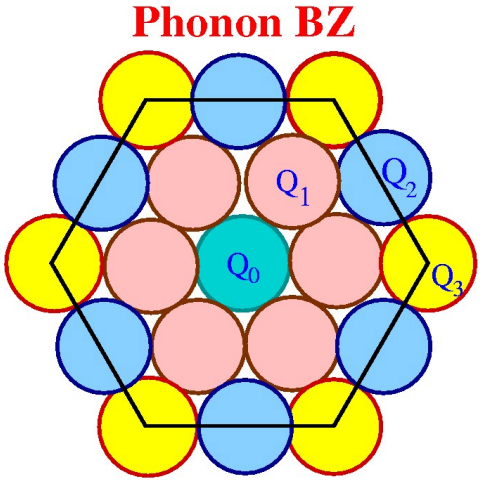
Example of one design criterion: doped 2D insulators

Select band structure to enable the phonons to use more of the Brillouin zone

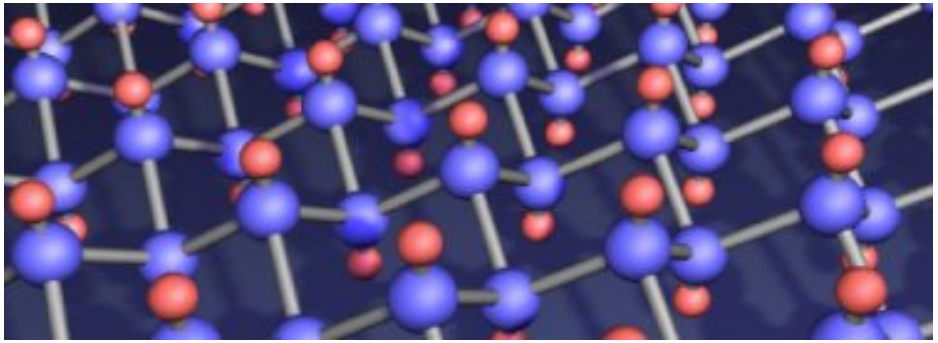








MgB_2-like materials (a brief mention)



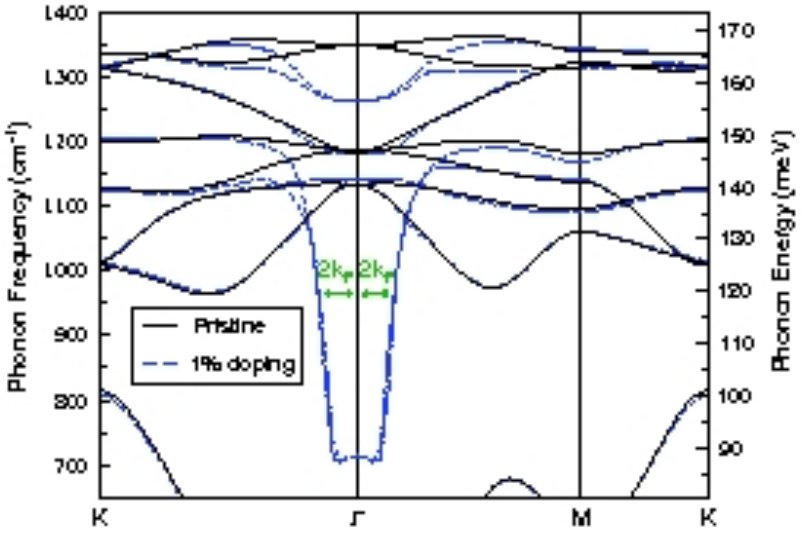
Graphane

"up to 90K"

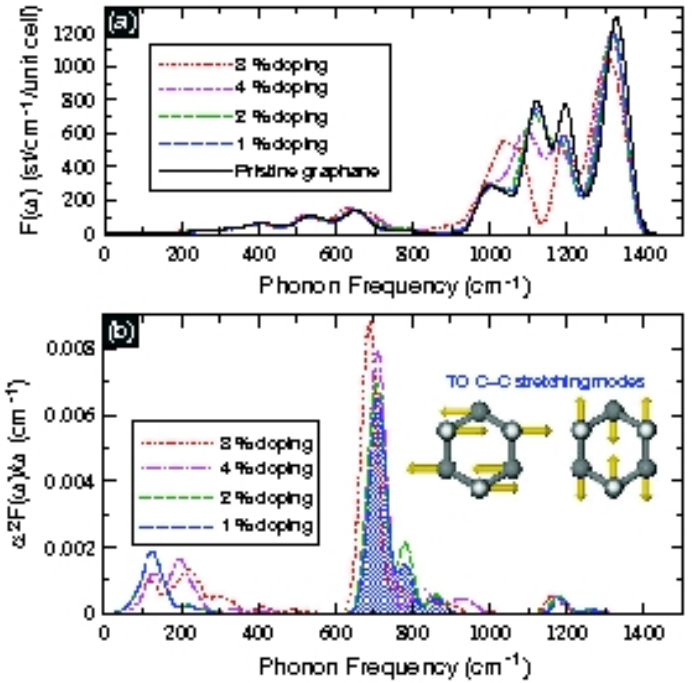
PRL 105, 037002 (2010) PHYSICAL REVIEW LETTERS week ending 16 JULY 2010

First-Principles Prediction of Doped Graphane as a High-Temperature Electron-Phonon Superconductor

G. Savini,[1,2] A. C. Ferrari,[1,*] and Feliciano Giustino[3]



Doped graphane CH



Coupling character

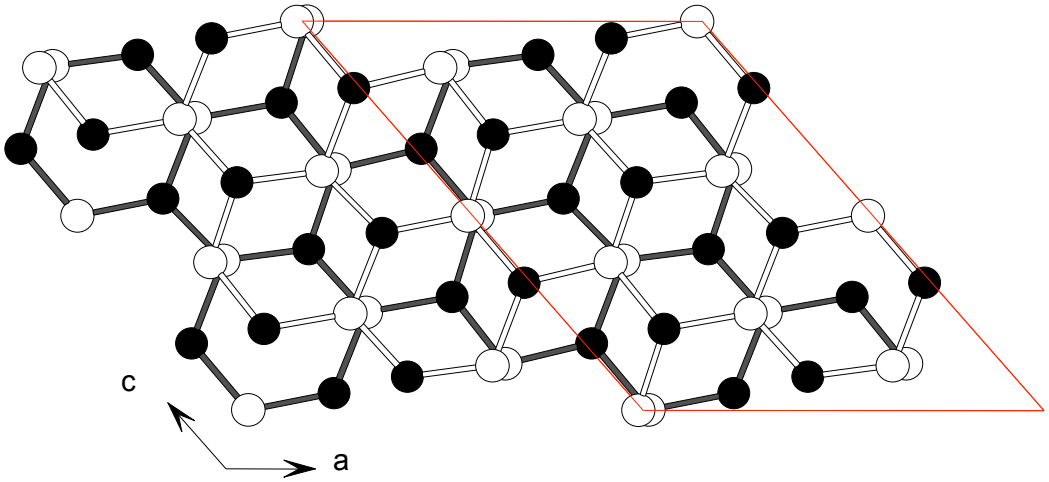
A newer MgB_2-like example,
hole-doped BeB_2C_2

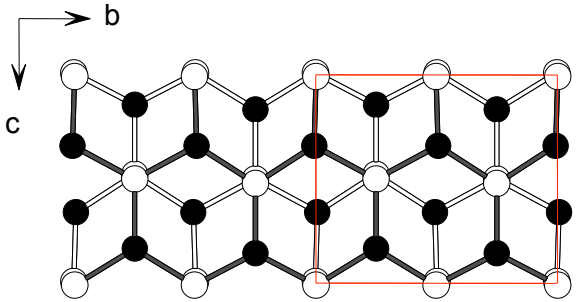
BeB_2C_2: isoelectronic with LiBC, isoelectronic with MgB_2

MgB_2C_2 has received some study: hex B-C layers, not flat due to Mg positions.
Could be quite interesting if hole-doped; no superconductivity yet produced..

$Be_{1-x}B_2C_2$: Moudden, Eur. Phys. J. B 64, 173 (2008). Guessed at structure(s).
Found indications (predictions) of relatively high T_c.

2010: B. Albert's group determined the structure: $P2_1/c$? No. Pmmm, yes.



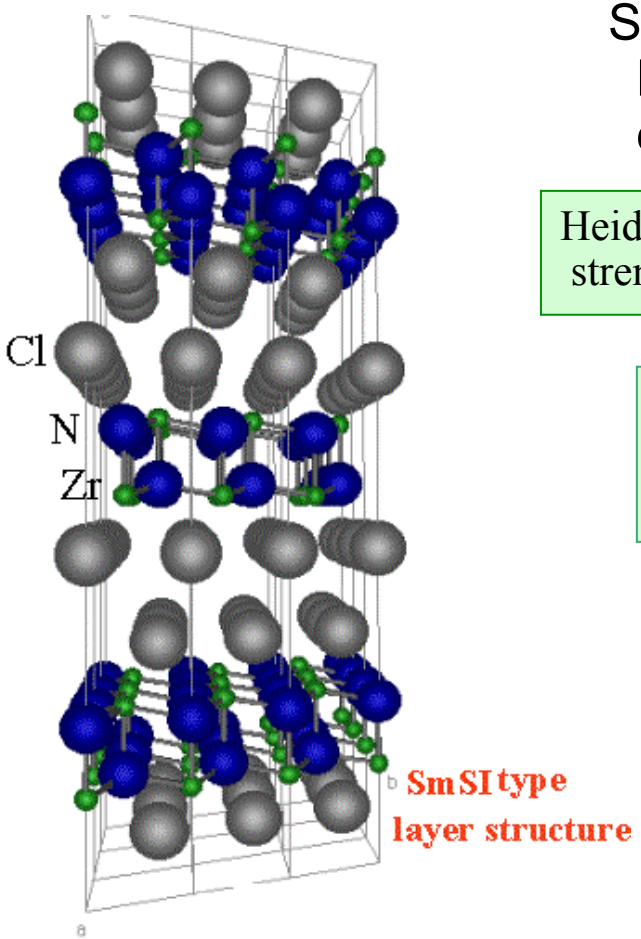


Calculations (Ylvisaker and WEP): when doped, very MgB_2-like.
Could have T_c ~ 50 K if structure can be retained.

A puzzle in 2D superconductivity electron-doped ZrNCl, HfNCl, TiNCl

Alkali-doped ionic insulators: A_xZrNCl (15 K), A_xHfNCl (25 K), A_xTiNCl (17 K)

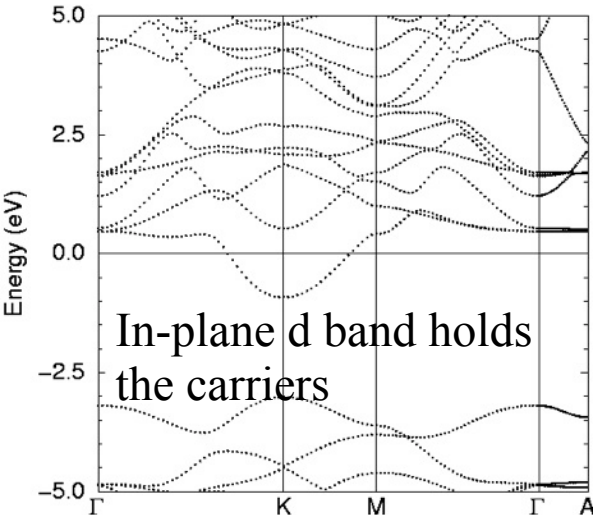
Yamanaka et al. 1998--; Shamoto et al. 1998



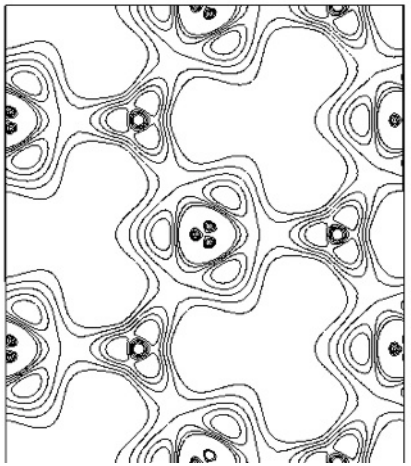
Structure is somewhat MgB_2-like; so is it electron-phonon?

