Two Dimensionality in Conventional and Unconventional Superconductors

Warren E. Pickett, UCDavis

Acknowledgments: too many to list

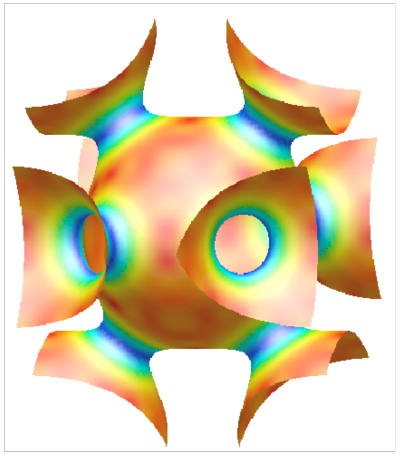
Workshop on Higher Temperature Superconductivity, June 22, 2009

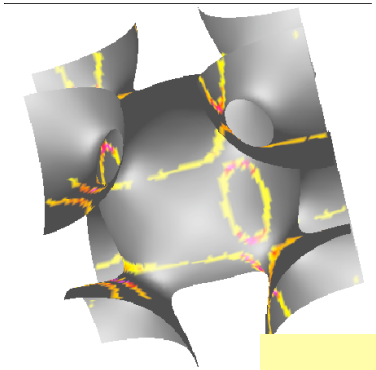
Part I

Electron-Phonon Coupling in 2D

"Recipe for Room Temperature Superconductivity"

Pressure as a Tool to Produce Superconductors: Elemental Metals under Pressure: T_c=20-25K





Li: T_c up to 20 K

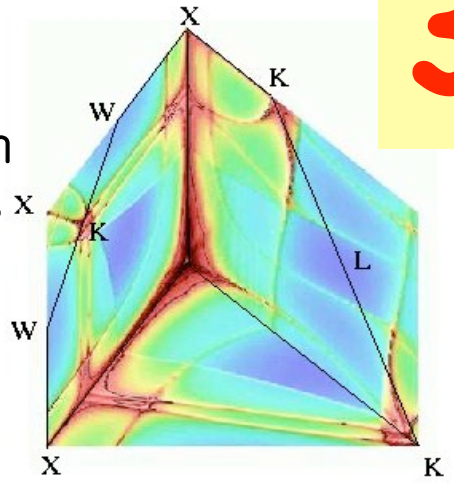
Y: T_c up to 20 K

Ca: T_c up to 25 K

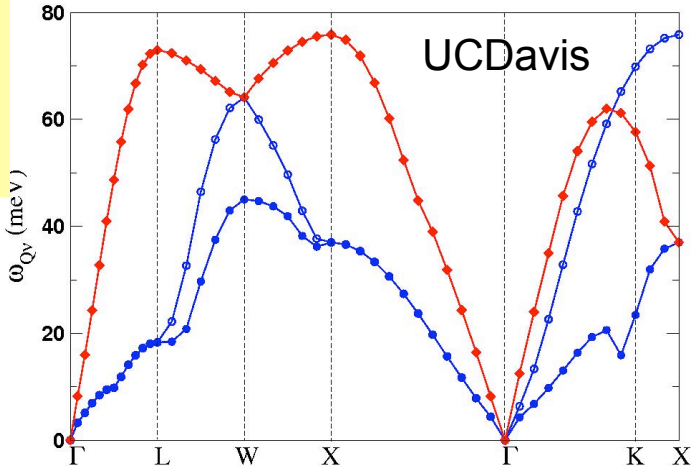
!

3D

Nesting function in three planes



Lithium



fcc Li: strong coupling, phonon anomalies, instabilities under pressure

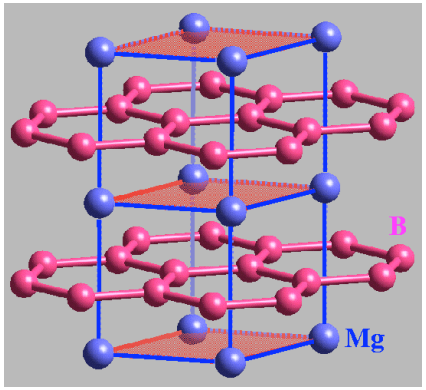
$$\xi_{\vec{Q}} = \sum_k \delta(\varepsilon_k)\delta(\varepsilon_{k+Q}) = V_c \int_{\mathcal{L}} \frac{d\mathcal{L}(k,Q)}{|\vec{v}_k \times \vec{v}_{k+Q}|}$$

Akimitsu's Discovery: 2001

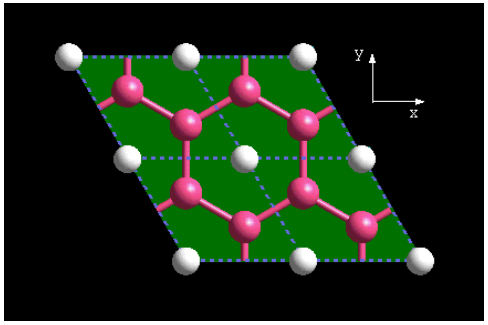
MgB_2, a common chemical reagent.

2D

Searching for ferromagnetism, superconductivity at 40 K was discovered



Quickly reproduced and synthesis techniques were extended by several groups

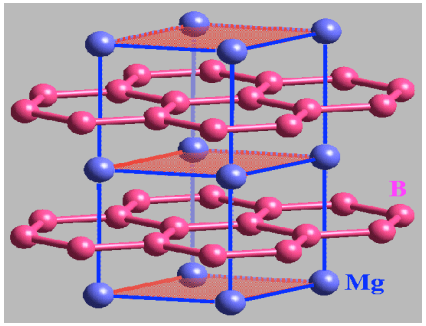


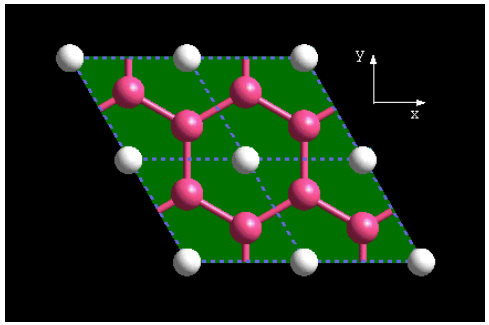
Crystal structure is simple. Quasi-2D.

