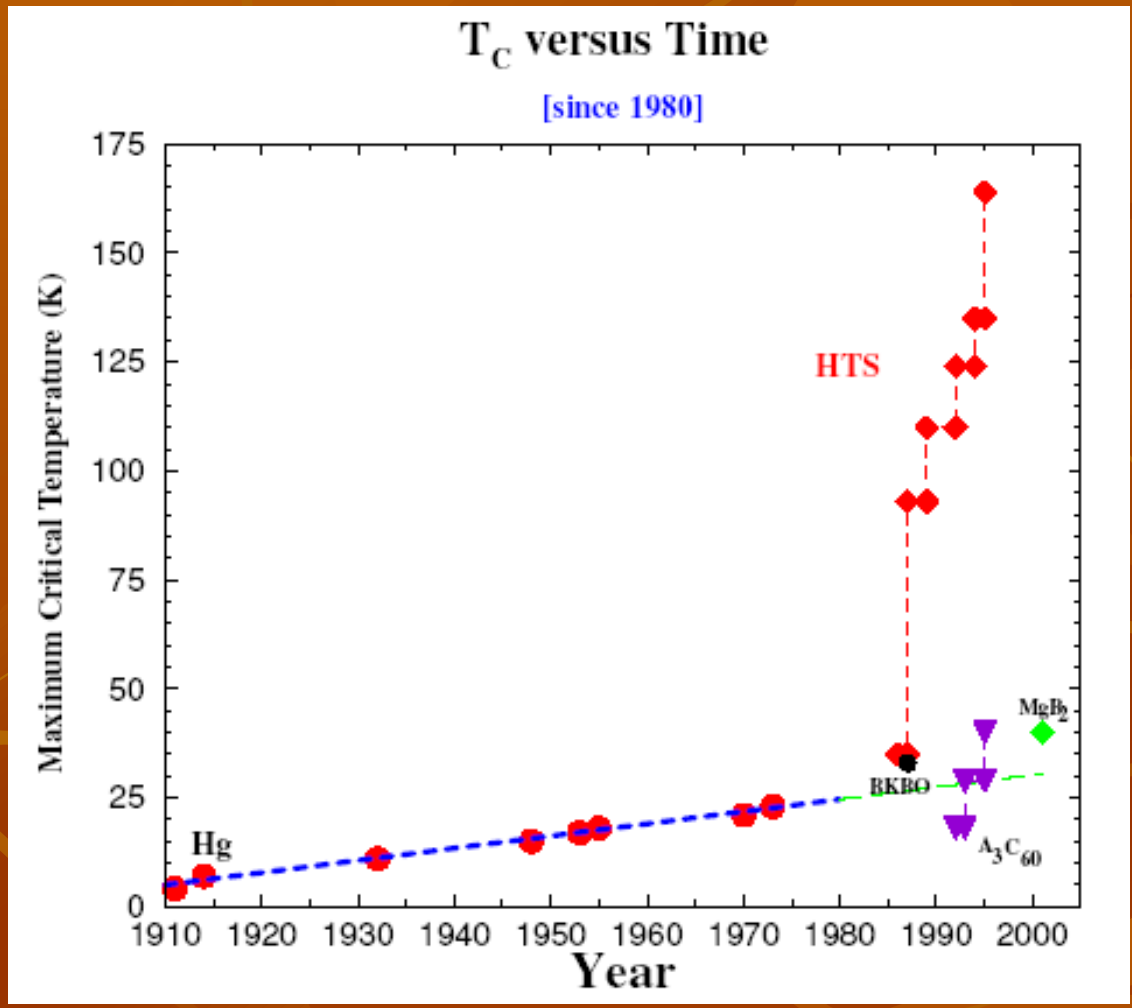
Possibility of Room Temperature Superconductivity

Why is MgB_2 So Pathetic?

Warren E. Pickett

Acknowledgments to:

Joonhee An, Michelle Johannes, Deepa Kasinathan, Kwan-woo Lee
Helge Rosner, Ruben Weht
Alex Kitiagorodsky
Neil Ashcroft


T_C versus Time
[since 1980]
Maximum Critical Temperature (K)
175
150
125
100
75
50
25
0
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
Year
HTS
Hg
BKBO
MgB_2
A_3C_{60}

The Other High Temperature Superconductors

40 K MgB_2: a new s-p class with only one member (?$C_{2-x}B_x$?)

40 K Cs_3C_{60}: the lowest density A_3C_{60} fulleride

35 K $(Ba,K)BiO_3$ (BKBO): s-p system, no excuse for this Tc

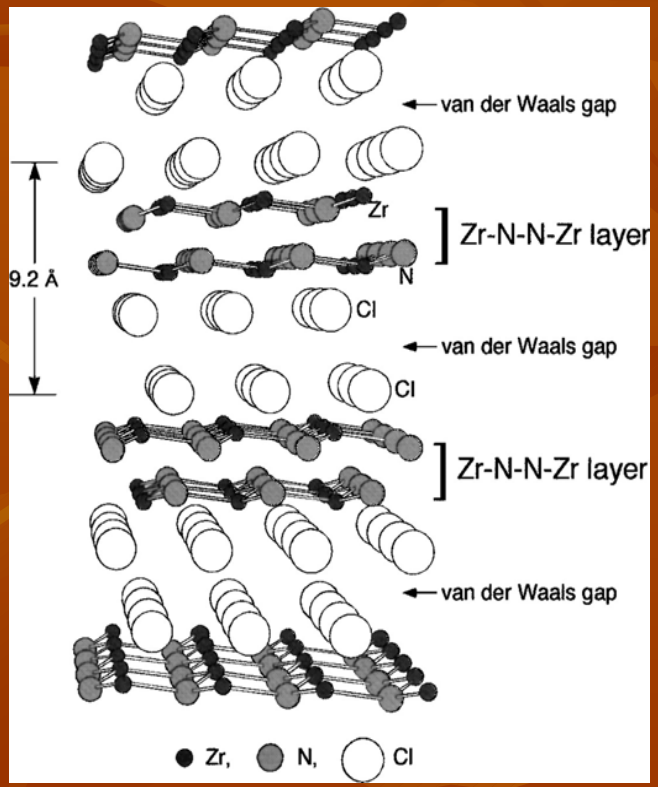
25 K $Li_x(ZrNCl)_2$: 2D layers, simple(?), low N(0)