Heid & Bohnen (2006) el-ph coupling strength is not large enough

Bill et al. (2003) Coupling to/ screening by low energy plasmons is important



- Double hex Zr-N layer
- Strongly 2D bands
- Electron-doped
- Inverse 'isotope shift'
- Weak el-ph coupling



Superconductor-insulator transition at x=0.06

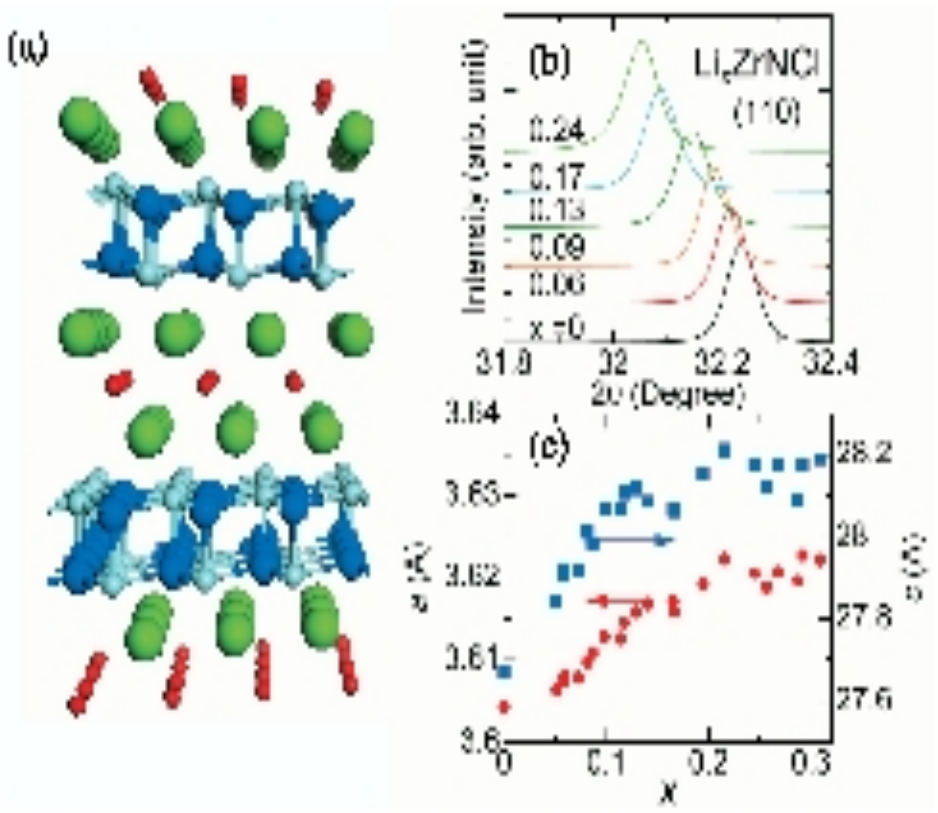
Increase in T_c upon Reduction of Doping in Li_xZrNCl Superconductors

PRL, 2009

Y. Taguchi,[1,2] A. Kitora,[1] and Y. Iwasa[1,2]

[1]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

[2]*CREST, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan*



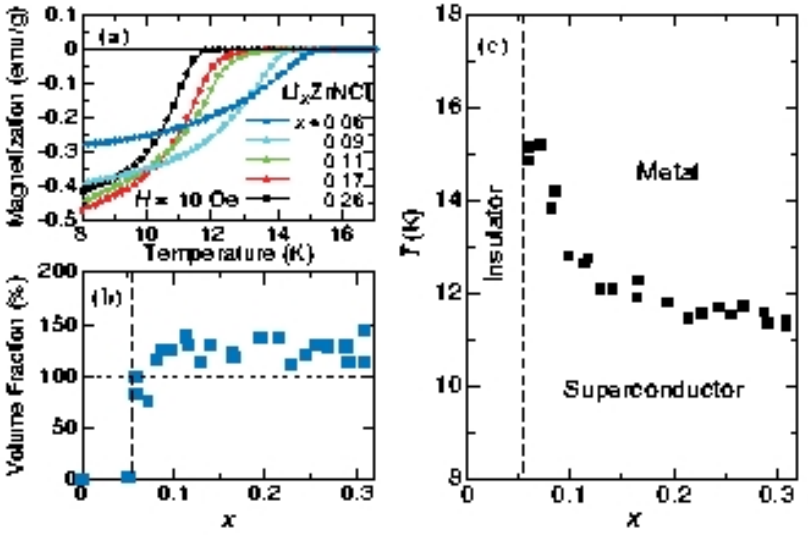


FIG. 4 (color). (a) Magnetization at a field of 10 Oe (without correction for demagnetizing field) is plotted against temperature for selected samples. (b) x dependence of the superconducting volume fraction determined by MH measurements at 2 K (or 5 K). Imperfect correction of the demagnetizing field is the reason the estimated volume fraction exceeds 100%. (c) x dependence of T_c, exemplifying rapid increase in T_c below $x = 0.12$.

Insulator-superconductor transition to optimal superconducting T_c = 15.5 K at x=0.06. Weak phonon coupling, no magnetism.

Doped HfNCl: T_c = 26 K.

Li_xZrNCl, x=0, x=1/6

Phonons and el-ph coupling:
Heid and Bohnen, PR B (2005)

Nearly circular Fermi surfaces at the zone corner K points: almost perfect nesting at K!
Focusing of scattering

Calculated el-ph coupling strength is 0.5, insufficient to account for T_c=15 K

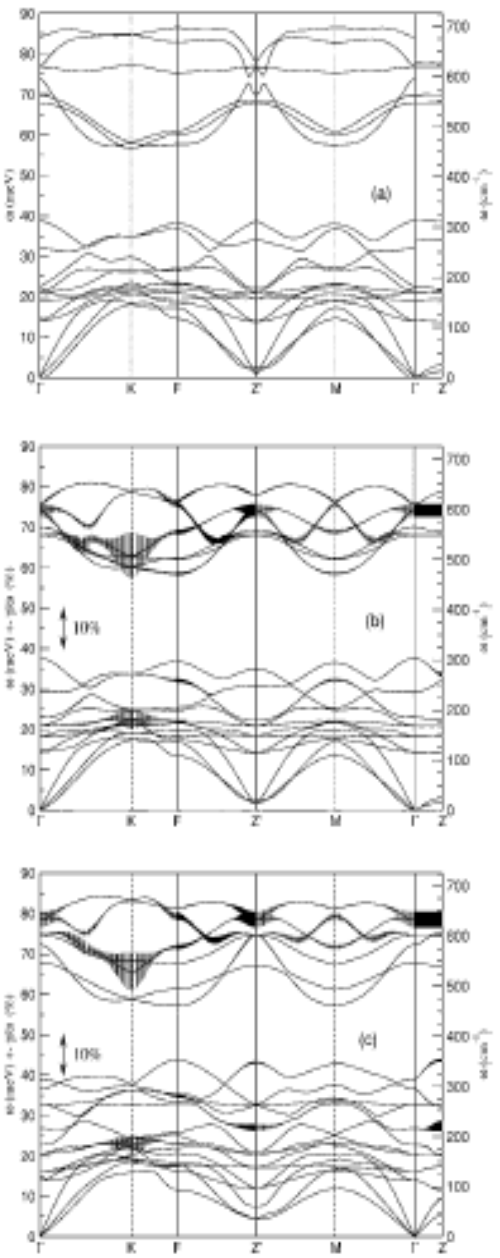


FIG. 5. Phonon dispersions of β-ZrNCl (a) and Li-doped ZrNCl model A (b) and model B (c), respectively. The vertical bars indicate the relative phonon linewidths γ/ω in % as calculated from the electron-phonon coupling [see Eq. (1)].

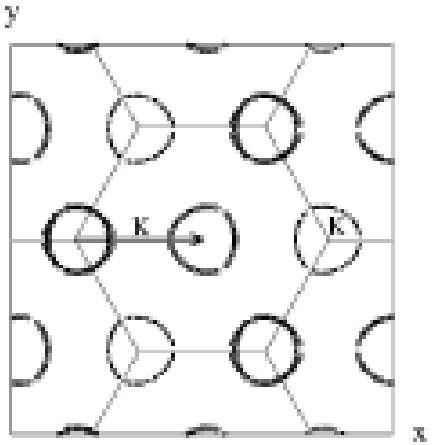


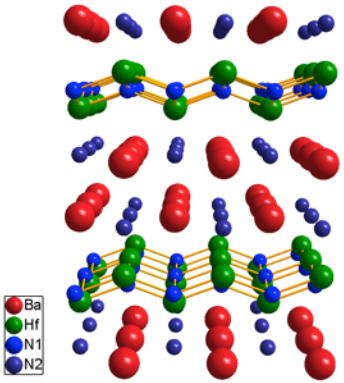
FIG. 7. Cut through the Fermi surface orthogonal to the rhombohedral axis. Full circles indicate the original Fermi surface, open circles the Fermi surface shifted by the momentum K.

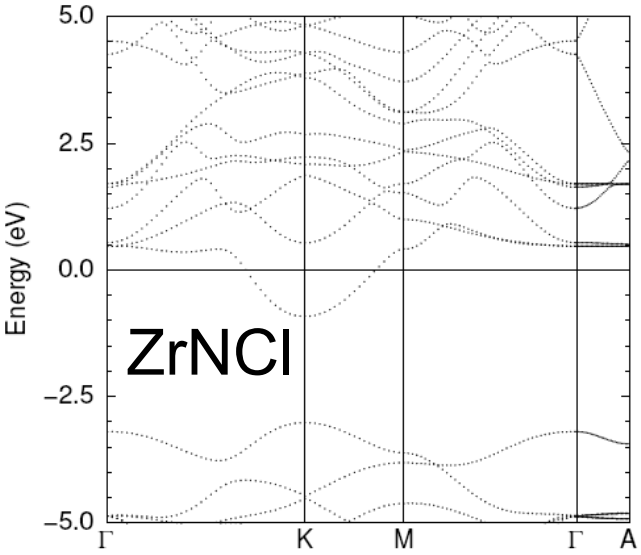
Electron doping of 2D ionic insulator $BaHfN_2$: Ba^{2+}, Hf^{4+}, N^{3-}

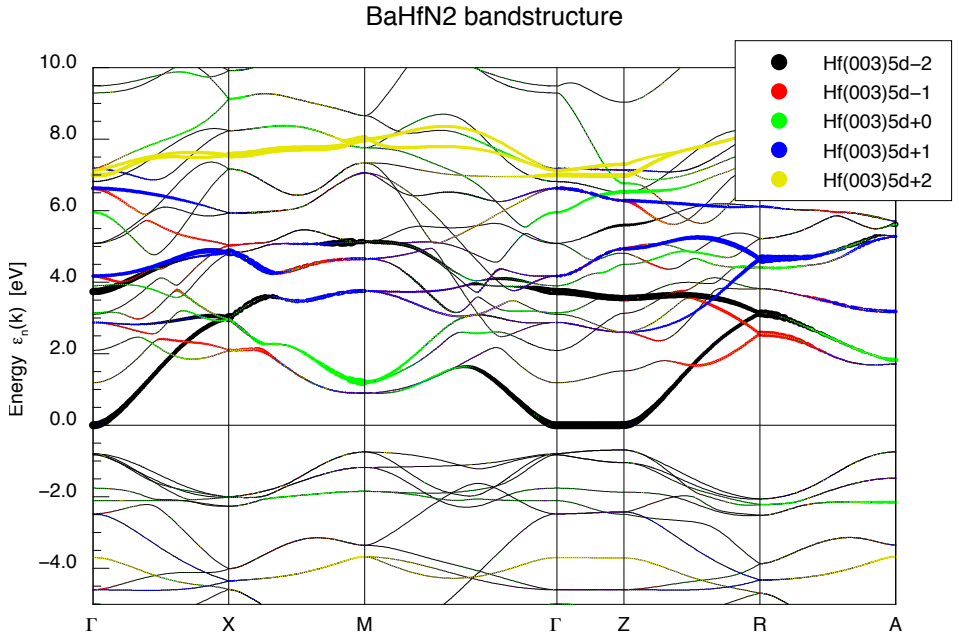
HfN bilayer is related to, but different from, ZrNCl.
$BaHfN_2$ has only one reactive cation, allowing vapor phase growth.

Expt.: D. H. Gregory et al. JSSC 137, 62 (1998)
Theory: A. Kaur et al., PRB 82, 155125 (2010)

- Structure: ionic-covalent square Hf_2N_2 layer, cladded by BaN on each side-->neutral slabs
- ? Intercalate with Li, Na, … to get superconductivity? as in ZrNCl.







Features of doped ionic 2D band insulators Relevant for the effective el-el interaction [Examples: A_xZrNCl and isovalent: T_c = 15-25K]

- Low density 2DEG (one carrier for each ~4x4 supercell)

  - static lattice: weak screening behavior at small distance
    -- study $\varepsilon^{-1}(r,r';\omega)$ in a material-dependent way, look for attractive interaction in certain reqions of q,ω

  − for 2D plasmons, $\omega_p(q) \sim q^{1/2}$ implying potential low energy dynamics and screening (Andreas Bill et al.)

  - dynamic lattice: calculate dynamic ionic polarizability, intermediate range interaction not well screened out

  - dynamic lattice: separated electrons sloshing in a sea of vibrating highly charged ions Zr^{4+}, N^{3-}, etc.

  - include dynamic electronic+charged lattice polarizability simultaneously (taking care of likely non-adiabatic effects, polaronic behavior, etc)

Total dielectric function: Algebraic sign, electron-lattice response, and superconductivity

P B Allen, M L Cohen, D R Penn, PRB 1988

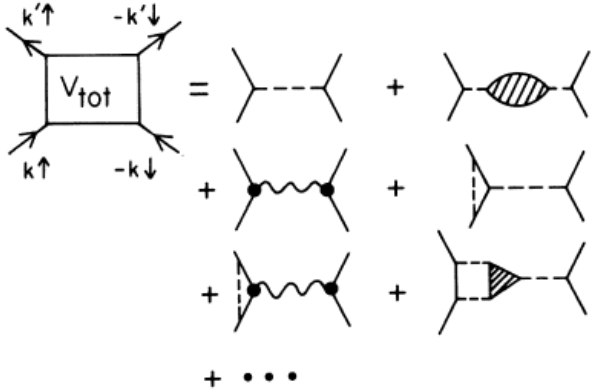


FIG. 2. Feynman graphs for the effective electron-electron interaction which binds a Cooper pair in the BCS theory.