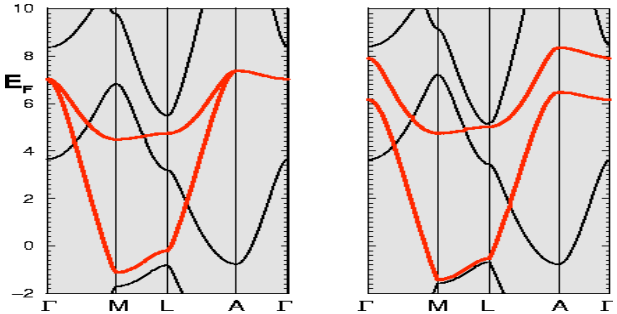
Electronic structure is simple: s-p electrons.

Nagamatsu, Nakagawa, Muranaka, Zenitani, and Akimitsu, Nature **410**, 63 (2001)

Four Months Later: Puzzle Solved!







T. Yildirim (NIST)

1. MgB_2: covalent bonds become metallic
2. Deformation potential *D*=13 eV/A
   (amazingly large for a metal)
3. 2D (cylinder) Fermi surfaces focus strength
4. Yet structure remains stable: intrinsic covalency

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…….

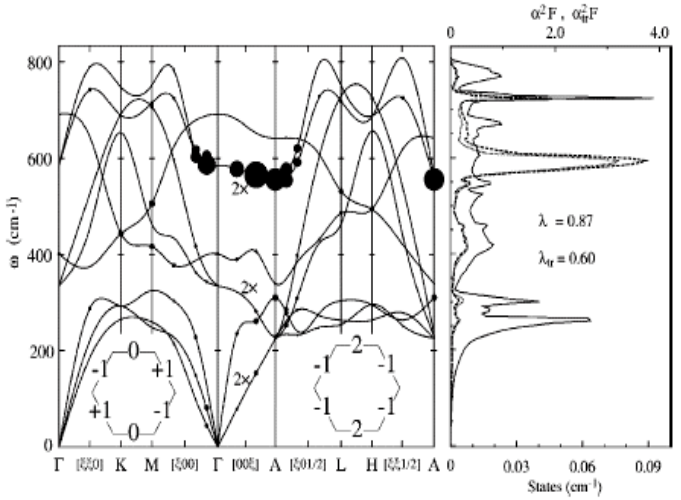


FIG. 1. Left: Calculated phonon dispersion curves in MgB_2. The area of each circle is proportional to the mode λ. The insets at the bottom show the two Γ*A* *E* eigenvectors (not normalized), which apply to the holes at the top of the σ bands (bond-orbital coefficients) as well as to the optical bond-stretching 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)

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

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

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

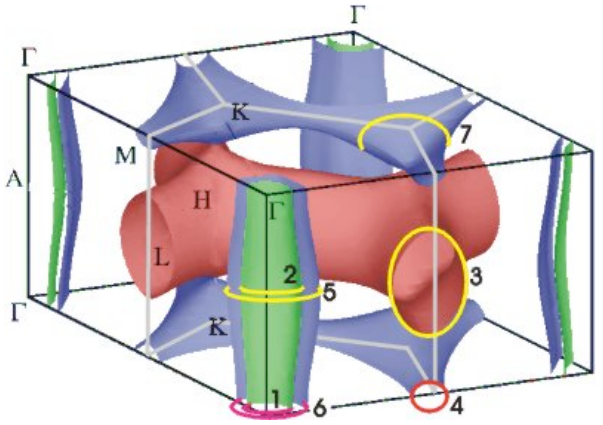
$$\gamma_{Q\nu} = \frac{\Omega_{q\nu}}{\omega_{Q\nu}} Im\ \Pi(Q,\omega_{Q\nu})$$

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

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

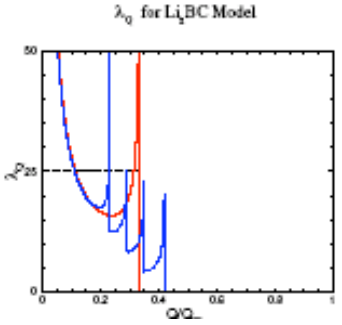
3% of phonons have $\lambda \sim 25$!

Rest of phonons have $\lambda \sim 0.3$

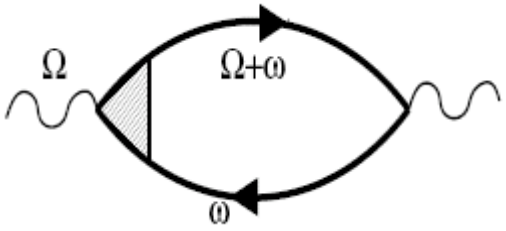


$$\lambda_{\vec{Q},\nu} = 4\frac{2}{\omega_{\vec{Q},\nu}}\sum_k |M_{k,k+Q}|^2\delta(\varepsilon_k)\delta(\varepsilon_{k+Q})$$

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



Phonon Renormalization (Self Energy)



Cylinder Fermi surface leads to sharp Kohn anomaly

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

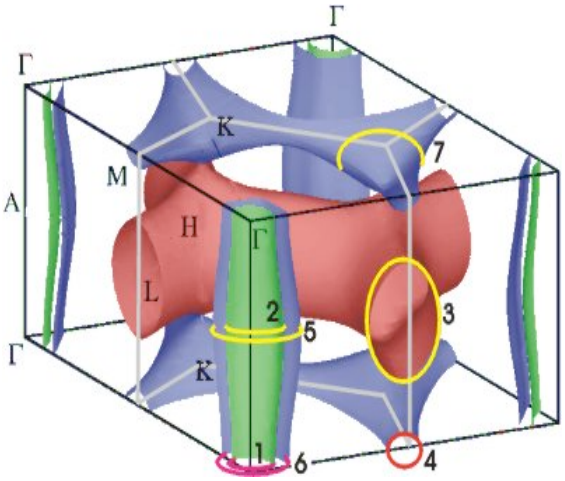
Extreme Electron-Phonon Coupling: Kohn Anomalies

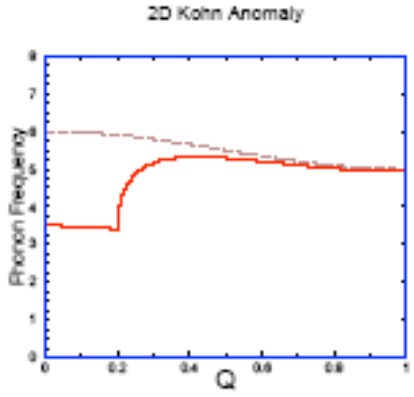
$$\omega_{Q\nu}^2 = \Omega_{Q\nu}^2 + 2\Omega_{Q\nu}^2 \Pi(Q, \omega_{Q\nu})$$