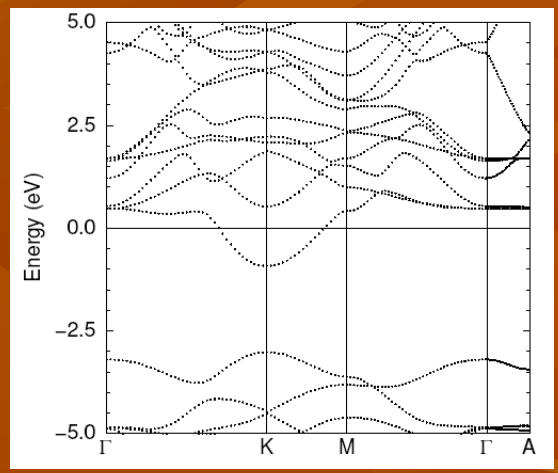
20 K Li at 40 GPa: simple 2s metal pushed to its limits (2p)

19 K $PuCoGa_5$: 5f electron system, a new game entirely

Li_xZrNCl: $T_c = 25$ K

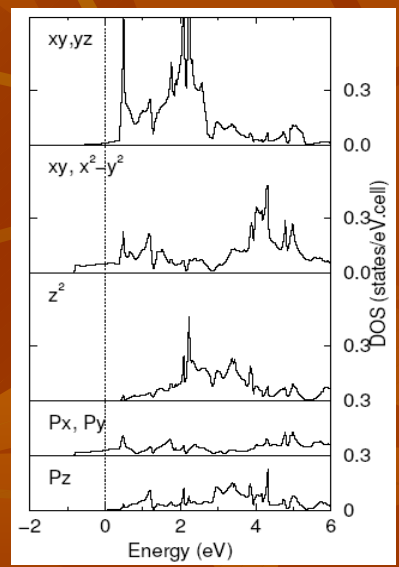
Layered, covalent-metallic bonded ZrN, van der Walls ZrNCl layers





Simple, high velocity bands at Fermi level

In-plane d band holds the carriers



Edward Teller's Last Guess

J. Supercond. 14, 299 (2001)

"Under special circumstances, it may be possible to observe an unusual phenomenon: a superconducting state which exists only at high temperatures." ….E.T., abstract.

The concept: the low temperature phase may be a broken symmetry one is which has occurred in order to alleviate the 'tension' in the system arising from a high $N(E_F)$, viz. as from a band Jahn-Teller effect.

The higher $N(E_F)$ in the symmetric high-T phase may be enough to overcome the normal pair-breaking effect of raising the temperature.

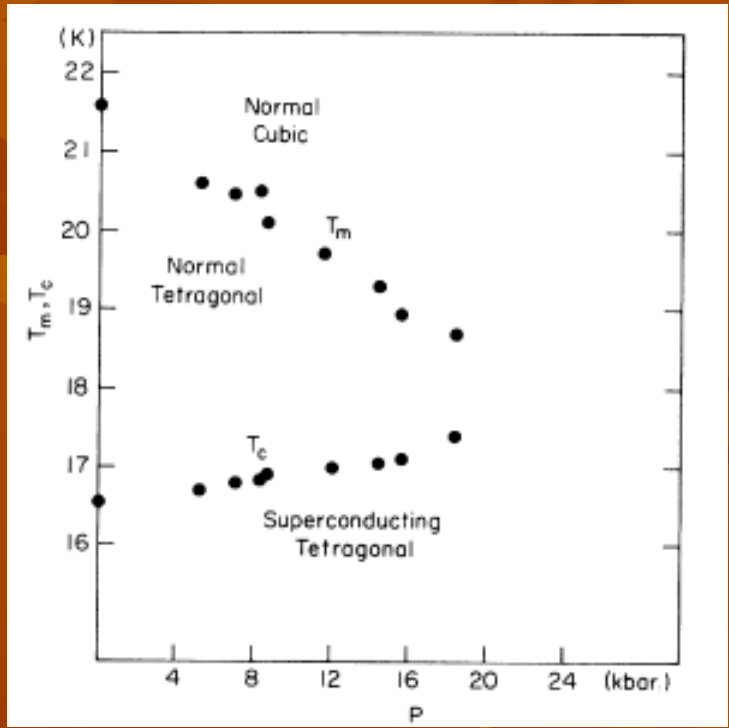
There is a history of such transitions interfering with superconductivity, with T_c being driven down by a structural transition. The inference is that one should look at structural (other?) transitions at higher temperature.

Strong Coupling; Structural Instability

1965-1975: strong coupling superconductivity observed to be accompanied by (near or actual) structural instabilities

Strong/very strong coupling:

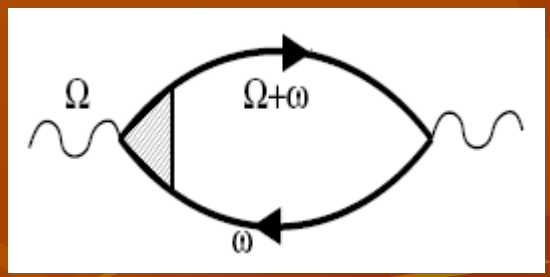
$\lambda = 1.5 - 2.5$



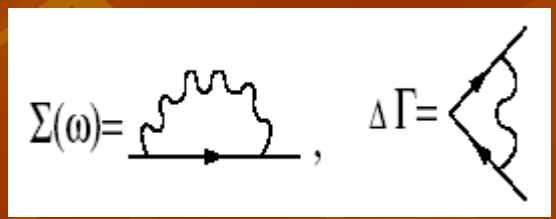
Experimental phase diagram of V_3Si. Chu and Testardi, 1974.

Phonon-paired Superconductivity

Electrons become paired by (attractive) exchange of virtual phonons, which overcomes the (repulsive) electron-electron repulsion if the el-ph coupling is sufficiently strong. Pairs coalesce into a macroscopic broken-gauge-symmetry state with long-range phase coherence.