Total effective interaction in mean field approximation

$$V_{12,\mathrm{MF}} = v_{1/2}\epsilon^{-1}_{s,\mathrm{MF}}v_{1/2} ,$$

$$\epsilon_{s,\mathrm{MF}} = 1 - v_{1/2}\chi_0 v_{1/2} .$$

$$V_{12,\mathrm{MF}} = V_{\mathrm{el}} + \sum_{\alpha,\beta}\phi_\alpha(\mathbf{Q}+\mathbf{G})D_{\alpha\beta}(Q\omega)\phi_\beta(\mathbf{Q}+\mathbf{G}') , \qquad (67)$$

where the first term is the purely electronic part of the screened interaction

$$V_{\mathrm{el}} = \epsilon^{-1}_{\mathrm{MF,el}}(\mathbf{Q}+\mathbf{G},\mathbf{Q}+\mathbf{G}',\omega)\frac{4\pi e^2}{\Omega(\mathbf{Q}+\mathbf{G})^2} . \qquad (68)$$

Effective el-el coupling: screened el-el interaction + el-lattice-el interaction

Dynamic lattice response

$$D^{-1}_{\alpha\beta} = M(\omega^2 - \Omega_0^2)\delta_{\alpha\beta} - \sum_{\mathbf{G}_1,\mathbf{G}_2} f_\alpha(\mathbf{Q}+\mathbf{G}_1)[\delta_{\mathbf{G}_1\mathbf{G}_2} + v_{1/2}(\mathbf{Q}+\mathbf{G}_1)\chi_{\mathrm{MF,el}}(\mathbf{Q}+\mathbf{G}_1,\mathbf{Q}+\mathbf{G}_2,\omega)v_{1/2}(\mathbf{Q}+\mathbf{G}_2)]f_\beta(\mathbf{Q}+\mathbf{G}_2) ,$$

Doped Band Insulating Oxides: a comparison to ponder

Two superconducting doped, highly ionic insulators

$BaBiO_3$

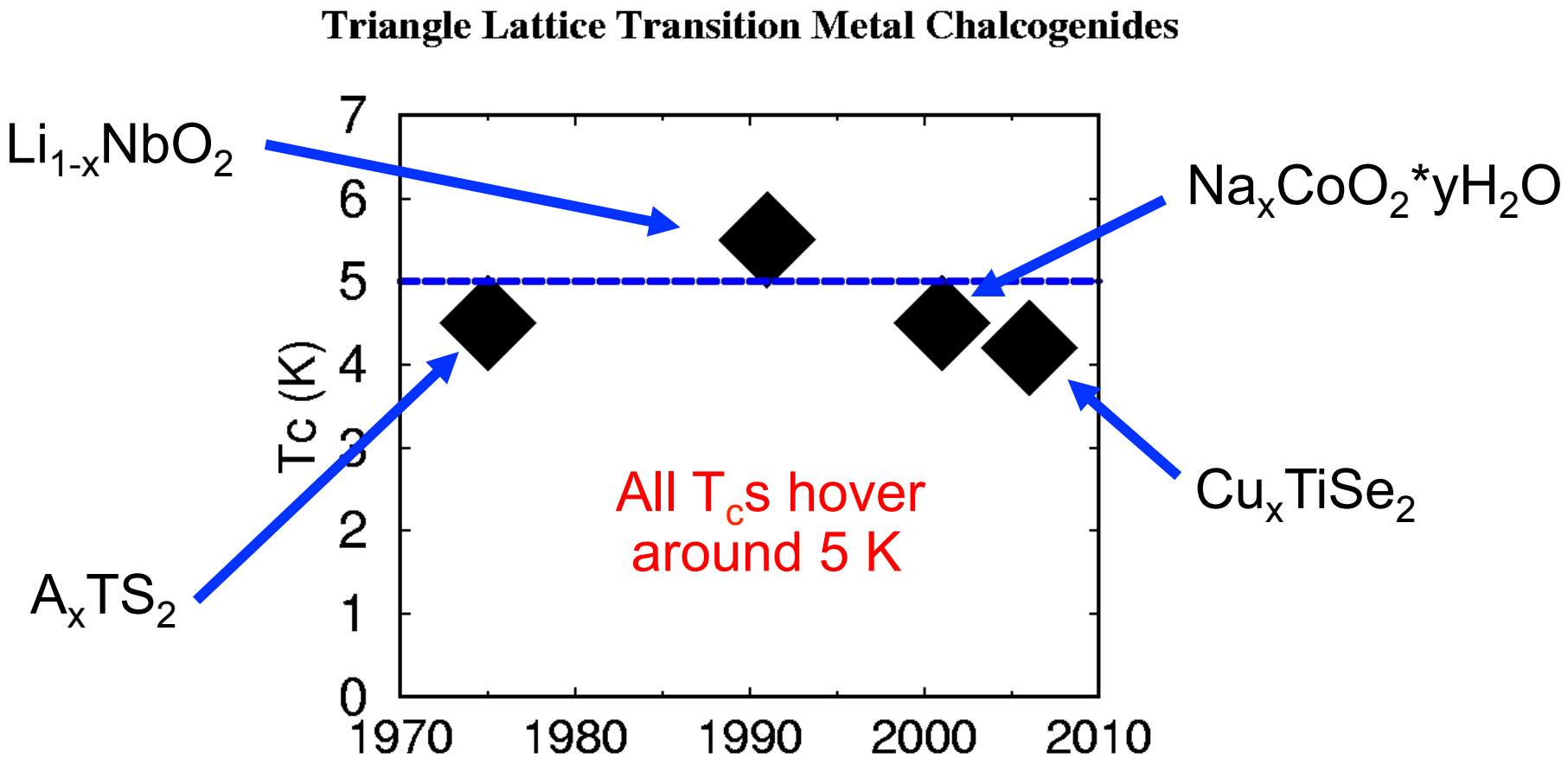
$Ba^{2+}_{1-x}K^{+}_{x}Bi^{4+}(O^{2-})_3$ (BKBO): T_c = 30+ K at x=0.35-0.40
wide band perovskite, sp electron carrier system
discussed as a negative-U, or valence skipping, system

$SrTiO_3$

$Sr^{2+}_{1-x}La^{3+}_{x}Ti^{4+}(O^{2-})_3$ (SLTO): T_c < 0.7 K at x<0.001
wide band perovskite, s-p electron carrier system
van der Marel, van Mechelen, Mazin, arXiv:1109.3050:
an anti-adiabatic electron-phonon system

Why (1) are these two doped insulators so different?
Why (2) do most doped perovskites not superconduct at all?

Synopsis: T_c in 2D Triangular Oxides/Chalcogenides



A doped triangular lattice TM oxide: Li_xNbO_2

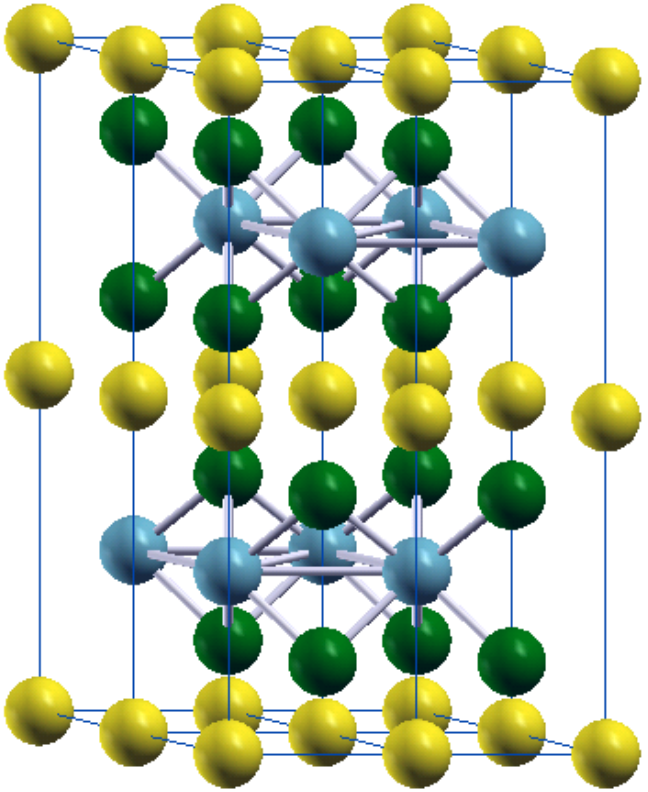
Li_xNbO_2: T_c = 5.5 K

$3d^{1+x}$ system

- a = 2.90 Å
- c = 10.46 Å
- Triangular Nb lattice
- Double layer unit cell
- Strongly layered structure
- T_c independent of x

- Li can be de-intercalated
- Nb trigonal prismatically coordinated*

[A. Stacy group (Berkeley, 1991-92)]



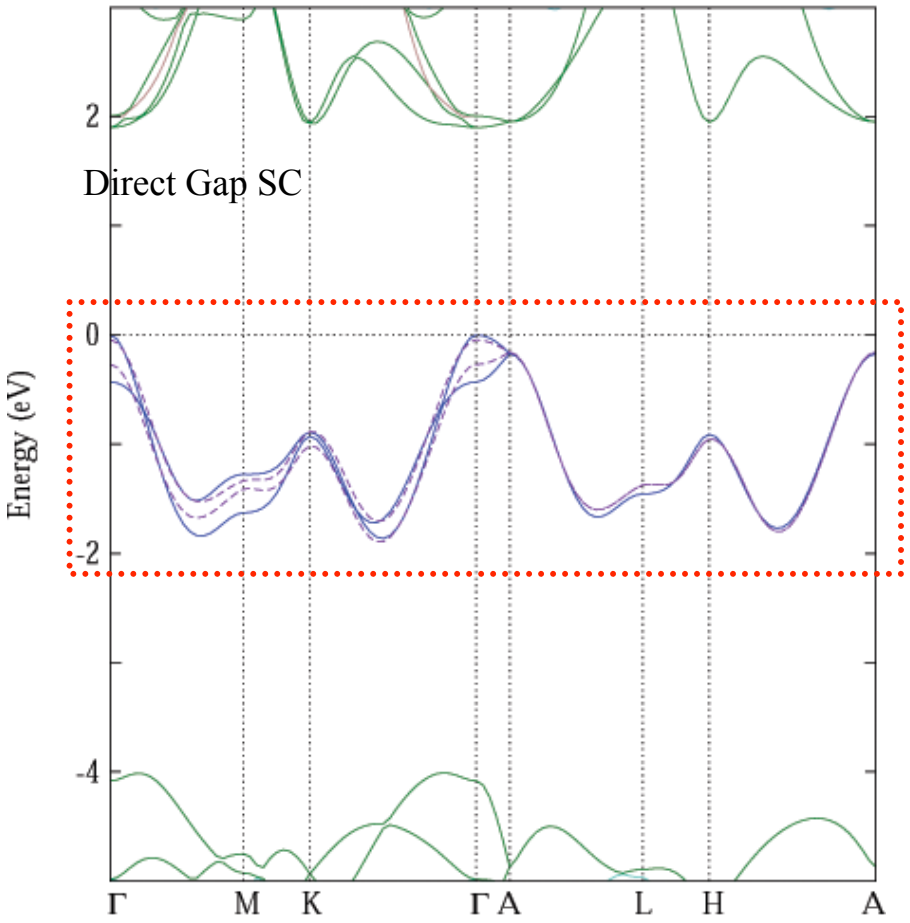
Experimental structure from Meyer and Hoppe, Angew. Chem. Int. ***13,*** *744 (1974)*

A Single Band System: The $LiNbO_2$ Band Structure

[E. Ylvisaker and WEP]

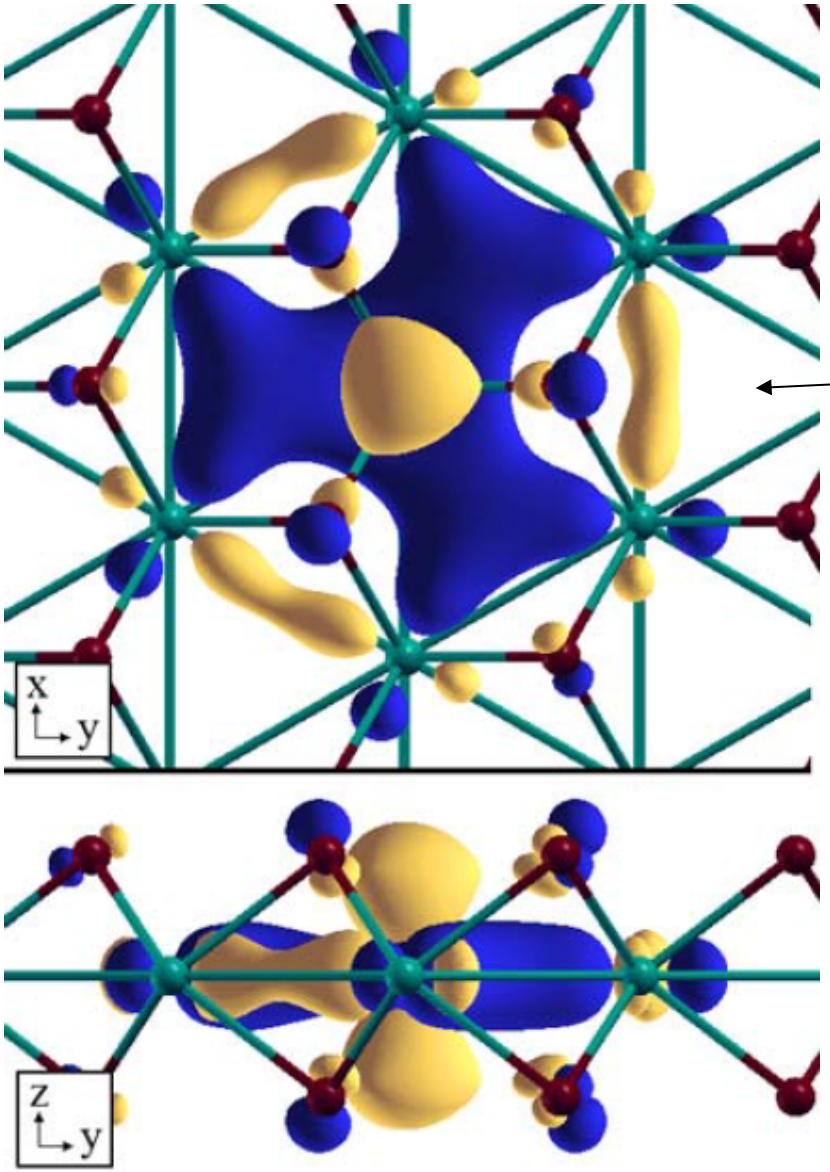
- Nb^{4+} d^1 configuration
- Crystal field splitting gives
- single $d(z^2)$ band (per Nb)
- Bandwidth 1.8 eV
- Large **second** neighbor
- Substantial el-ph coupling

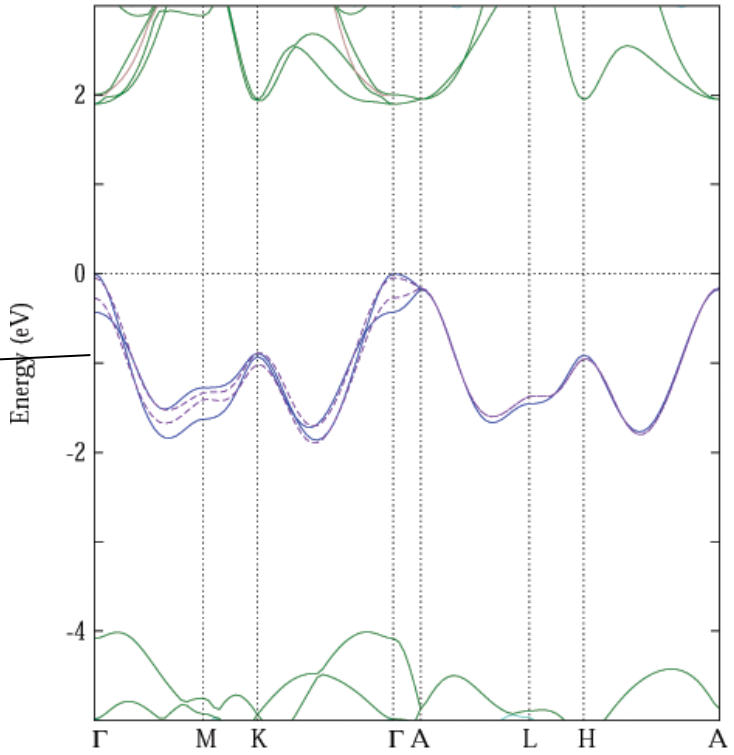
z_O	t_1	t_2	t_3	t_z
0.117	24	**107**	17	231
0.126	73	**104**	43	27
0.136	**136**	97	68	28