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

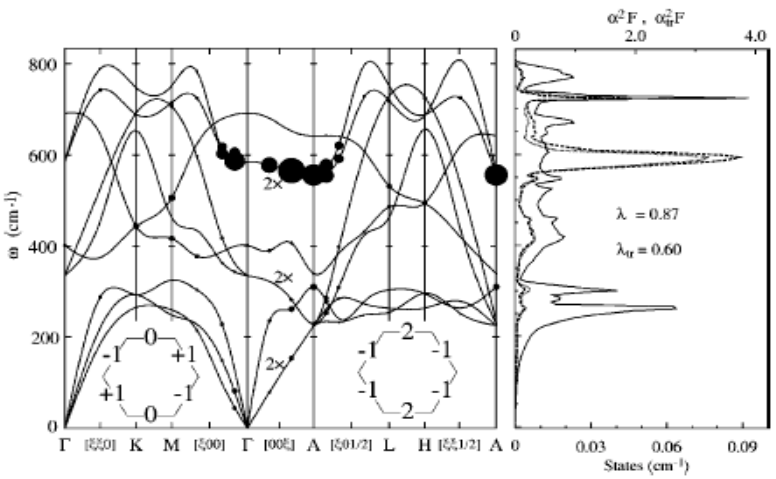
2D dispersion, slowly varying matrix elements give

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





Pinpointing of Strong Electron-Phonon Coupling



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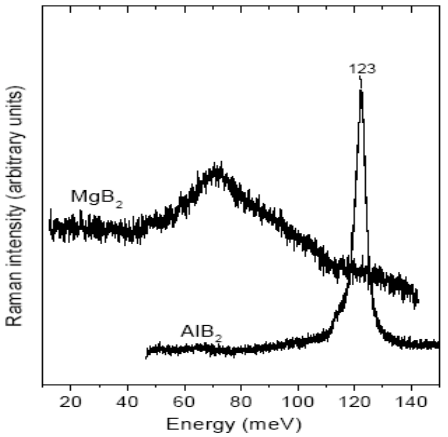
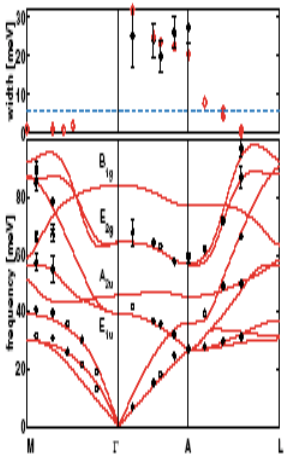


Raman spectrum
Bohnen, Heid, Renker (2002)



Shukla et al. Phys. Rev. Lett. (2003)
Inelastic x-ray scattering measurements

3% of phonons have $\lambda \sim 25$!
Rest of phonons have $\lambda \sim 0.3$

W. Weber et al.,
PRL (1978)

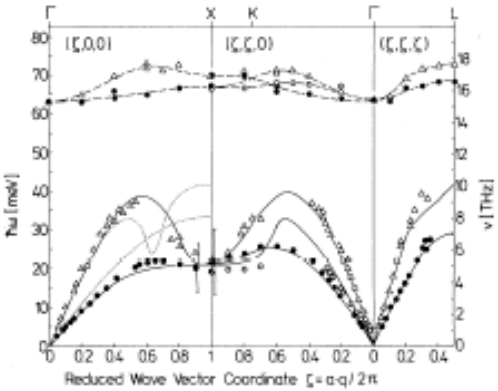
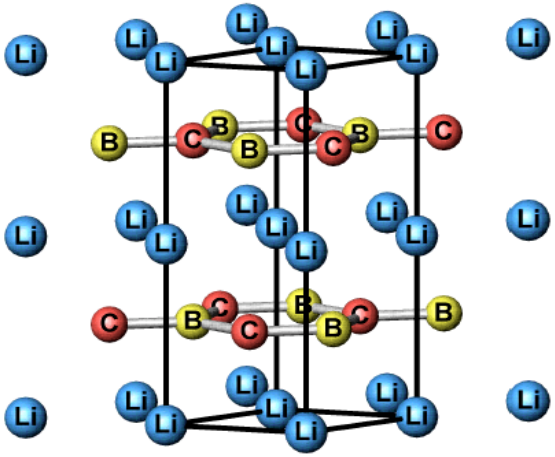


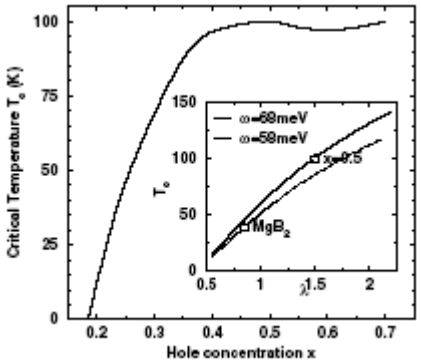
FIG. 1. Phonon dispersion curves for $VN_{0.86}$ (open

Prediction of a "better MgB_2": $Li_{1-x}BC$

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



Structurally, chemically, similar to MgB_2
Semiconductor, so hole-doping is required
(de-intercalation of Li)
Deformation potential 50% larger than MgB_2
T_c =75 K (or higher) might be possible



Not so simple experimentally!

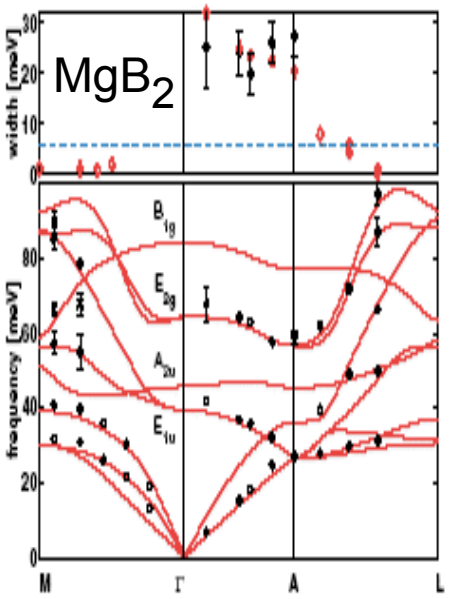
Several reports of inability to prepare $Li_{1-x}BC$
Reports that $Li_{1-x}BC$ is not superconducting:

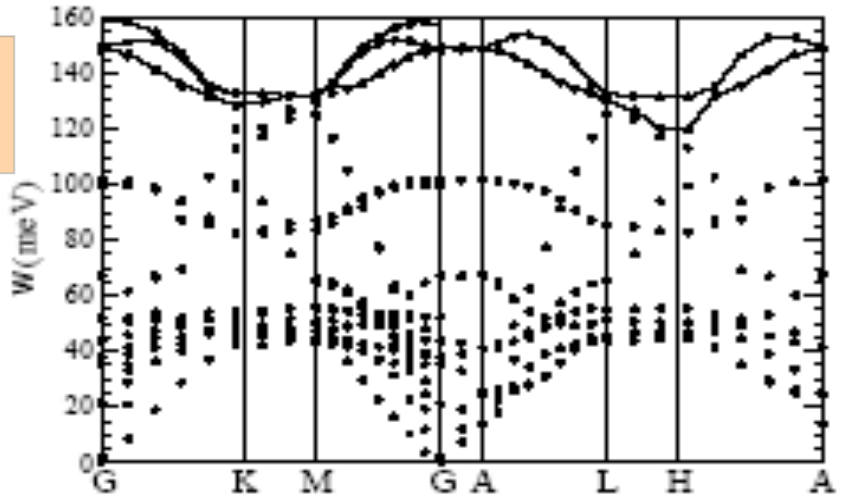
Zhao, Klavins, Liu, J. Appl. Phys. (2003)
Fogg, Claridge, Darling, Rosseinsky (2003)

But the $Li_{1-x}BC$ samples are not well characterized(?).

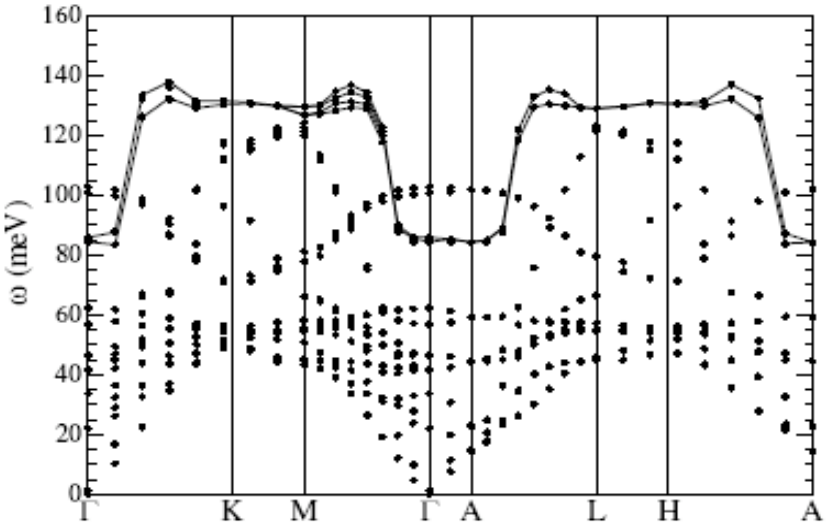
Electron-Phonon Coupling Strength Calculated for $Li_{1-x}BC$

Semiconductor x=0
Simple vibrational spectrum





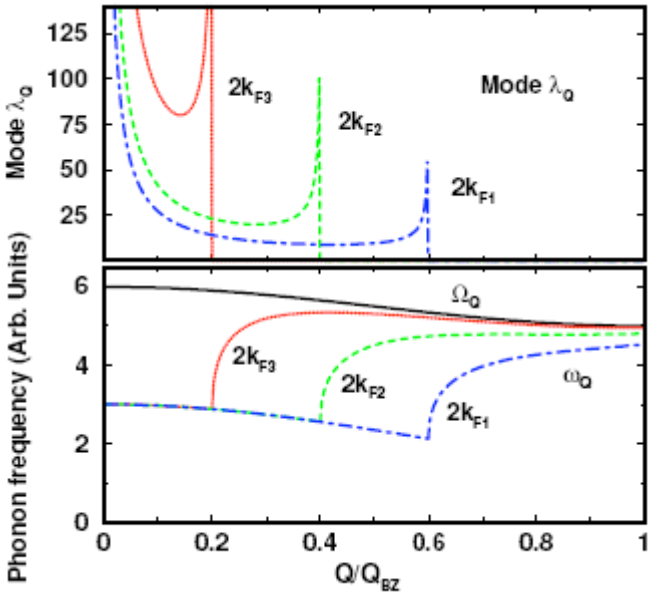
Metal for x=0.25
Extreme Kohn anomalies



EI-Ph Coupling in MgB_2-like Systems

Mode λ_Q and Total Coupling Strength λ

$$
\begin{aligned}
\lambda_Q &= \frac{2}{\pi N(0)} \frac{\gamma_Q}{\omega_Q^2} \\
\gamma_Q &= \pi \Omega_Q |g|^2 [N(0)]^2 d_b^2 \hat{\xi}(Q), \\
\hat{\xi}(Q) &= \frac{\sum_k \delta(\varepsilon_k)\delta(\varepsilon_{k+Q})}{[\sum_k \delta(\varepsilon_k)]^2} = \frac{A_{BZ}}{A_{FS}} \frac{1}{\pi} \frac{\theta(1-\eta)}{\eta\sqrt{1-\eta^2}} \\
\lambda &= \sum_{Q\nu} \lambda_{Q\nu} = d_b^2 \frac{N(0)\mathcal{D}^2}{M\omega_Q^2} \leftrightarrow \frac{N(\varepsilon_F) < I^2 >}{M < \omega^2 >} \\
&= \frac{d_b^2 N(0)\mathcal{D}^2}{M\Omega_Q^2 - d_b^2 N(0)\mathcal{D}^2}, \quad N(0) = \frac{m^*}{2\pi} \\
&= \frac{\lambda_o}{1-\lambda_o}, \quad \lambda_o \equiv \frac{d_b^2 N(0)\mathcal{D}^2}{M\Omega_Q^2}
\end{aligned}
$$



- mode λ_Q *scales inversely with carrier density* ($A_{FS} \equiv \pi k_F^2$)
- total λ is independent of carrier density

Why Isn't MgB_2 a Higher T_c Material?