Phonon self-energy bubble: electron-hole pair creation and reabsorption



Electron self-energy: phonon emission and reabsorption

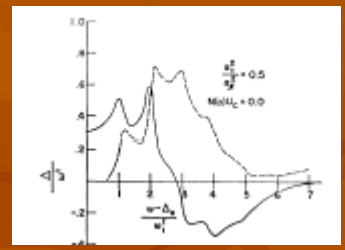
"Migdal's theorem": vertex corrections are order m/M (negligible) in normal state

Theory of Strong Coupling Superconductivity

G. M. Eliashberg, Sov. Phys. JETP (1960)
Scalapino, Schrieffer, Wilkins, Phys. Rev. (1966)

Starting from full electron+nuclei Hamiltonian

* Presume electrons form a Fermi liquid state
* Presume stable structure→conventional phonons
* Presume conventional el-ph theory holds (Migdal's theorem)
* Presume el-el interaction is not anomalous



Complex-valued energy-dependent gap function for Pb

Rowell, McMillan, Feldman (1969)

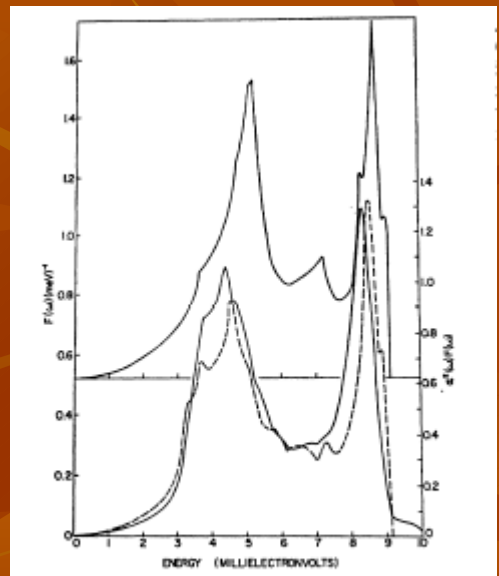


FIG. 1. Upper trace shows the phonon density $F(\omega)$ in Pb taken from Ref. 1. The lower dashed curve is the phonon density from Ref. 8. The area under the spectrum is normalized to 3. The lower solid line is the function $\alpha^2(\omega)F(\omega)$ determined from superconducting tunneling.

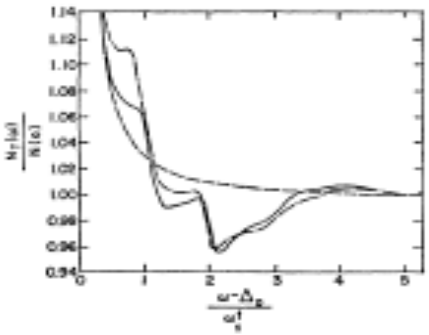


FIG. 10. The effective tunneling density of states $N_T(\omega)/N(0) = \mathrm{Re}\{\omega/(\omega^2-\Delta^2(\omega))^{1/2}\}$ versus $(\omega-\Delta_0)/\omega_1'$ (solid) obtained from Δ of Fig. 8. The ratio of the differential conductance of Pb in the superconducting to that in the normal state (Ref. 25) is plotted (dash-dot) as a function of $(\omega-\Delta_0)/\omega_1'$. The prediction of the simplified BCS model $\omega/(\omega^2-\Delta_0^2)^{1/2}$ is shown as the short dashed curve.

Electron-Phonon Coupling:
General Results for $\lambda_{Q\nu}$ and $\gamma_{Q\nu}$
P. B. Allen, PR B6, 2577 (1972)

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

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

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

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

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

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

"Matthias's Rules" for High T_c

- 1. Must have d electrons (not just s-p, nor f)
- 2. High symmetry is good, cubic is best
- 3. Certain electron concentrations are favored
- (peak in density of states at Fermi level)

McMillan (1968)

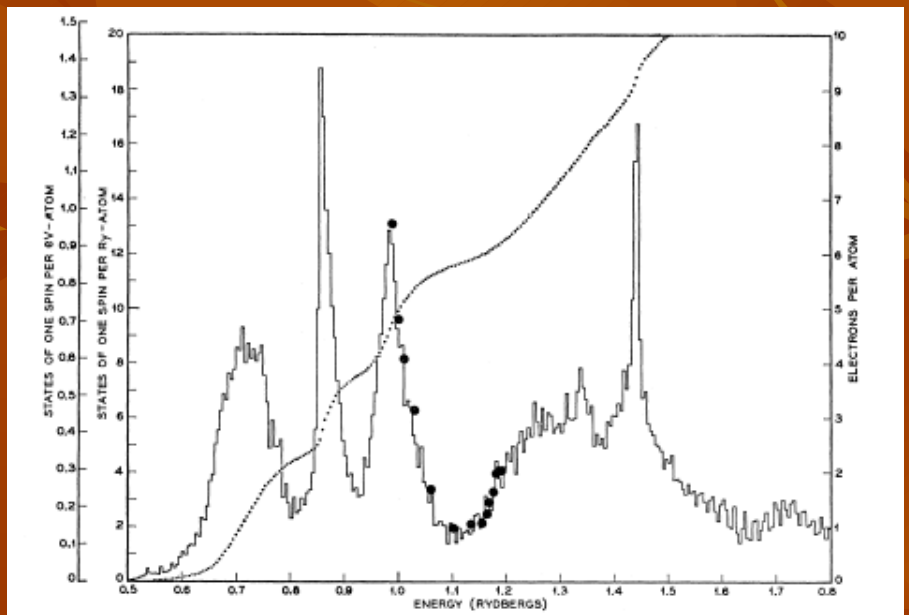


FIG. 10. The theoretical band-structure density of states versus energy for tungsten according to Matthias (Ref. 25), together with the empirical (solid-circles) data for the bcc 5*d* alloys from Tables III and VI.