Tight binding fit shown dashed

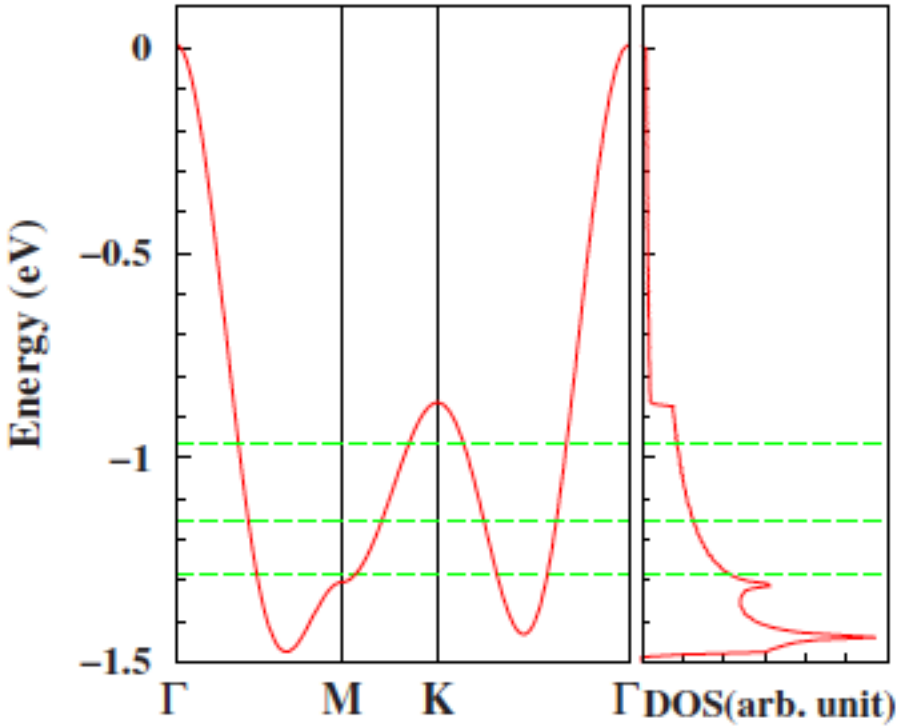
A Single Band System: The $LiNbO_2$ Wannier Function



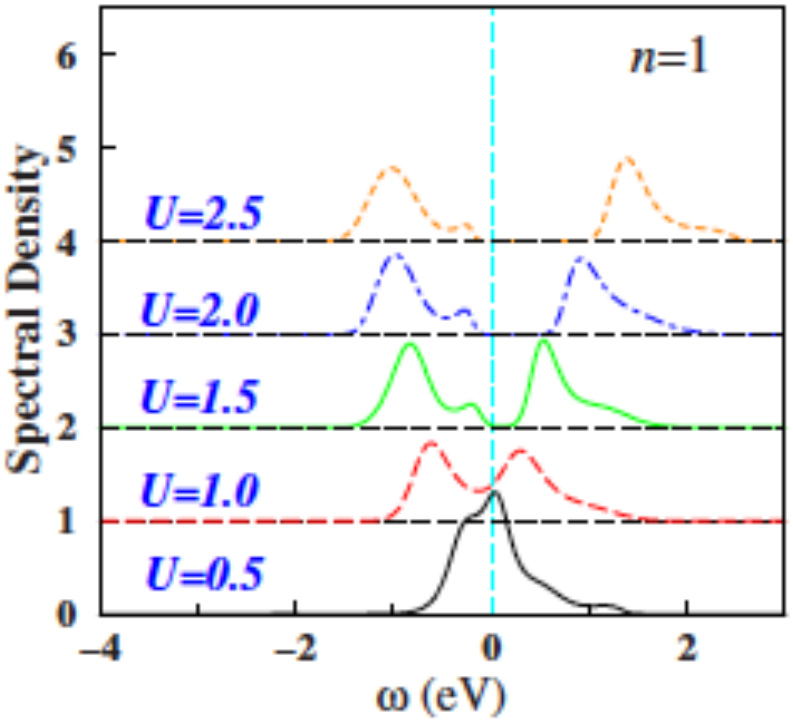


A Single Band System $LiNbO_2$: a DMFT study

Lee, Kunes, Scalettar, WEP, PRB 2007



Band and DOS



Spectral density vs U at half filling

Likely $Li_{1/2}NbO_2$ is a correlated electron system.
However, U for the Wannier function is not known.
The origin of pairing is a mystery at present.

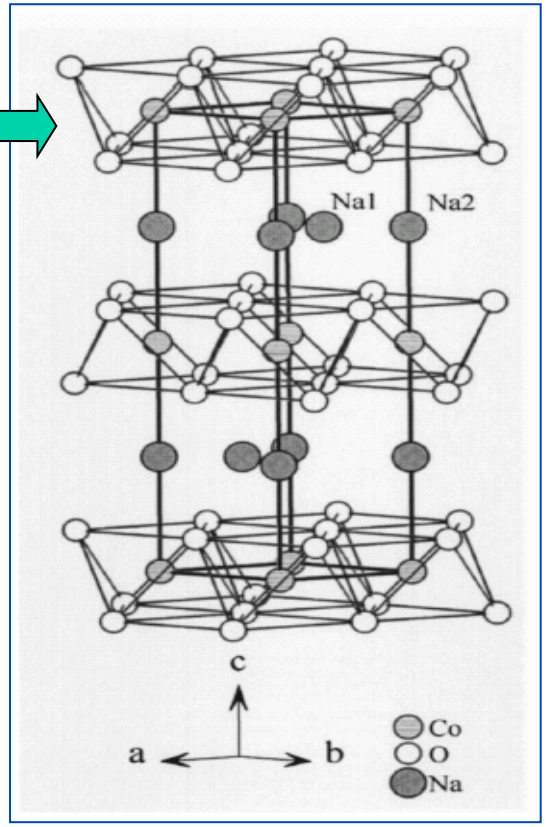
A doped triangular lattice TM oxide:
$Na_xCoO_2*nH_2O$

Na_xCoO_2, the Dehydrated Superconductor
Just add water!

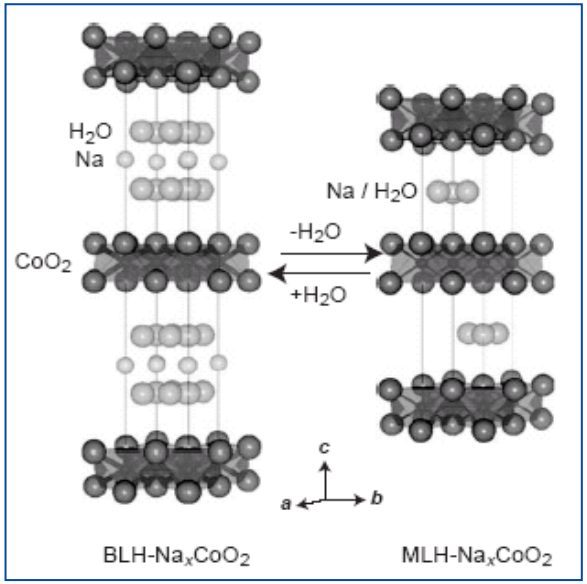
Edge-sharing CoO_6 Octahedra

By the trigonal symmetry of the Co site:

t_{2g}: e_g'+ a_g



Water



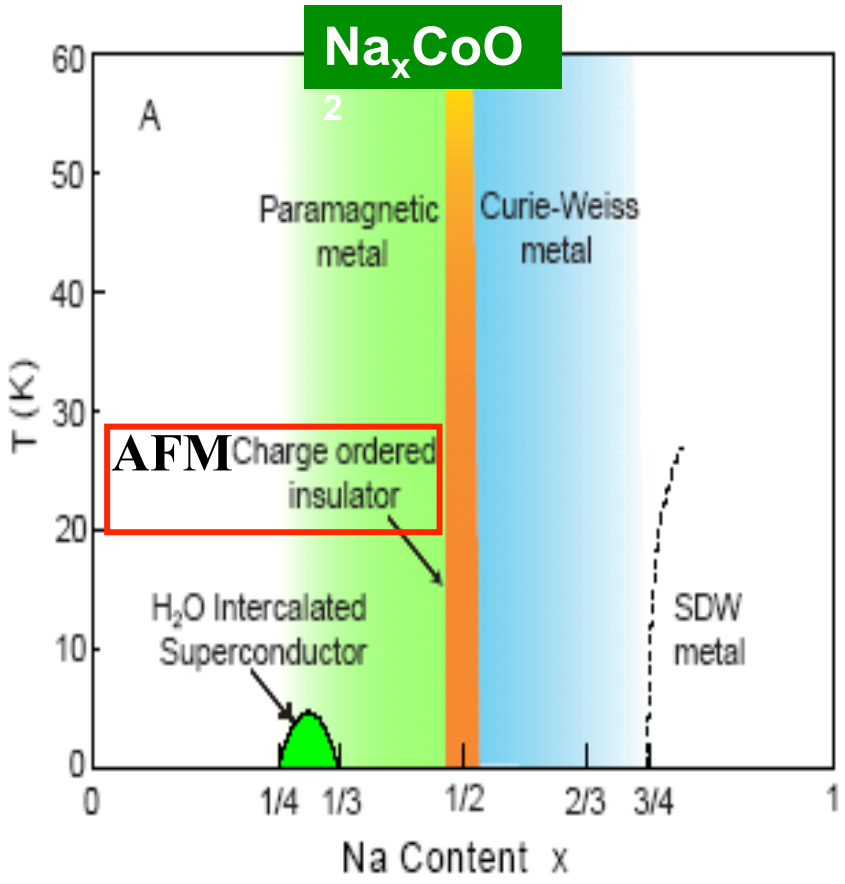
$$Na_{0.35}CoO_2 1.3(H_2O)$$

$$Na_{0.35}(H_3O)_{0.17}CoO_2 1.22(H_2O)$$

J.D. Jorgensen et al. (ANL)
Phys. Rev. B 68, 214517 (2003)

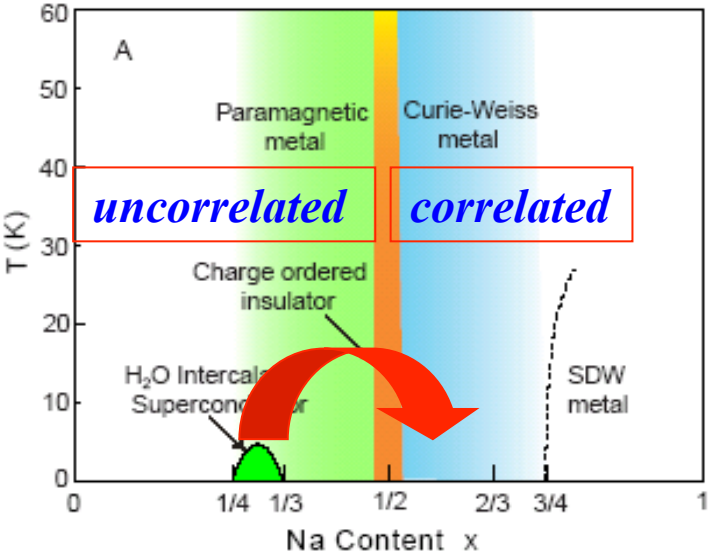
K. Takada et al., Nature 422, 53 (2003);
Adv. Mater. 16, 1901 (2004) [NIMS, Tsukuba]

Phase Diagram of Na_xCoO_2



Several reports of H_2O-to-oxonium $(H_3O)^+$ conversion in sample; shift in Co mean valence

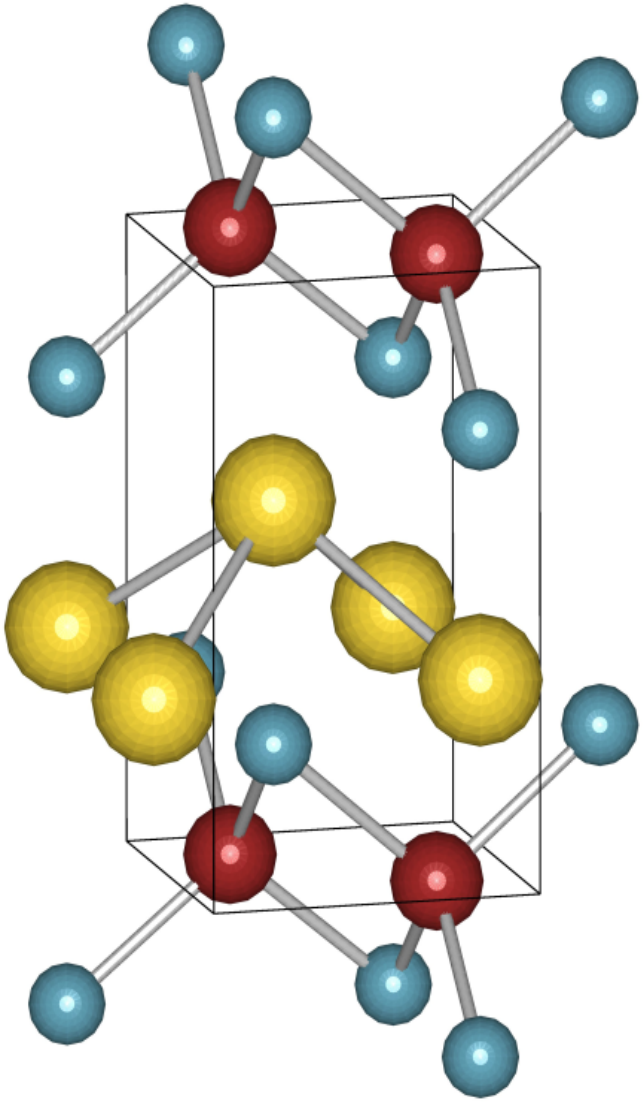
- Takada et al., J Mater Chem 14, 1448 (2004)
- Karpinnen et al., Chem Mater 16, 1693 (2004)
- Milne et al., Phys Rev Lett 93, 247007 (2004)
- Takada et al., Adv. Mater. 16, 1901 (2004)
- Chen et al., cond-mat/0501181