How could MgB_2 have been better? Relations to use:

$$\lambda_o \equiv \frac{d_b^2 N(0)\mathcal{D}^2}{M\Omega^2}; \quad \lambda = \frac{\lambda_o}{1-\lambda_o}$$

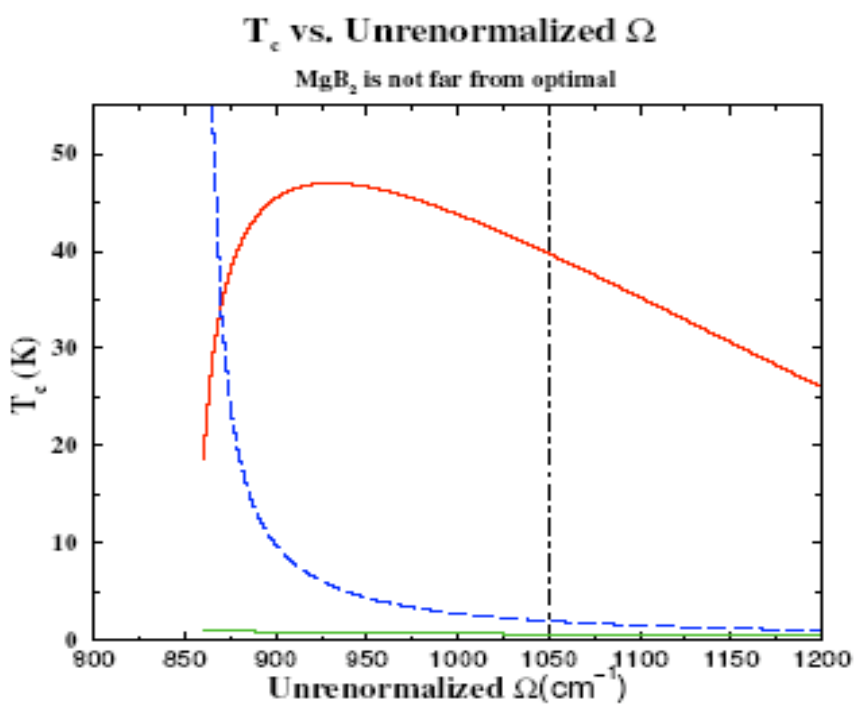
$$T_c \approx \frac{<\omega>}{4}[e^{2/\lambda_{eff}} - 1]^{-1/2}; \quad \lambda_{eff} = \frac{\lambda - \mu^*}{1 + 0.75\lambda\mu^* + 2\mu^*}$$

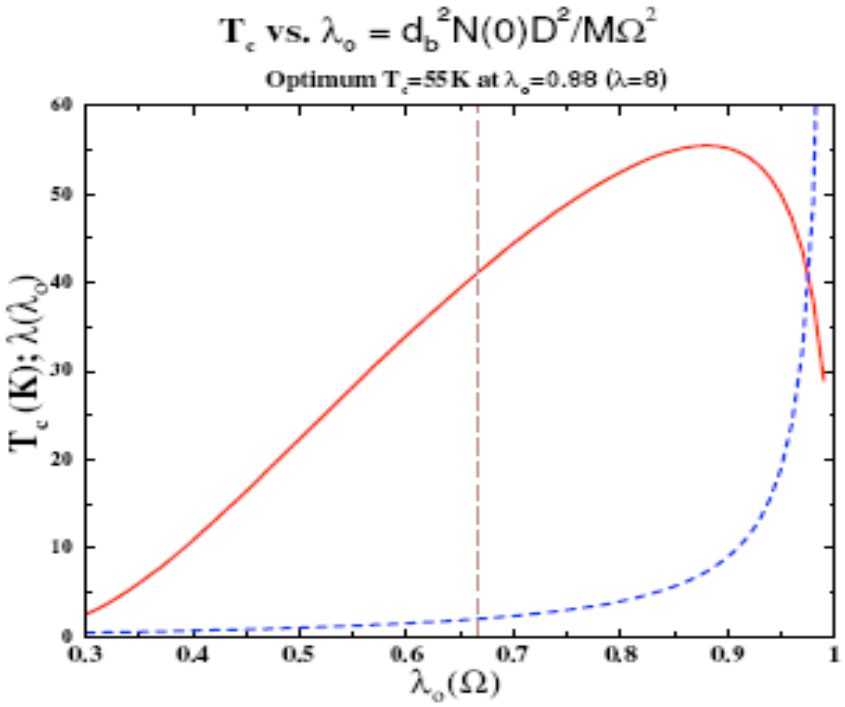
• Suppose Ω had been different from what it is, Ω_{AlB_2} =1050 cm^{-1}. With other factors the same, the parent system would have been unstable if $\Omega = 850$ cm^{-1}. Hence MgB_2 is not so far from not having existed.

• What if Ω were even bigger? λ_o and λ would be smaller but the energy/temperature scale (prefactor in T_c) would have been higher.

• What if the coupling (deformation potential $\mathcal{D}$) had been larger? If $\mathcal{D}$) were 20% larger ($\mathcal{D}^2$ 44% larger), $\lambda_o \to 1$ and MgB_2 would be unstable.

Engineering an Optimized MgB_2





An Optimized MgB_2 would have T_c=55-60K

Is there some other way to win?

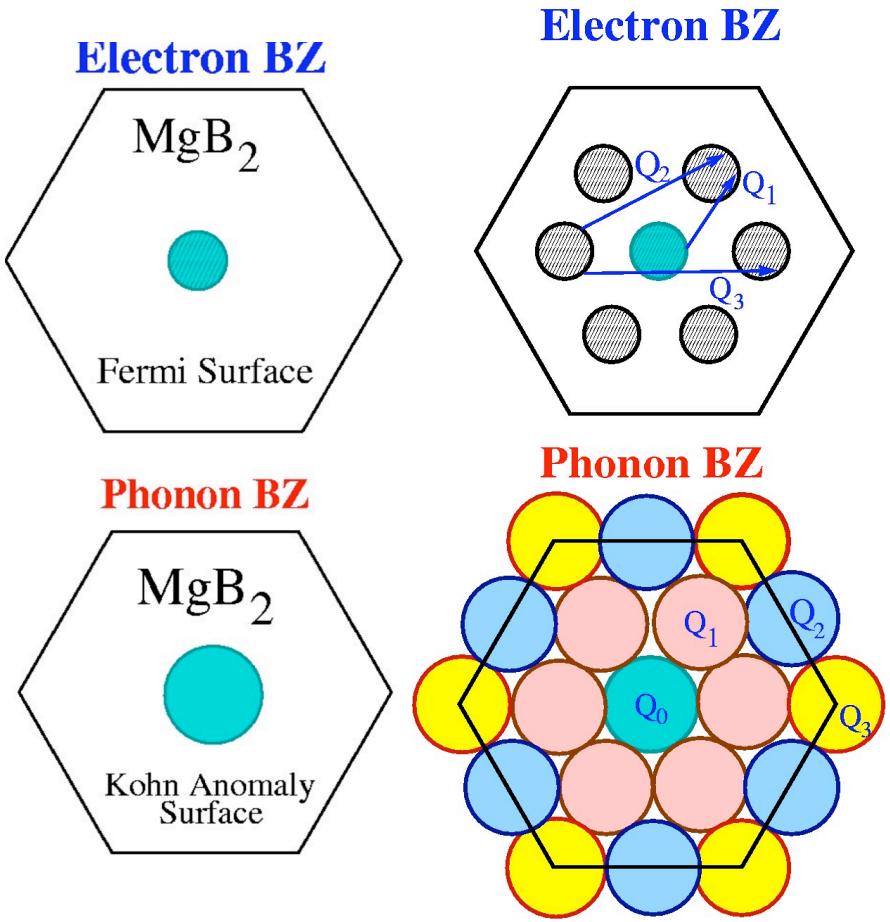
Yes.