Strong Coupling: Good News, Bad News

P. B. Allen

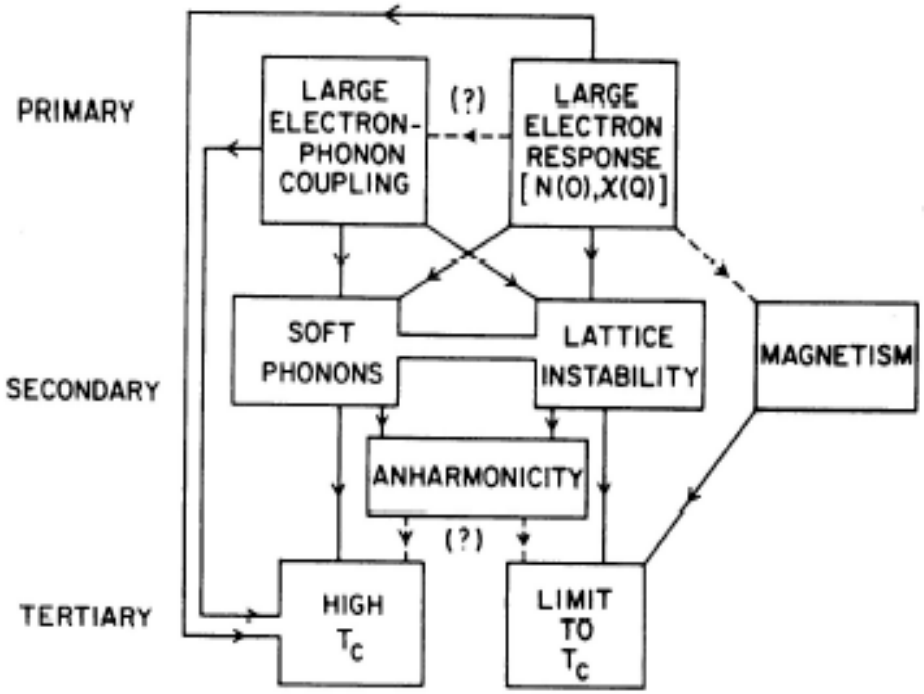
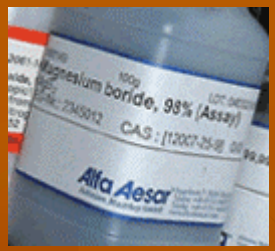


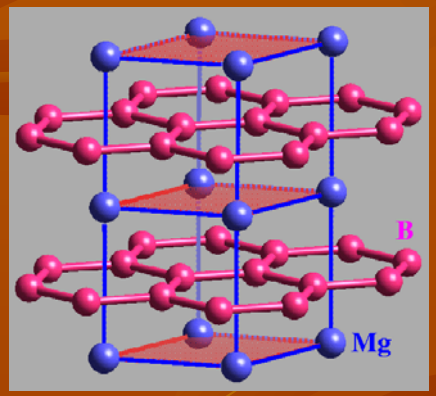
Fig. 3. Causative relations are indicated by arrows. High T_c is partly a direct consequence of the primary factors, and partly indirect through the phonon dispersion. Dashed lines with arrows represent less certain relationships.



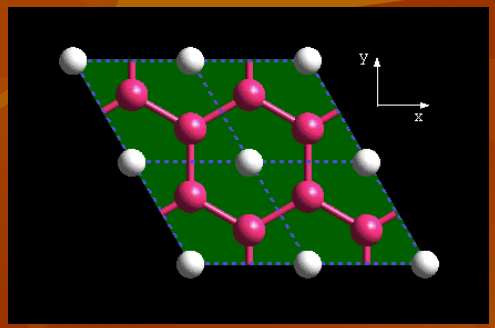
Akimitsu's Discovery: 2001

MgB_2, a common chemical reagent.

Searching for ferromagnetism, superconductivity at 40 K was discovered



Quickly reproduced and synthesis techniques were extended by several groups

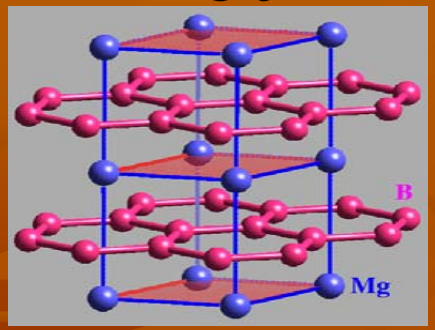


Crystal structure is simple. Quasi-2D.

Electronic structure is simple: s-p electrons.

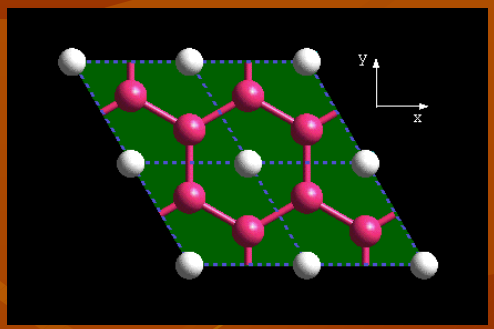
Nagamatsu, Nakagawa, Muranaka, Zenitani, and Akimitsu, Nature **410**, 63 (2001)

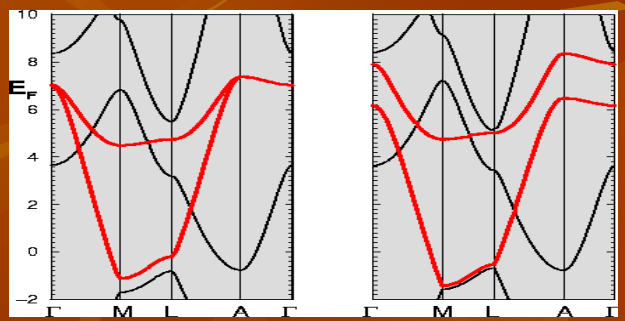
Four Months Later: Puzzle Solved!



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…….