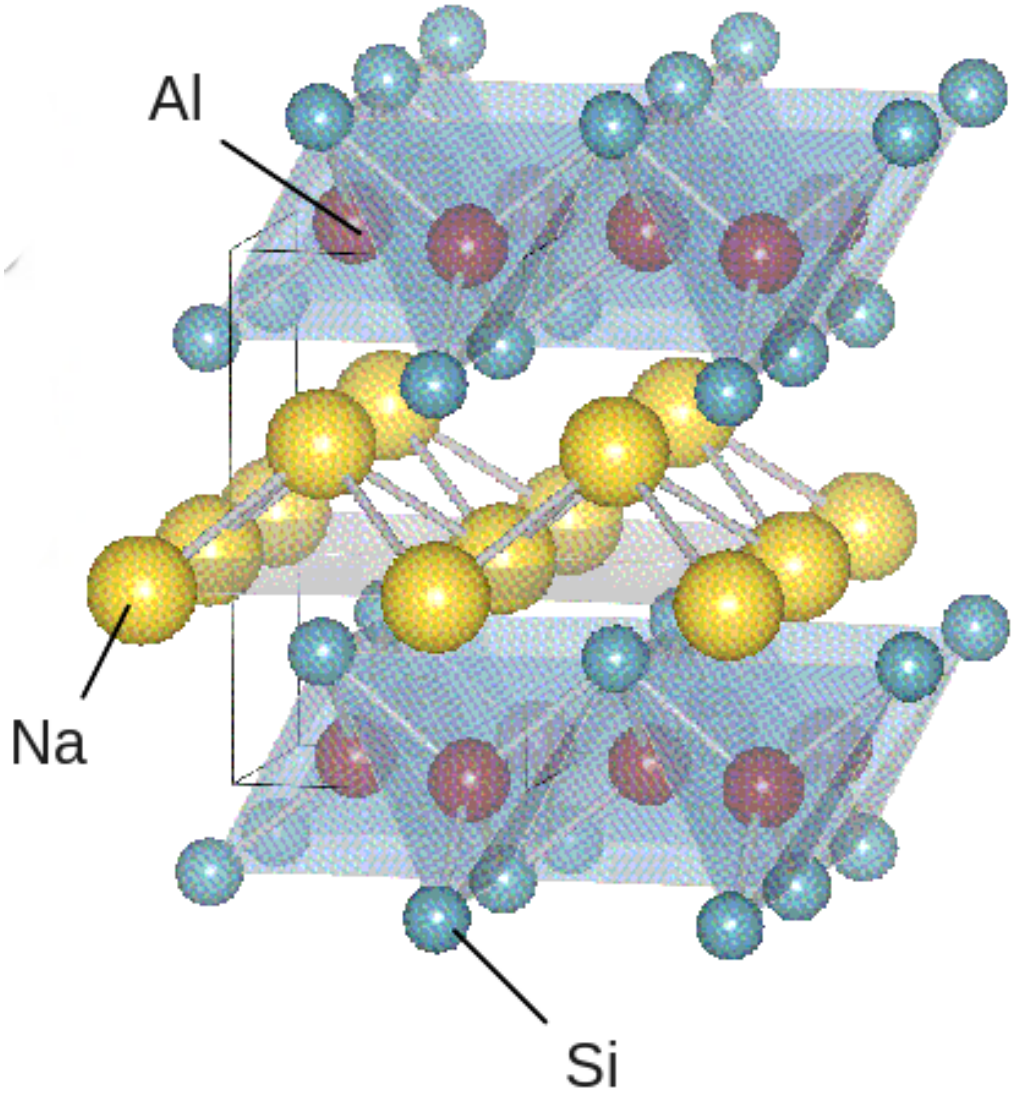


M.L. Foo et al. (Princeton), Phys. Rev. Lett. 92, 247001 (2004)

Another self-doped s-p 2D superconductor besides MgB_2: NaAlSi

NaAlSi





Structural similarities to the
Fe pnictide superconductors.
Completely different electronic properties.

NaAlSi: self-doped semimetallic superconductor with Al free electrons and covalent Si holes

[NaAlSi: Z=11:13:14]

[LiBC: Z= 3: 5: 6]

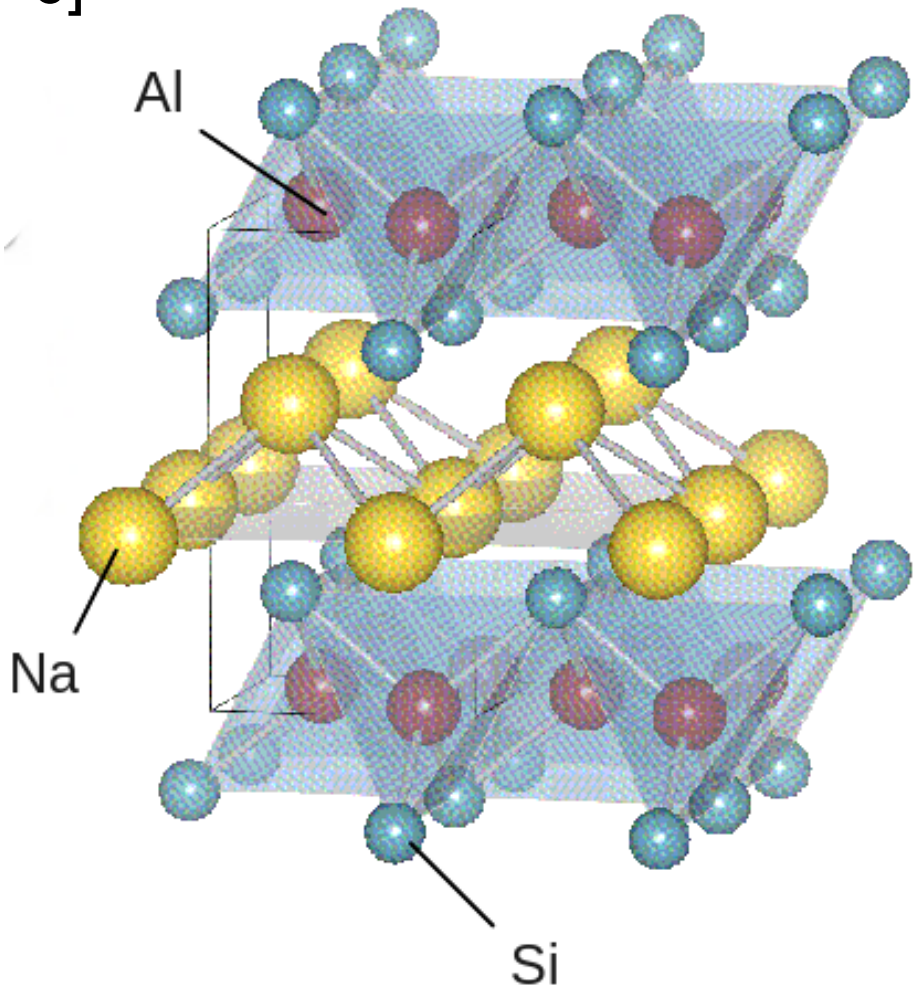
sp electron superconductor, semimetal

T_c = 7 K [Kuroiwa *et al*., Physica C (2007)]

Related systems

- Isovalent to LiBC and (sort of) MgB_2
- More closely related to CaAlSi
- Al_2Si_2 layer structure like Fe-pnictides:

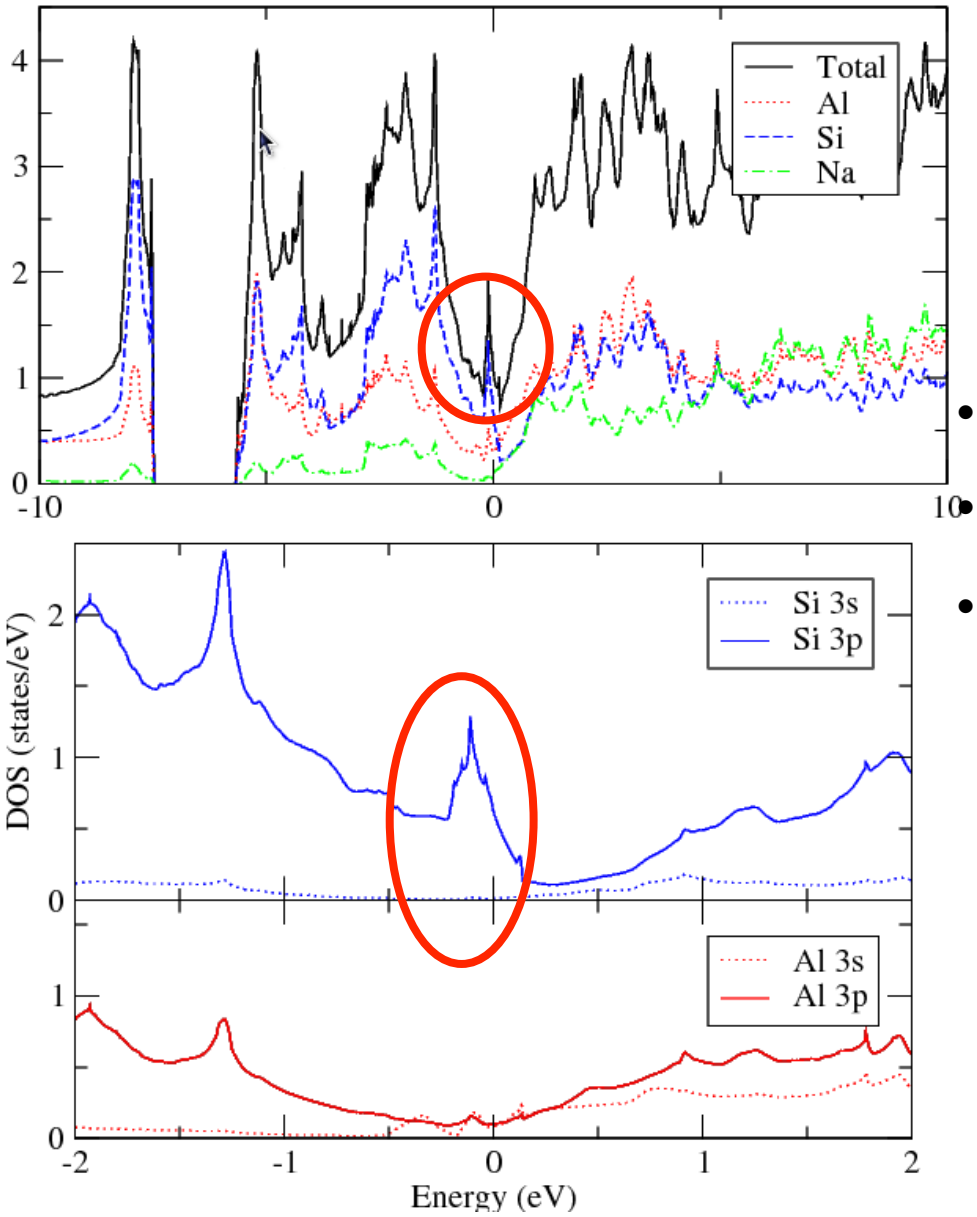
  Si-Al-Si layer ↔ As-Fe-As layer



Rhee, Banerjee, Ylvisaker, WEP, Phys Rev B (2010)

NaAlSi

unusual semimetallic
quasi-two-dimensional
superconductor



- Sharp narrow peak within deep pseudogap
- Peak is Si 3p character
- Steep slope means high thermopower:

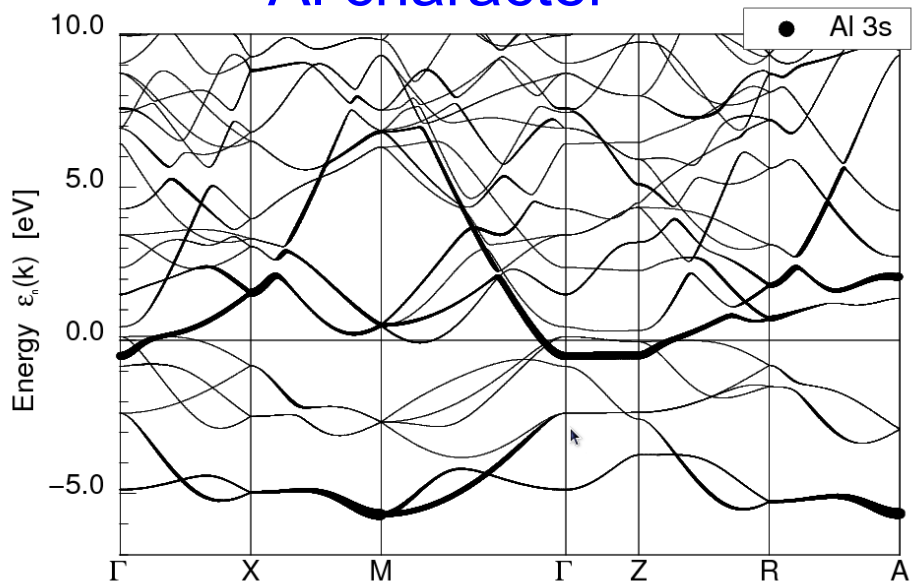
Thermoelectric Application?

$$\mathbf{S}(T) \rightarrow -\frac{\pi^2 k_B}{3e} \left. \frac{d \ln \boldsymbol{\sigma}(E)}{dE} \right|_{\varepsilon_F} k_B T$$

$$\boldsymbol{\sigma}(E) = 4\pi e^2 \langle \vec{v}(E) \vec{v}(E) \rangle N(E) \tau(E)$$

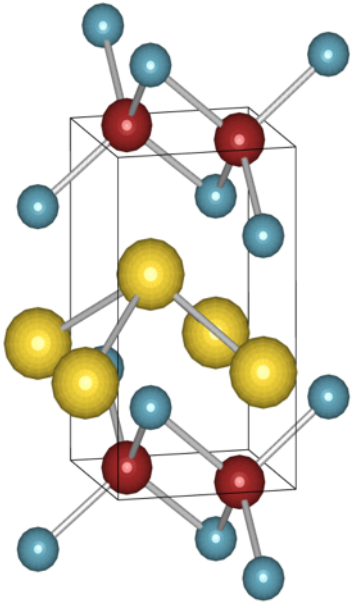
$$d \ln N(E)/dE|_{\varepsilon_F} = -4.0 \text{ eV}^{-1}$$