Make serious use of
two-dimensionality in the boson coupling.

Design of higher T_c superconductors: is it viable?

Rational Design/Search for new hTS

Example of one design criterion



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

Part II

Doped 2D Insulators

But: ionic band insulators, not Mott insulators

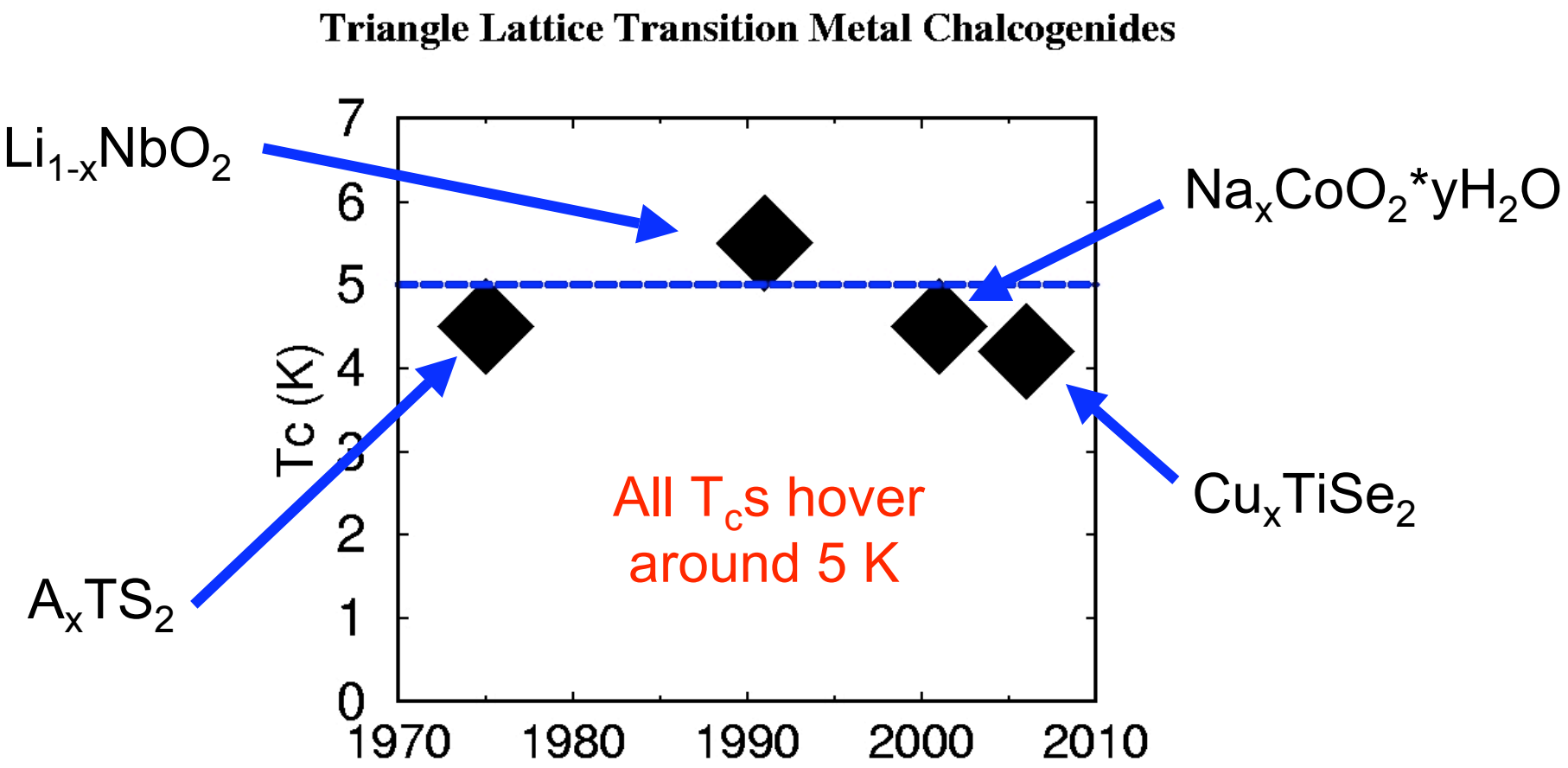
Observations about Carrier-doped Layered Transition Metal Oxides

- Electron-doped TaS_2
- Hole-doped $LiNbO_2$
- Hole-doped $NaCoO_2$ (hydrated)
- Electron-doped $TiSe_2$

Observation about Carrier-doped Layered Transition Metal Nitride

- Electron-doped ZrNCl, HfNCl
- Electron-doped TiNCl
- Electron-doped $BaHfN_2$???