T. Yildirim (NIST)

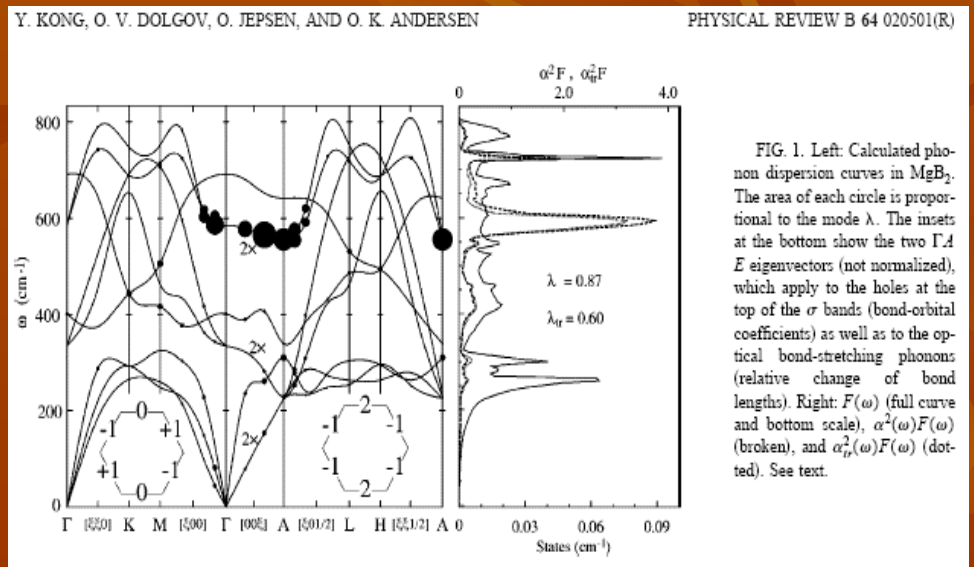
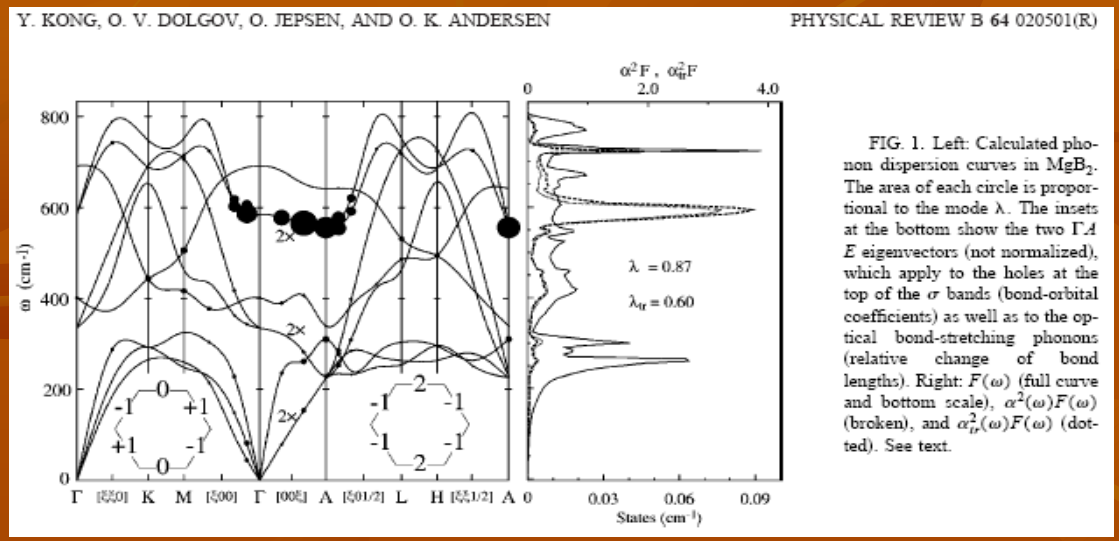


FIG. 1. Left: Calculated phonon dispersion curves in MgB_2. The area of each circle is proportional to the mode λ. The insets at the bottom show the two Γ*A* *E* eigenvectors (not normalized), which apply to the holes at the top of the σ bands (bond-orbital coefficients) as well as to the optical bond-stretching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

Pinpointing of Strong Electron-Phonon Coupling



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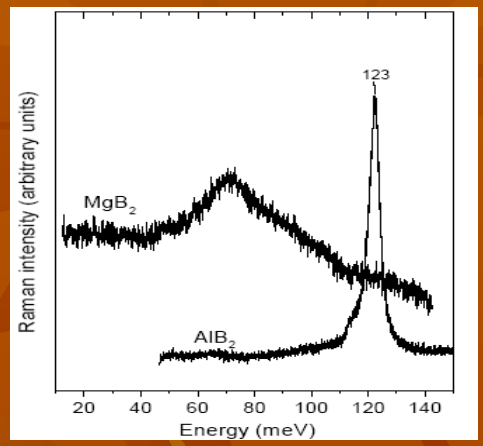
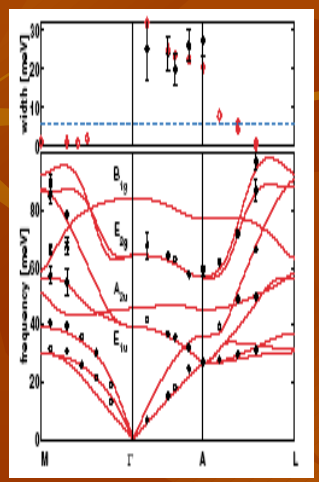


Raman spectrum
Bohnen, Heid, Renker (2002)



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

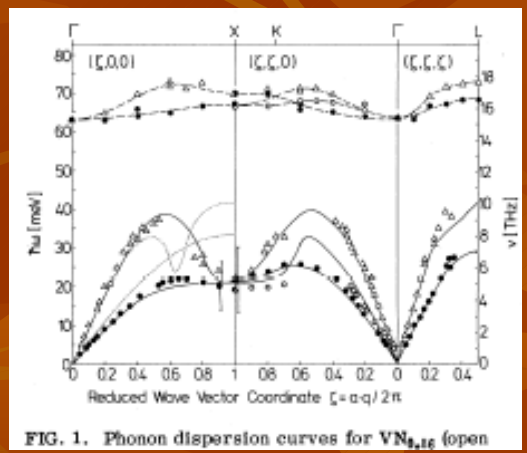


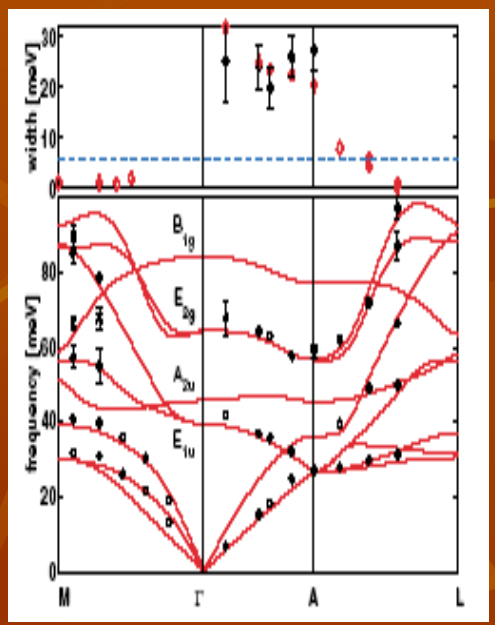
FIG. 1. Phonon dispersion curves for $VN_{0.95}$ (open