Al character



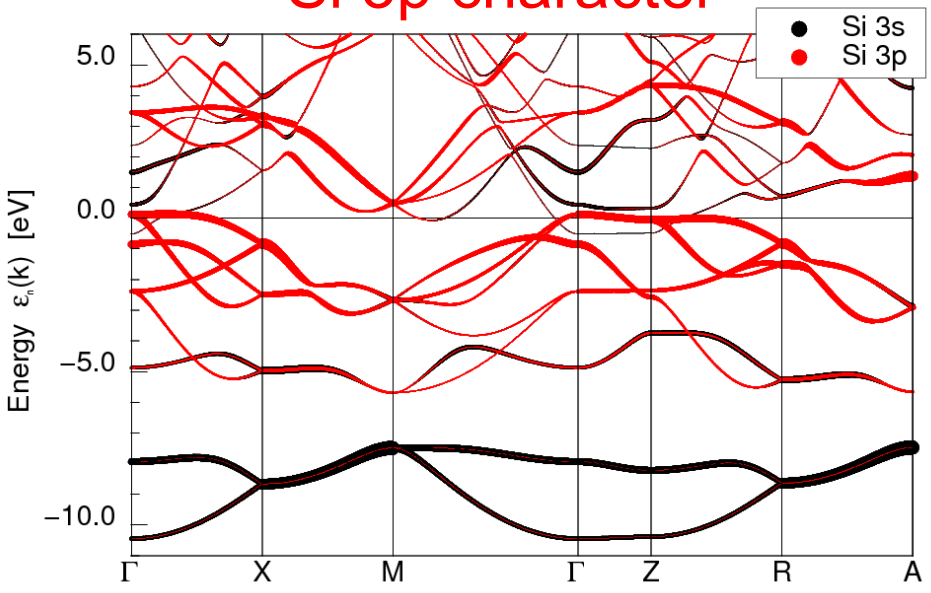
NaAlSi

T_c = 7K



Al 3s: nearly free electrons, semimetallic

Si 3p character



- Al electron pockets, Si hole pockets
- Ionic Na, covalent (and ionic) Al-Si
- Free-electron-like Al 3*s* bands
- Valence states Si-derived, 2D
- s-p electrons, no magnetism

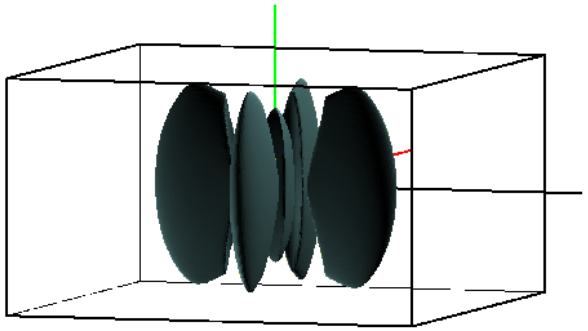
Si 3s,3p holes: covalent-like bands

NaAlSi Fermi Surfaces

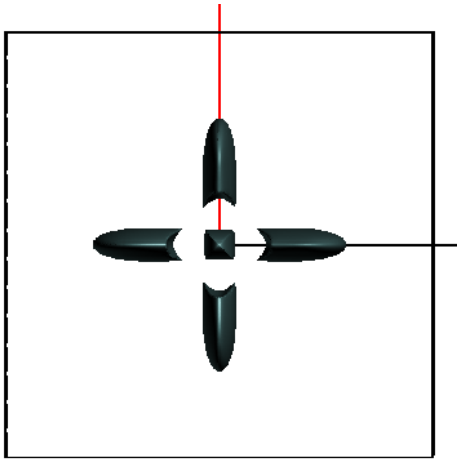
Black: holes. Yellow: electrons.

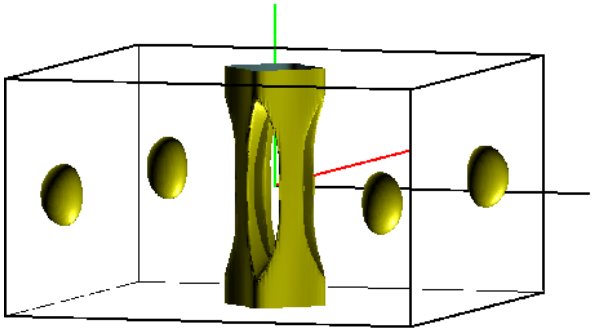
Side view

Paddlewheel

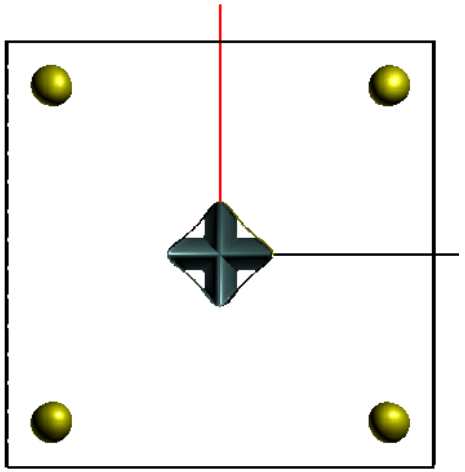


Top view





Side view



Top view

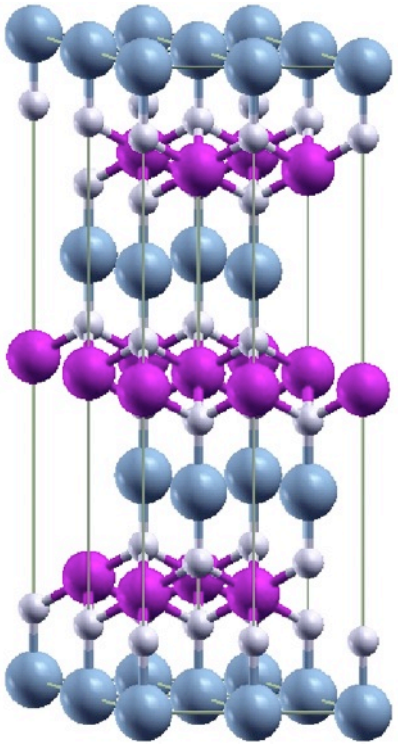
What is λ & T_c (calculated)?
No answer yet to this question.

DFT linear response el-ph coupling calcs?

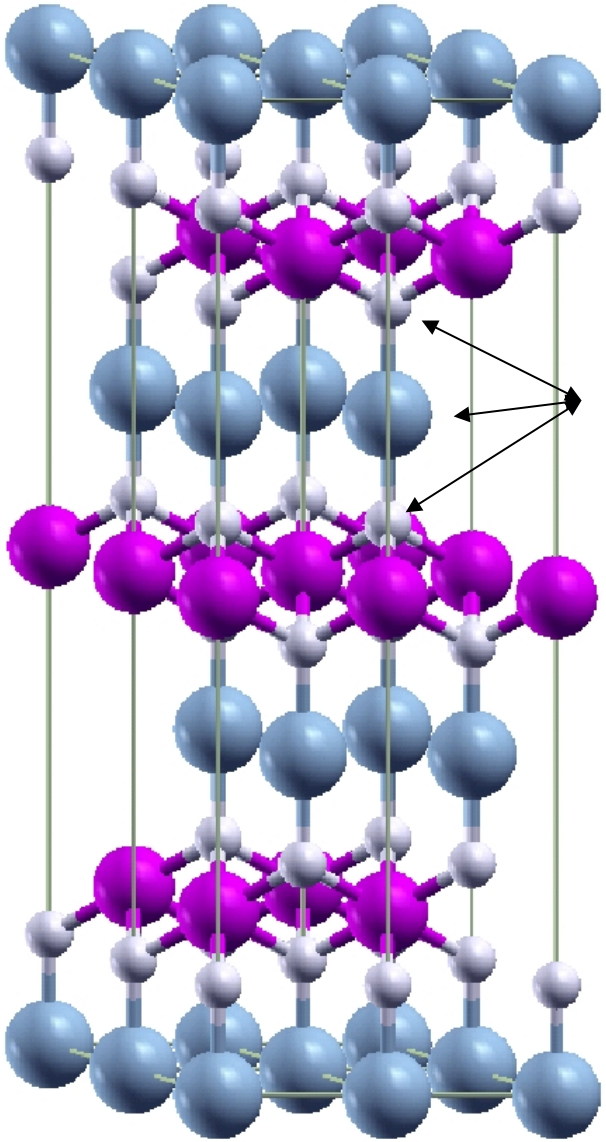
Accurate integrated λ value is difficult to obtain due to small Fermi surfaces and code architectures

An unusual new cuprate superconductor; a high temperature superconductor?

hole-doped delafossite $CuAlO_2$



Triangular lattice delafossite $CuAlO_2$



Linear O-Cu-O trimers

Layered structure, rhombo stacking

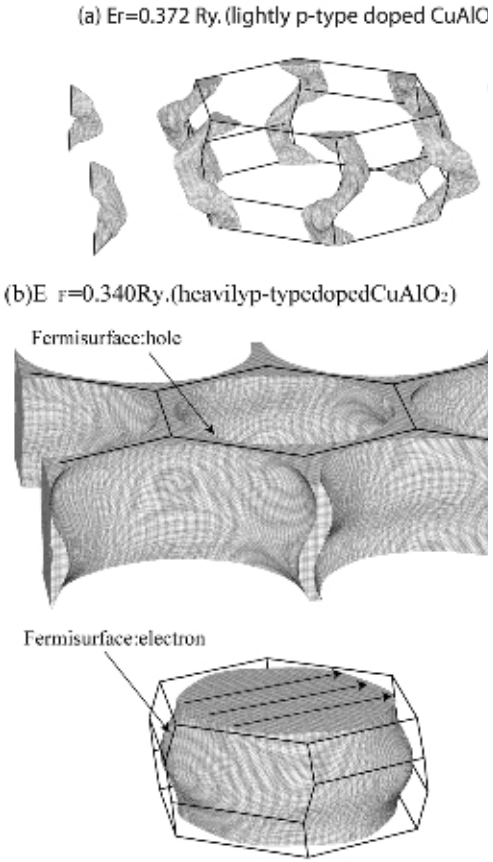
AlO_4 units (hexagonal)

Formally: $Cu^{1+}Al^{3+}(O^{2-})_2$
~3 eV gap insulator

Mostly studied as a transparent metal & thermoelectric
(is naturally a slightly hole-doped conductor)

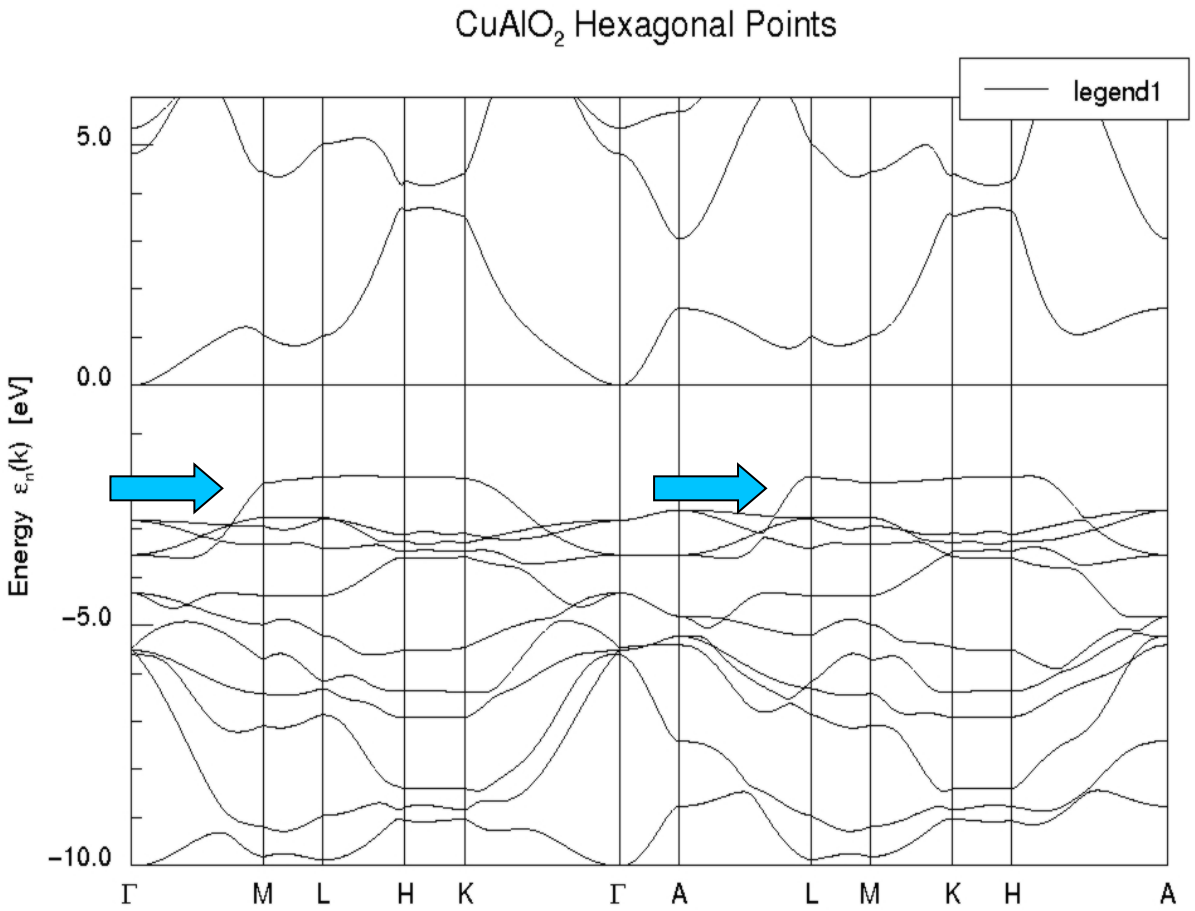
$CuAlO_2$ Electronic structure

Rigid band Fermi surfaces



Nakanishi & Katayama-Yoshida

Band plot along hexagonal lines in BZ

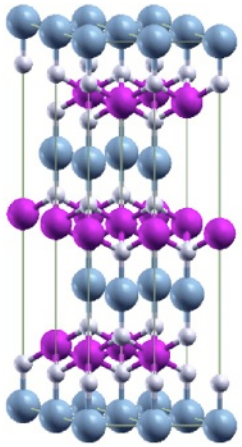


Flat band all around sides of "hexagonal BZ"