Synopsis: T_c in 2D Triangular Oxides/Chalcogenides



Observations about Carrier-doped Layered Transition Metal Oxides

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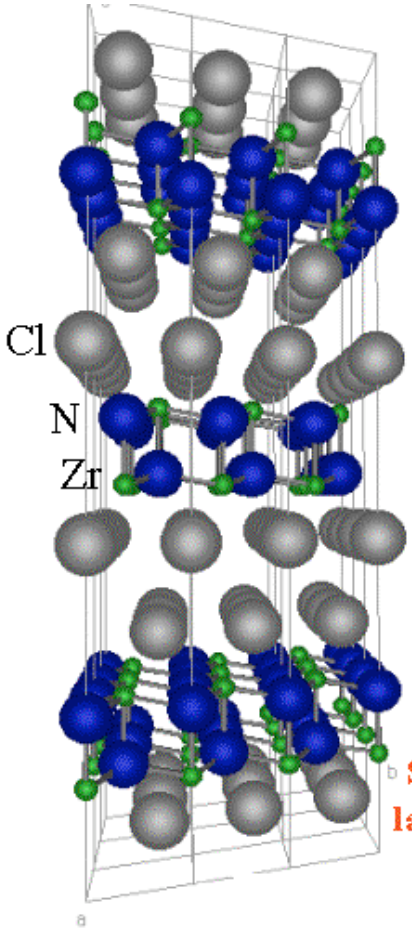
Observation about Carrier-doped Layered Transition Metal Nitrides

- Electron-doped ZrNCl, HfNCl
- Electron-doped TiNCl
- Electron-doped $BaHfN_2$???

Alkali-doped A_xZrNCl (15 K) & A_xHfNCl (25 K)

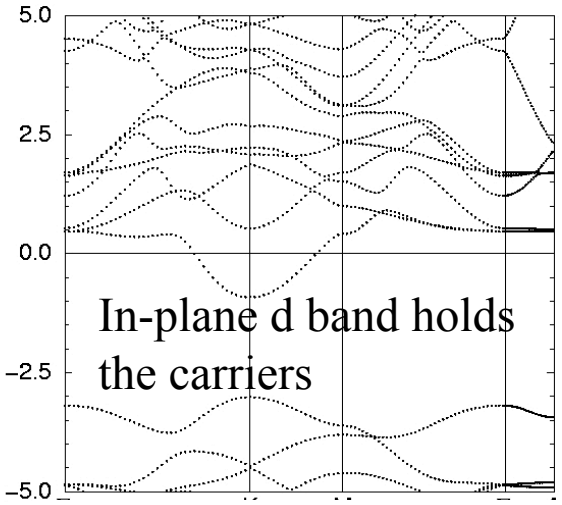


SmSI type layer structure

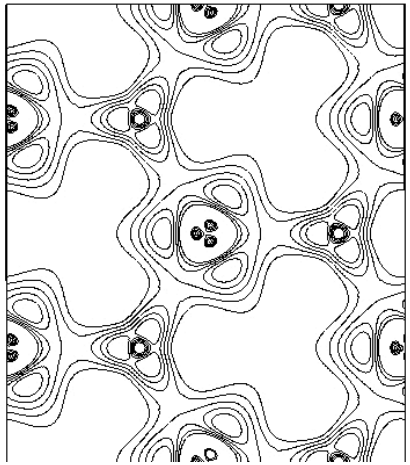
Structure is somewhat MgB2-like; so is it electron-phonon?

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 Zr-N layer
- Strongly 2D bands
- Electron-doped
- Inverse ‘isotope shift’
- Weak el-ph coupling

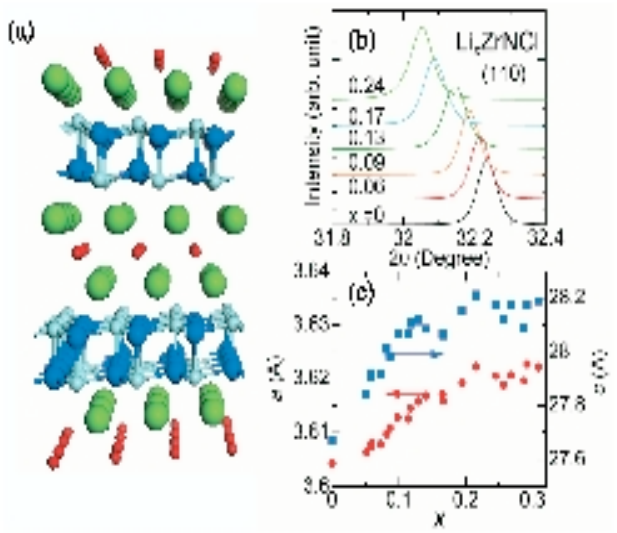


Superconductor-insulator transition at x=0.06

Increase in T_c upon Reduction of Doping in Li_xZrNCl Superconductors

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*

PRL, 2009



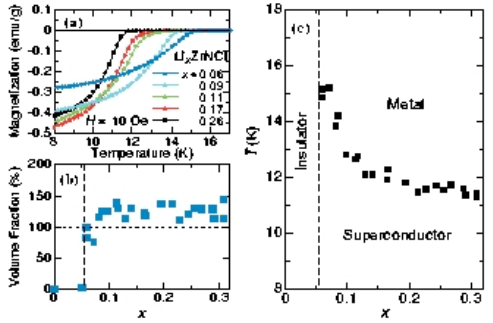


FIG. 4 (color). (a) Magnetization at a field of 10 Oe (without correction for demagnetizing field) is plotted against temperature for selected samples. (b) x dependence of the superconducting volume fraction determined by MH measurements at 2 K (or 5 K). Imperfect correction of the demagnetizing field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

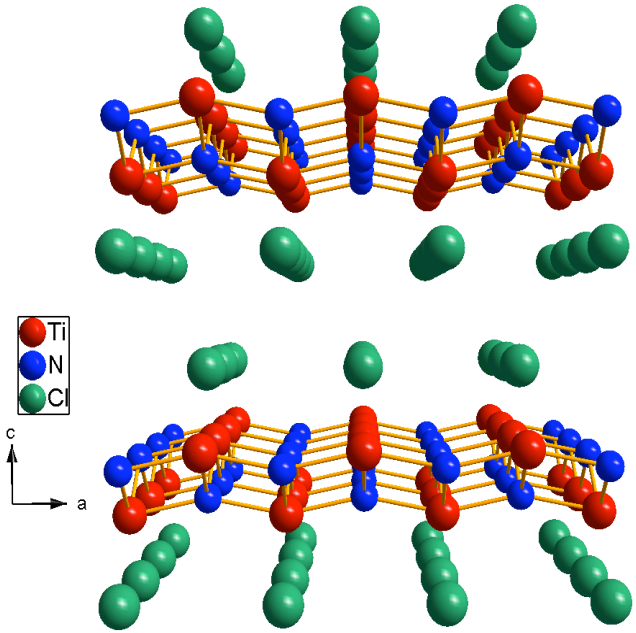
Insulator-superconductor transition to optimal superconducting Tc at x=0.06