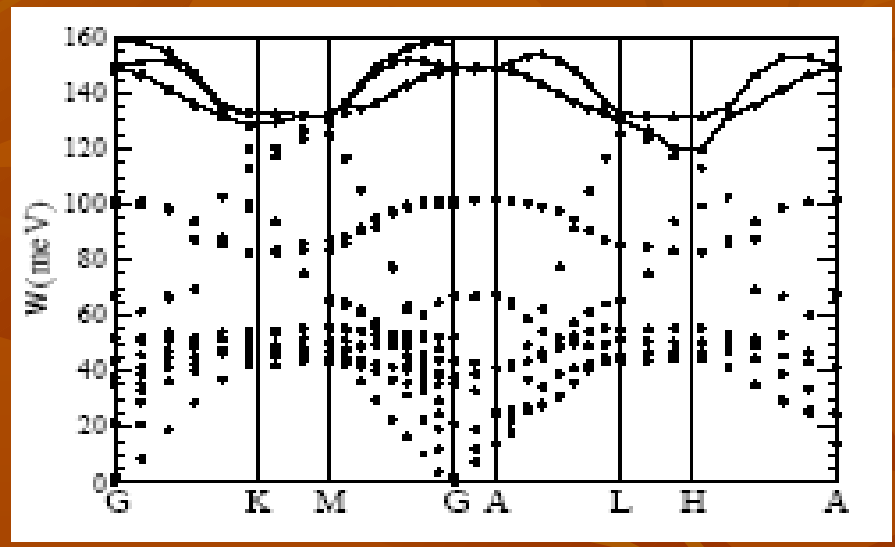
W. Weber et al.,
PRL (1978)

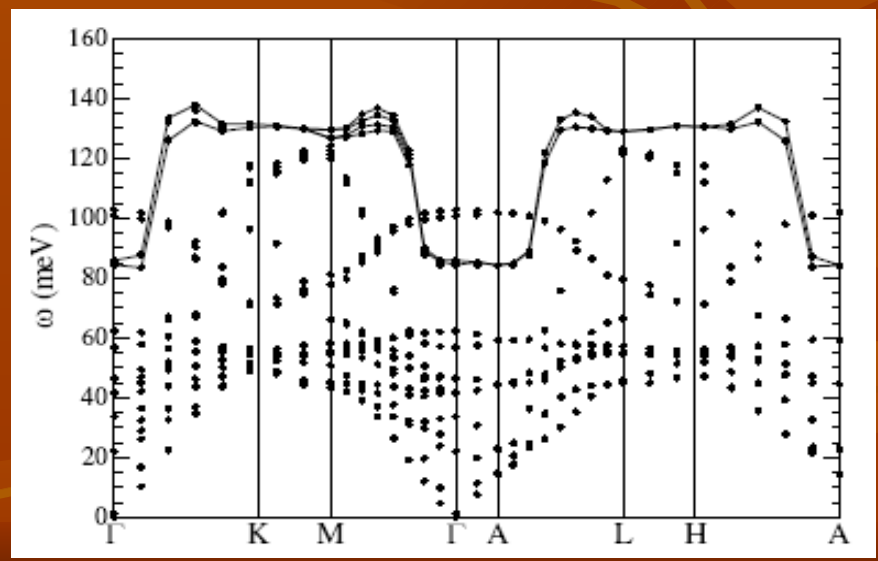
Electron-Phonon Coupling Strength Calculated for $Li_{1-x}BC$

Semiconductor x=0
Simple vibrational spectrum

Metal for x=0.25
Extreme Kohn anomalies







The Miraculous Nature of MgB2

Complete and utter scorn of the conventional wisdom

1. Total violation of Matthias's Rules.

2. Focusing of coupling to a few select modes
   $Q<2k_F$ comprises 12% of the BZ area
   2 of 9 phonon branches only
   →0.12 x 2/9 → only 3% of phonons are being used!!

Phonons and Electrons in 2D

Limits to Strong Coupling in 2D

2D MgB_2-like material, circular Fermi surfaces

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

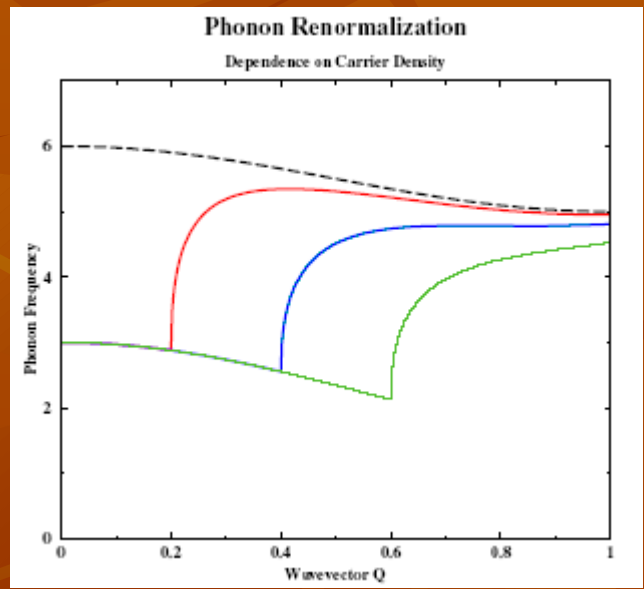
$$\Pi^\sigma(Q,\omega) = -2\sum_k |g_{k,Q}|^2 \frac{f_k - f_{k+Q}}{\varepsilon_{k+Q} - \varepsilon_k - \omega - i\delta},$$

$$\Re e\ \Pi^\sigma(Q,\omega_Q) \approx -2|g|^2 N(0) d_b^2 \hat{\chi}_L^{2D}(Q),$$

$$\hat{\chi}_L^{2D}(Q) = \theta(1-\eta_Q) + \left[1 - \sqrt{1-\eta_Q^{-2}}\right]\theta(\eta_Q - 1)$$

$$\eta_Q \equiv \frac{Q}{/2k_F}, \quad |g|^2 = \frac{\mathcal{D}^2}{2M\Omega}$$

$$\frac{\omega_Q^2}{\Omega_Q^2} = 1 - d_b^2 \frac{m^*}{2\pi} \frac{\mathcal{D}^2}{M\Omega_Q^2}, \quad Q < 2k_F$$