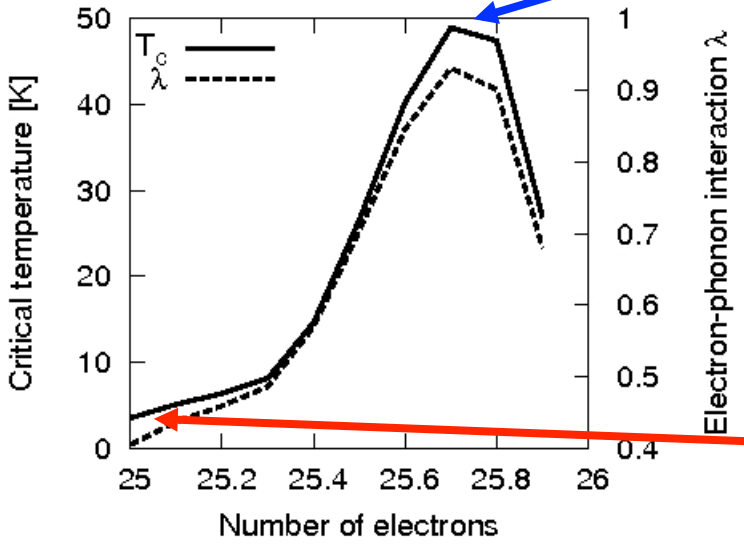
E. R. Ylvisaker & WEP (2002)

Nakanishi & Katayama-Yoshida PREDICTION (SSC 2012)

Superconductivity up to 50K in hole-doped delafossite $CuAlO_2$



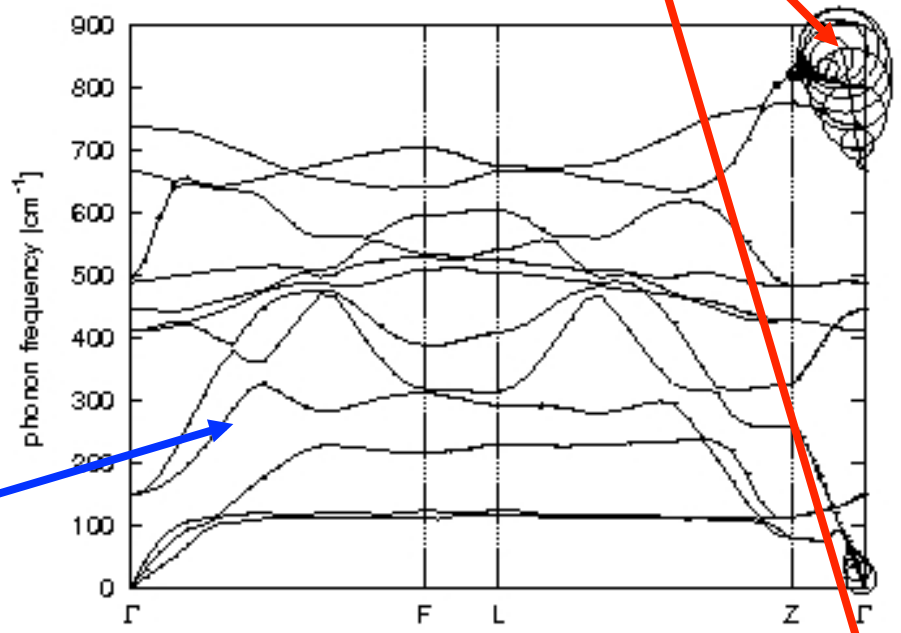
Rigid band doping; matrix elements from undoped material.

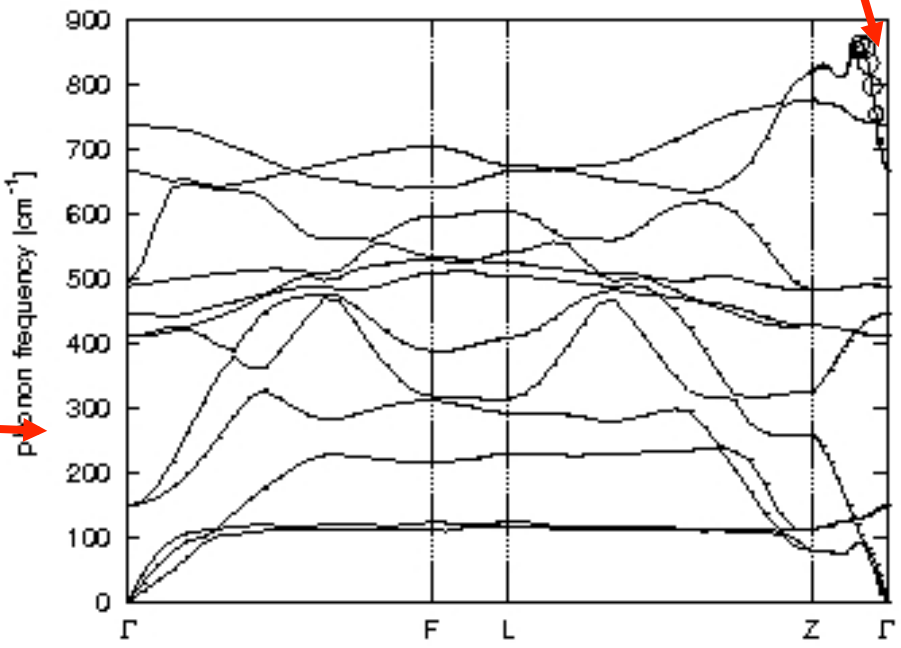


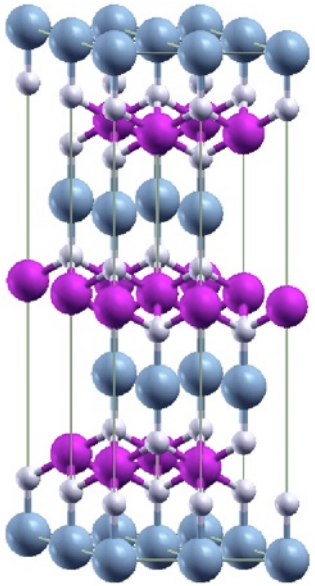
$CuAlO_2$ el-ph coupling λ, T_c

Very weak el-ph coupling almost everywhere, except …

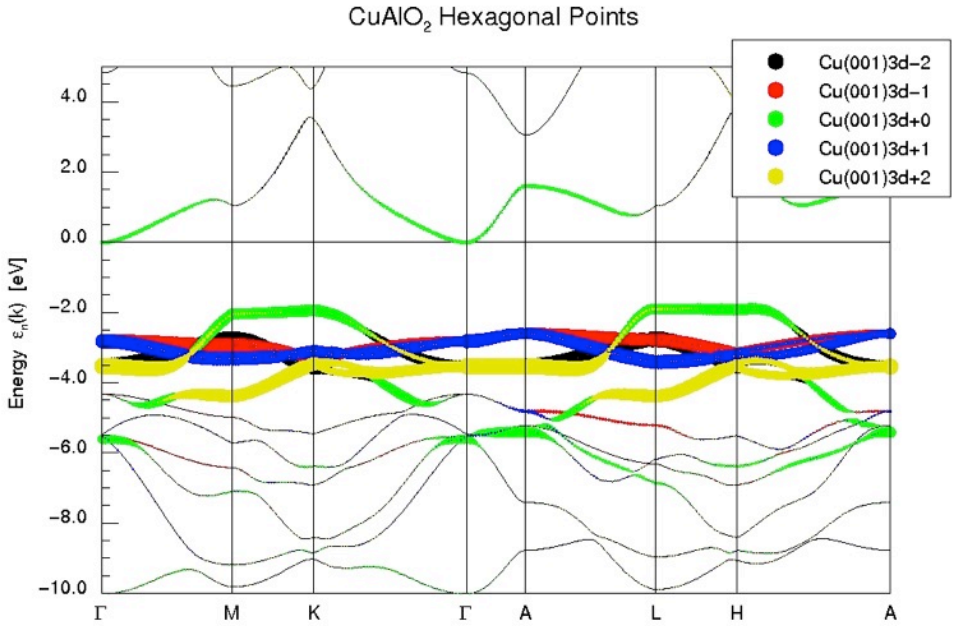
Q = (ε,ε',q), q<0.5π

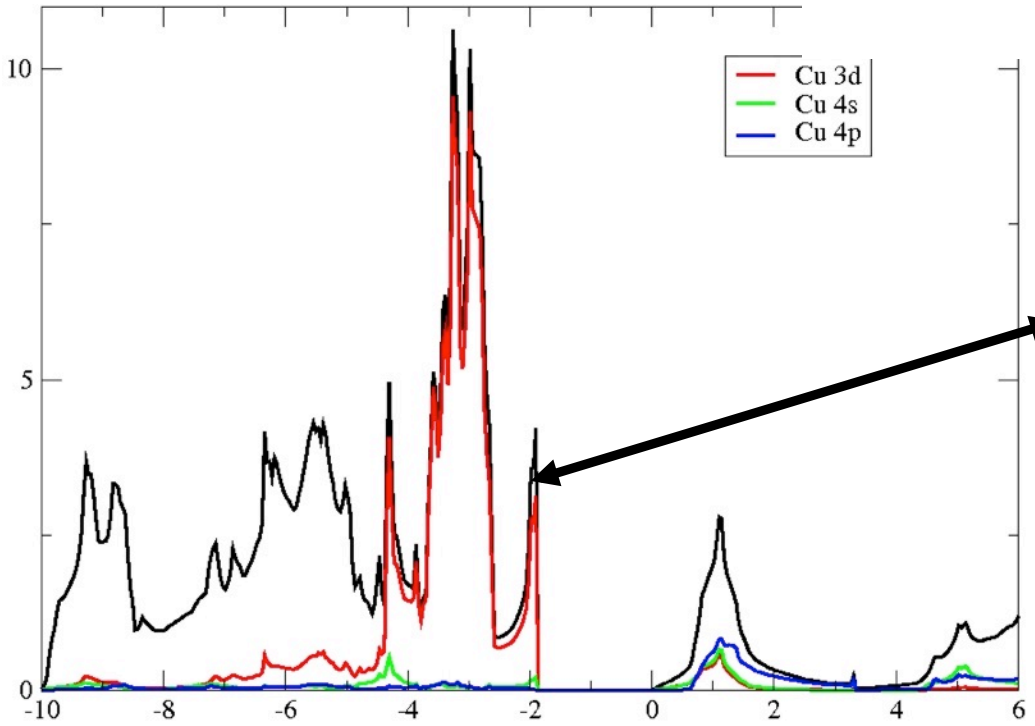






$CuAlO_2$ electronic character





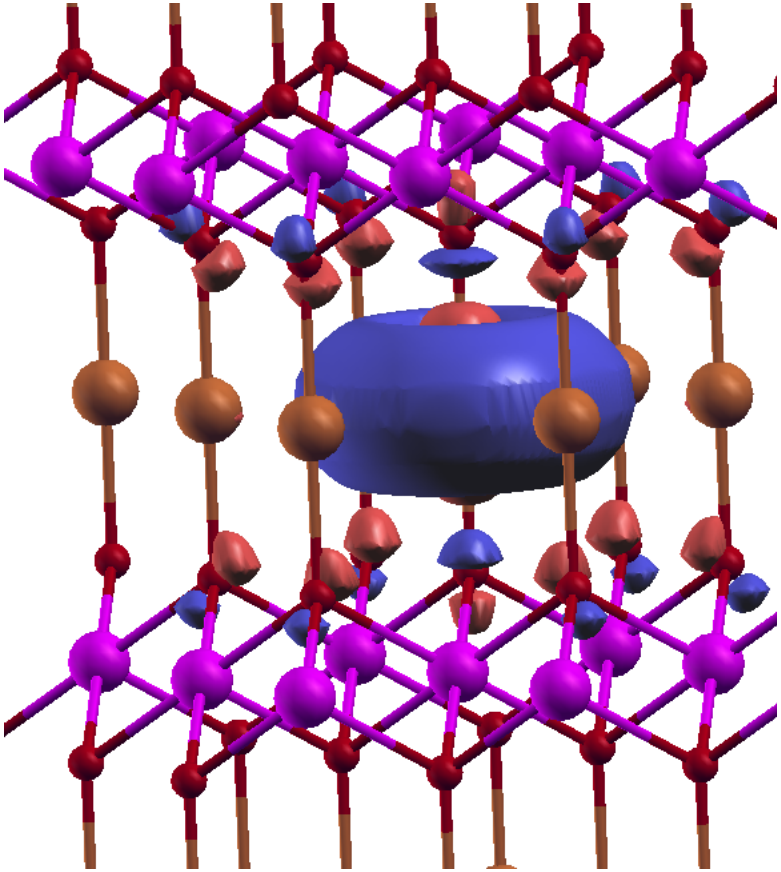
Cu really is Cu^{1+}: d^{10}

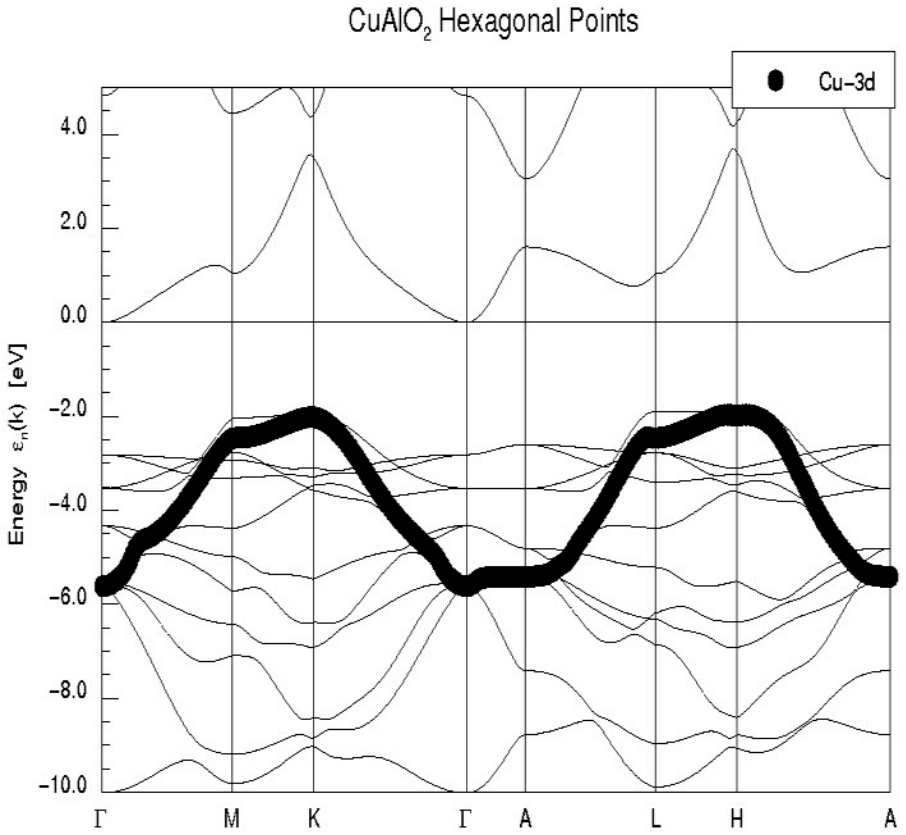
Hole-doping is into Cu $d(z^2)$ - O p_z antibonding states on triangular lattice

Flat valence band max around edge of hexagonal BZ gives “1D” DOS edge

Not near half-filling, but “narrow band.” Polaronic? Or some quasi-1D physics?