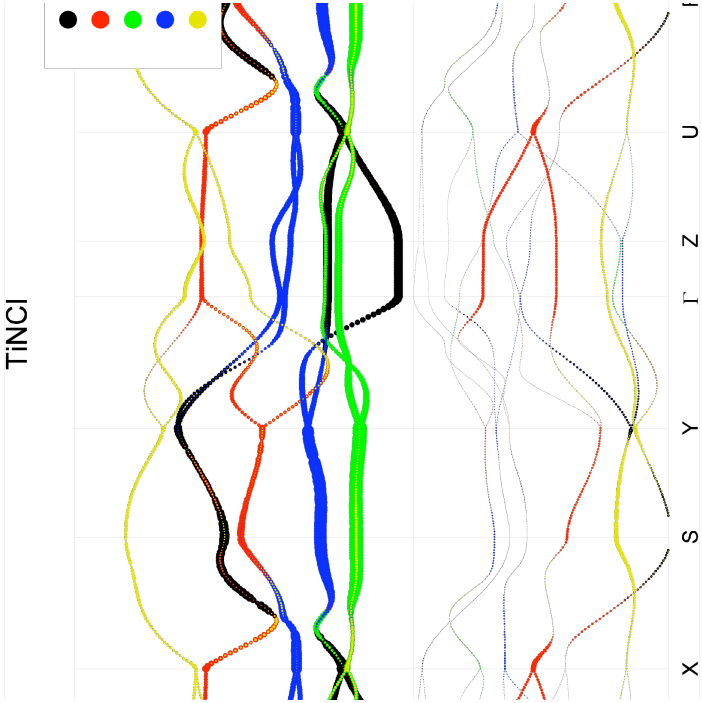
Electron doping of 2D van der Walls insulator TiNCl

S Yamanaka et al. J. Mater. Chem. 19, 2573 (2009)

T_c to 16.5K

- Structure: metallic-covalent square Ti_2N_2 layer, cladded by Ba on each side-->neutral slabs
- Intercalate with Li, Na, … to get superconductivity?

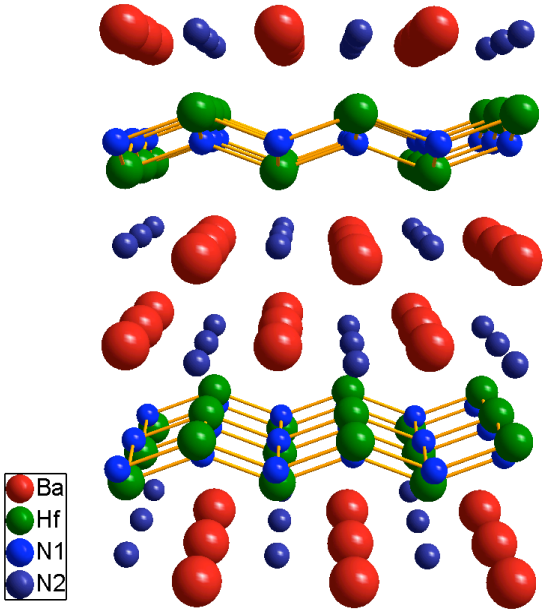


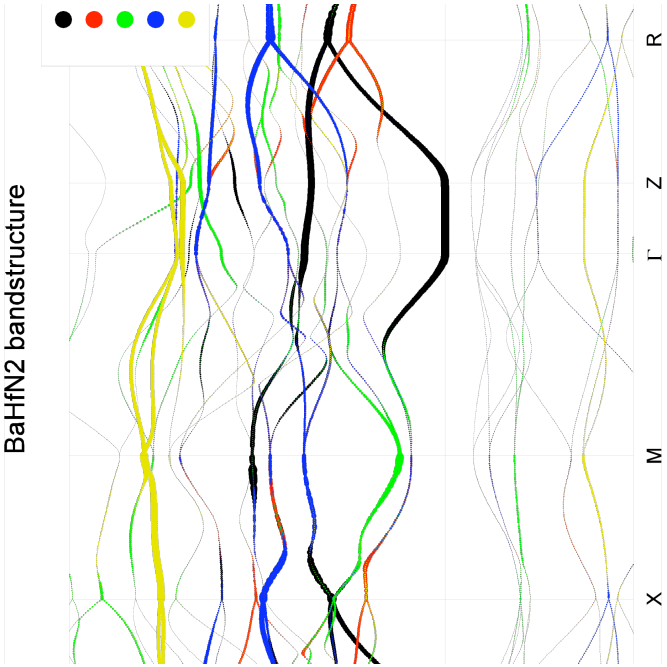


Electron doping of 2D van der Walls insulator $BaHfN_2$

D. H. Gregory et al. JSSC 137, 62 (1998)

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



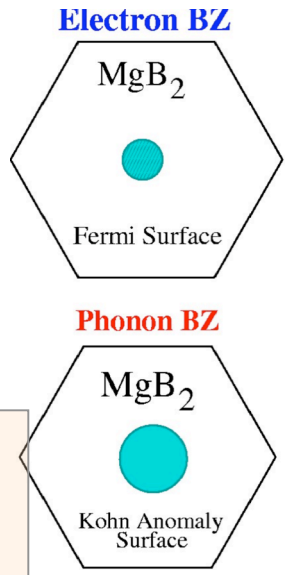


Mechanism of superconductivity in doped HfNCl, TiNCl?

Not phononic, not magnetic --> electronic.

Boson exchange: use of BZ is same as MgB_2

i.e. very far from optimal



2D plasmons: $\omega_q=[(2\pi ne^2/\varepsilon m^*)q]^{1/2}$

for $m^*=1$, $\varepsilon=9$, $n_{cr}=1/16$ (ZrNCl): ω_q^{max} = 0.5-0.75 eV

Doped insulator just beyond MIT: weak screening --> "charged phonons" (can have huge oscillator strengths)

Doped insulator just beyond MIT: coupled plasmon-phonon modes

A. Bill et al.

?Polaronic behavior: ?bipolaron pairing?

Discussion Questions

Hirschfeld

- Eliashberg-type theory for electronic pairing?
- Atomic-scale phenomena: very important for higher Tc.
- Can DFT play a role in strongly correlated materials?
- Prospects for theory of inhomogeneous superconductivity…..
- What could 30x more computational power accomplish?