El-Ph Coupling in MgB_2-like Systems

Mode λ_Q and Total Coupling Strength λ

$$\lambda_Q = \frac{2}{\pi N(0)}\frac{\gamma_Q}{\omega_Q^2}$$

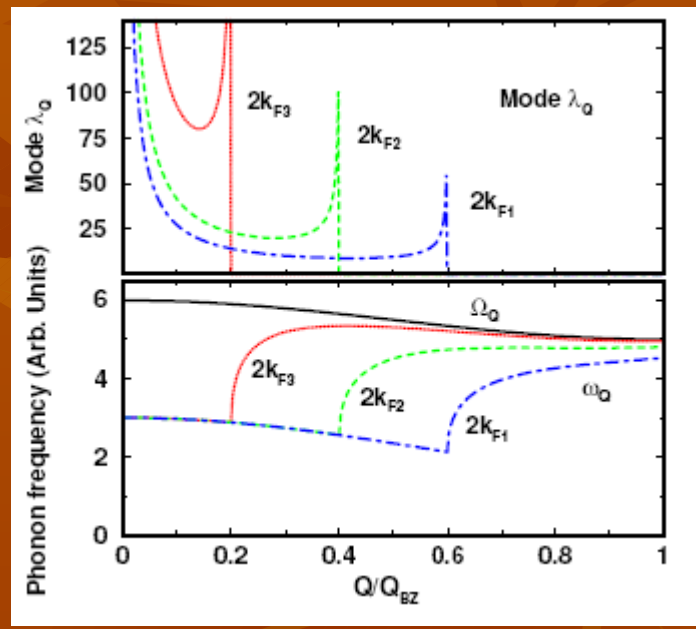
$$\gamma_Q = \pi\Omega_Q|g|^2[N(0)]^2 d_b^2\hat{\xi}(Q),$$

$$\hat{\xi}(Q) = \frac{\sum_k \delta(\varepsilon_k)\delta(\varepsilon_{k+Q})}{[\sum_k \delta(\varepsilon_k)]^2} = \frac{A_{BZ}}{A_{FS}}\frac{1}{\pi}\frac{\theta(1-\eta)}{\eta\sqrt{1-\eta^2}}$$

$$\lambda = \sum_{Q\nu}\lambda_{Q\nu} = d_b^2\frac{N(0)\mathcal{D}^2}{M\omega_Q^2} \leftrightarrow \frac{N(\varepsilon_F) < I^2 >}{M < \omega^2 >}$$

$$= \frac{d_b^2 N(0)\mathcal{D}^2}{M\Omega_Q^2 - d_b^2 N(0)\mathcal{D}^2}, \quad N(0) = \frac{m^*}{2\pi}$$

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



- 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?

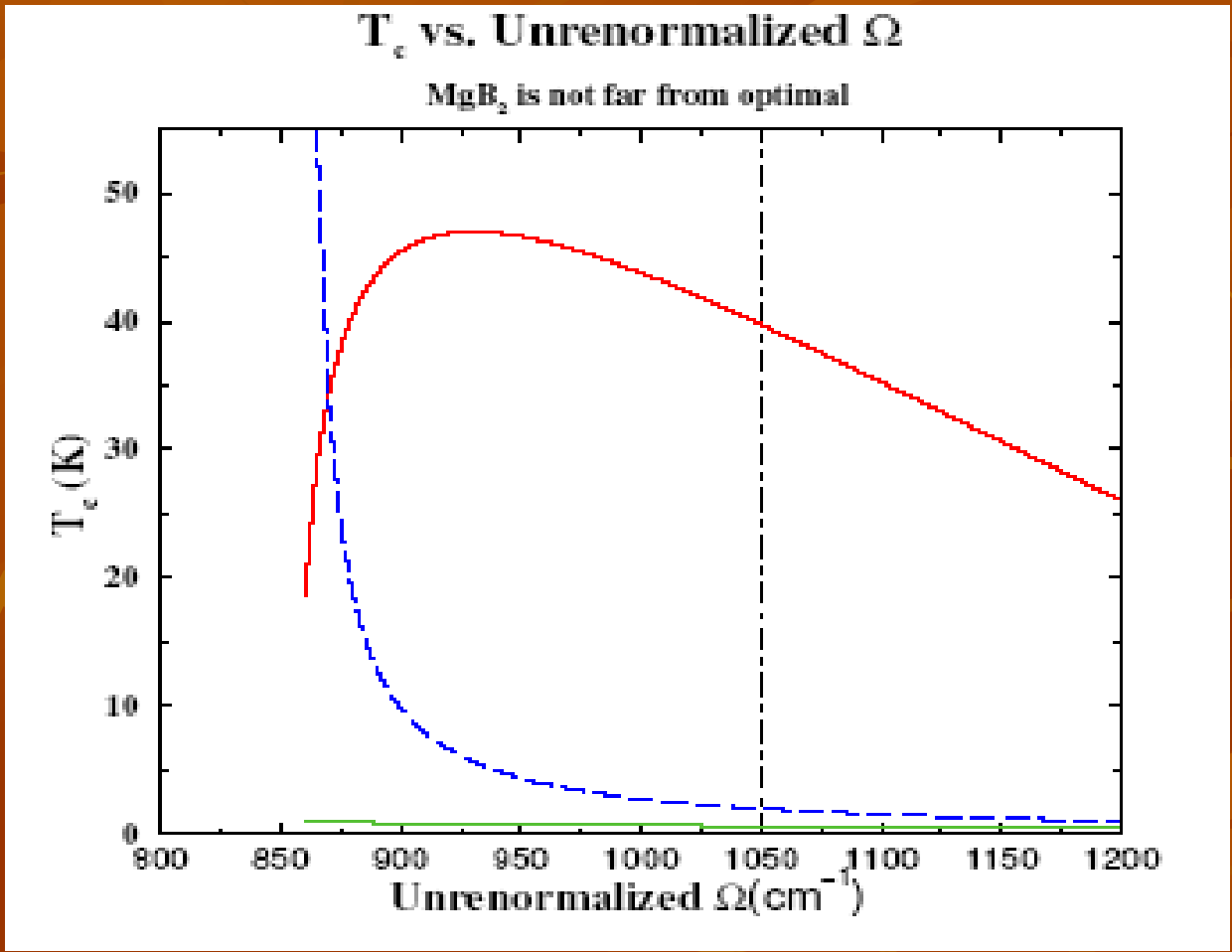
How could MgB_2 have been better? Relations to use:

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

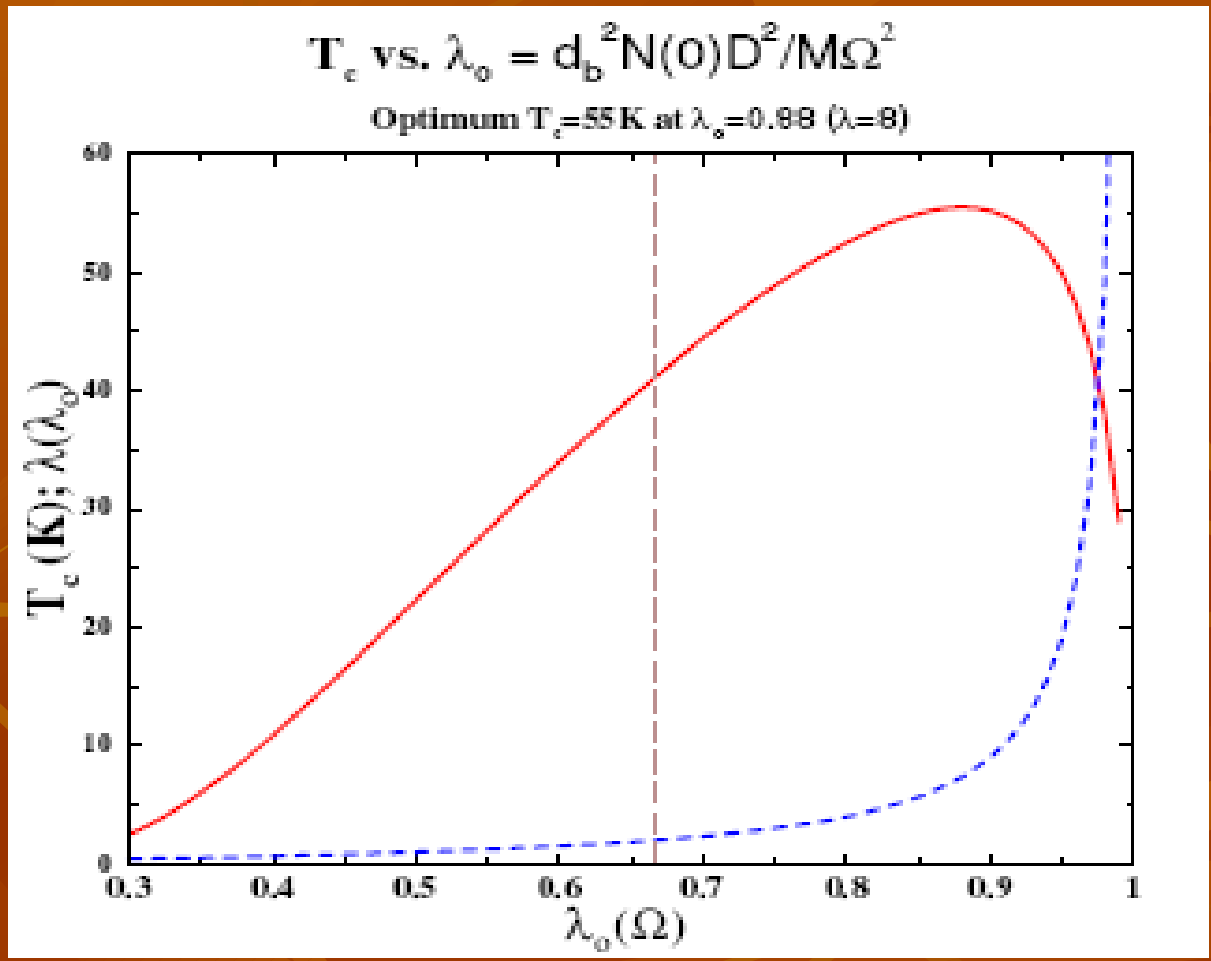
$$T_c \approx \frac{<\omega>}{4}[e^{2/\lambda_{eff}} - 1]^{-1/2}; \quad \lambda_{eff} = \frac{\lambda - \mu^*}{1 + 0.75\lambda\mu^* + 2\mu^*}$$

- 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.

$$T_c = \frac{<\omega>}{8}\left[e^{\frac{2}{\lambda_{eff}}} - 1\right]^{1/2}$$



$$T_c = \frac{<\omega>}{8.75}\left[e^{\frac{2}{\lambda_{eff}}} - 1\right]^{1/2}$$



Is there some way to win? Yes.

One must avoid the lattice instability, keep

$$\lambda_o \equiv \frac{d_b^2 N(0)\mathcal{D}^2}{M\Omega_Q^2} < 1,$$

In fact it should not get too near unity.

So, increase Ω. But keep λ_o remains optimal $\rightarrow$ increase $d_b^2 N(0)\mathcal{D}^2$ proportionally.

"Build a stiffer lattice, then beat it down with stronger coupling."

Options:

- increase N(0): maybe, but may get magnetism.
- increase $\mathcal{D}$. Find harder reference systems, then make them metallic.
- increase the band/Fermi surface degeneracy, use the power of 2.

What is the limit? In at least one nonsymmorphic (cubic) space group there is a sixfold degeneracy of one band symmetry at the R point (BZ corner). This could get a factor of $6^2 = 36$ if one needed it, and one probably would, to overcome the 3D DOS $N(\varepsilon) \propto \sqrt{|\varepsilon - \varepsilon_o|}$. {Think of B-doped diamond.}

So: why wasn't MgB_2 better than 40 K?

- Reference system (AlB_2) was too restricting
- - increasing d_b^2 x N(0) x D^2 would lead to T_c around 55 K,
- with instability to follow
- - decreasing the unrenormalized frequency, T_c would peak
- below 50 K (then crash to instability)
- The Hope: obtain a stiffer reference system,
- with very strong coupling; add carriers
- Need: very strongly bonded, light atom xtals