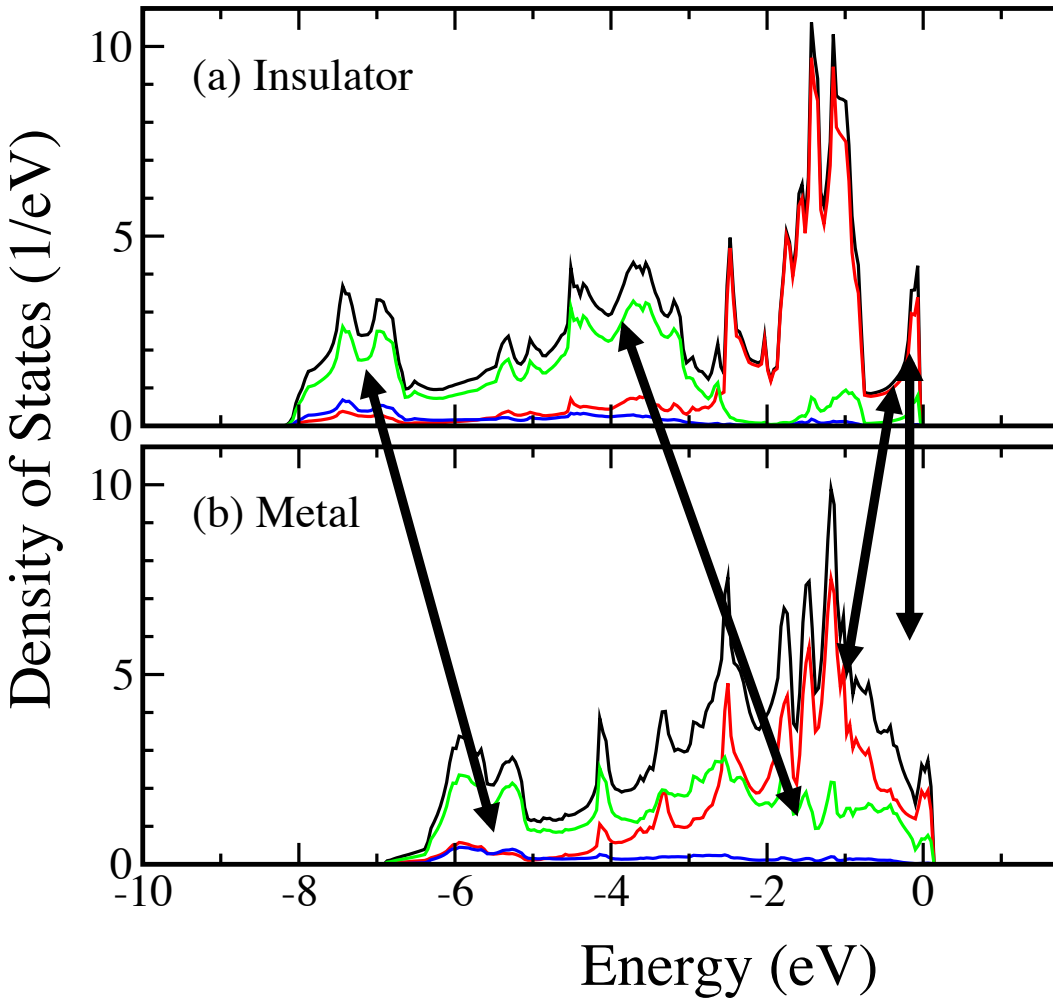
$CuAlO_2$: the active Cu $d(z^2)$ - O p_z Wannier function (valence band maximum): unexpected character

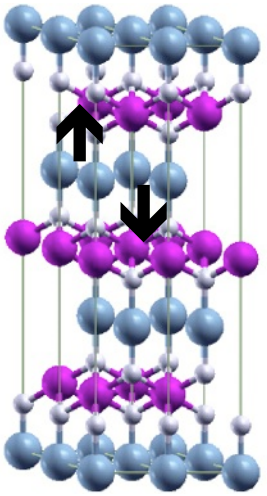




Unusual spectral density shift: doping 0.3 holes into $Cu(Mg,Al)O_2$

Not rigid band at all.





Doping holes
- from Al layer to Cu layer
- introduces dipole layer
  (recall polar catastrophe?!)
- large O 2p ←→Cu 3d shift

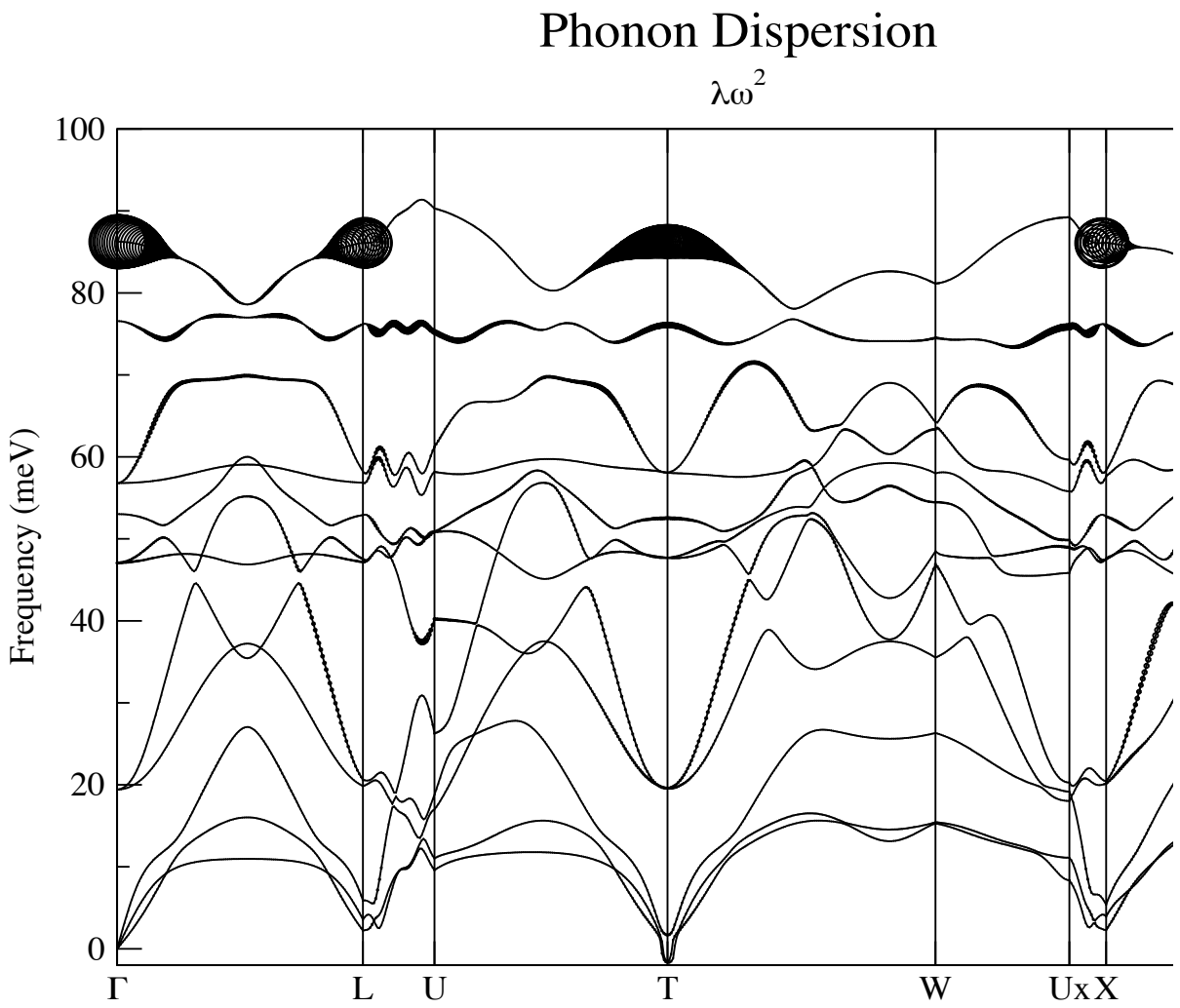
Effects:
- changes character around E_F
- screens the EP matrix elements

This is a 2D physics aspect:
- dipole layer / potential shift

$CuAl_{0.7}Mg_{0.3}O_2$ phonon dispersion, weighted by $\lambda\omega^2$

Full DFT linear response for metallic phase

E. R. Ylvisaker and WEP, EPL 2013



[24x24x24 mesh]

Calculated $\lambda \sim 0.2$;
so $T_c \sim 0$
rather than $T_c \sim 50K$

.

Not superconducting even at optimal doping.

Full self-consistent calculation for the doped system is necessary for definitive results.

Final Comments

Most interesting new sc'ors in last 25 years are

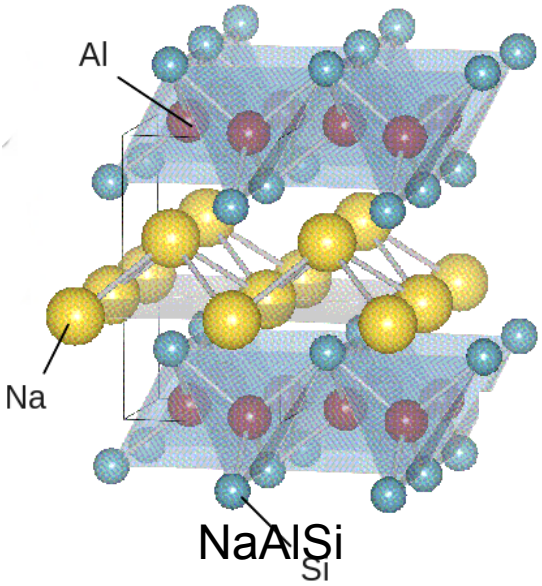
- 2D structurally and electronically, both the magnetic and nonmagnetic examples
- doped insulators (some hole, some electron)

These two features hold for both

- Mott insulating parent phases (viz. cuprates)
- Fe-based pnictide system
- MgB_2 is intrinsically self-doped
- band ionic insulator parent phases (viz. HfNCl)

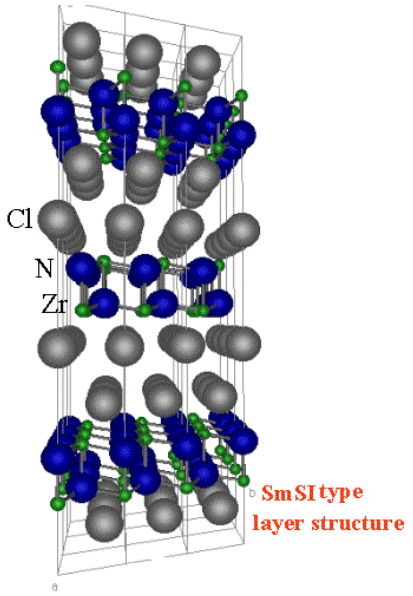
There surely are some very general characteristics favorable for superconductivity that we do not yet fathom (many new doped 2D insulators do not superconduct).

Superconductivity and two dimensionality: experimental facts, theoretical issues, novel materials

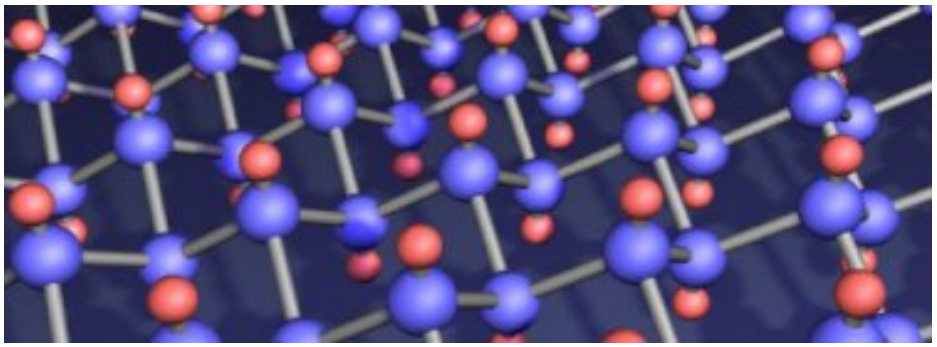


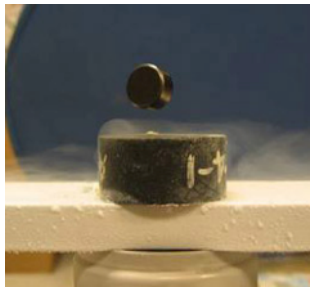
NaAlSi

An area for new discoveries in materials physics

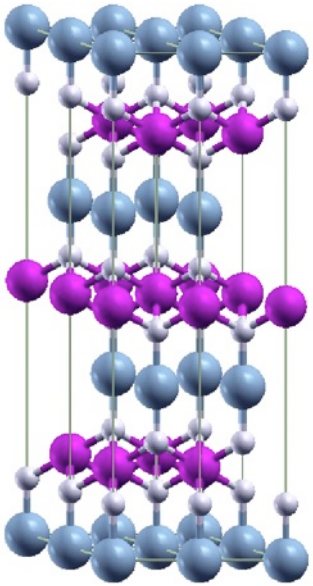


Graphane CH





$CuAlO_2$



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