Superconductivity: from BCS to modern electronic structure theory

Sandro Massidda
Physics Department, University of Cagliari
sandro.massidda@dsf.unica.it

Outline

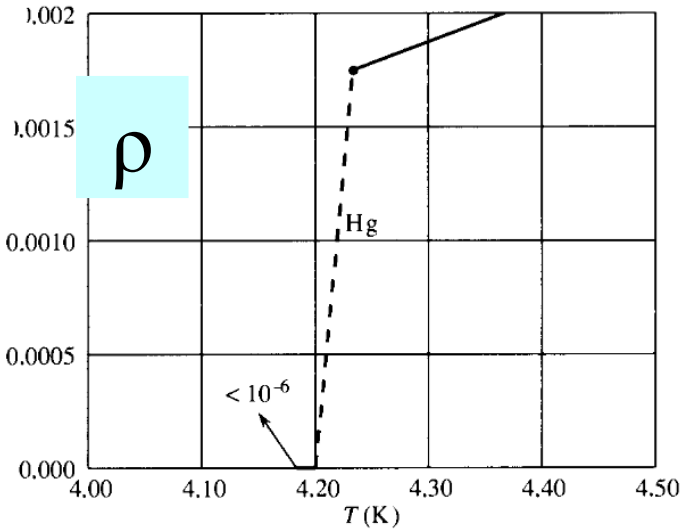
- Introduction: Basic concepts of the BCS theory:

1. Concepts of Fermi liquid theory and instability of the normal state.
2. Phonon mediated attractive interaction and the Cooper pairs.
3. The BCS gap equation.

- Limitations of BCS theory.
- The introduction of Coulomb repulsion.
- The electron-phonon interaction in real materials.
- Applications to real materials: MgB_2, alkali under pressure, CaC_6

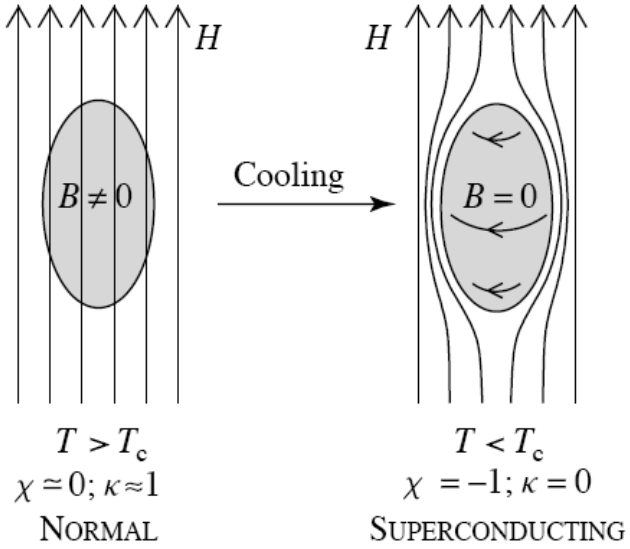
- Kohn anomaly,
- Fermi surface nesting,
- two-gap superconductivity.

Superconductivity: 100 years



Kamerling Onnes
Leiden 1911

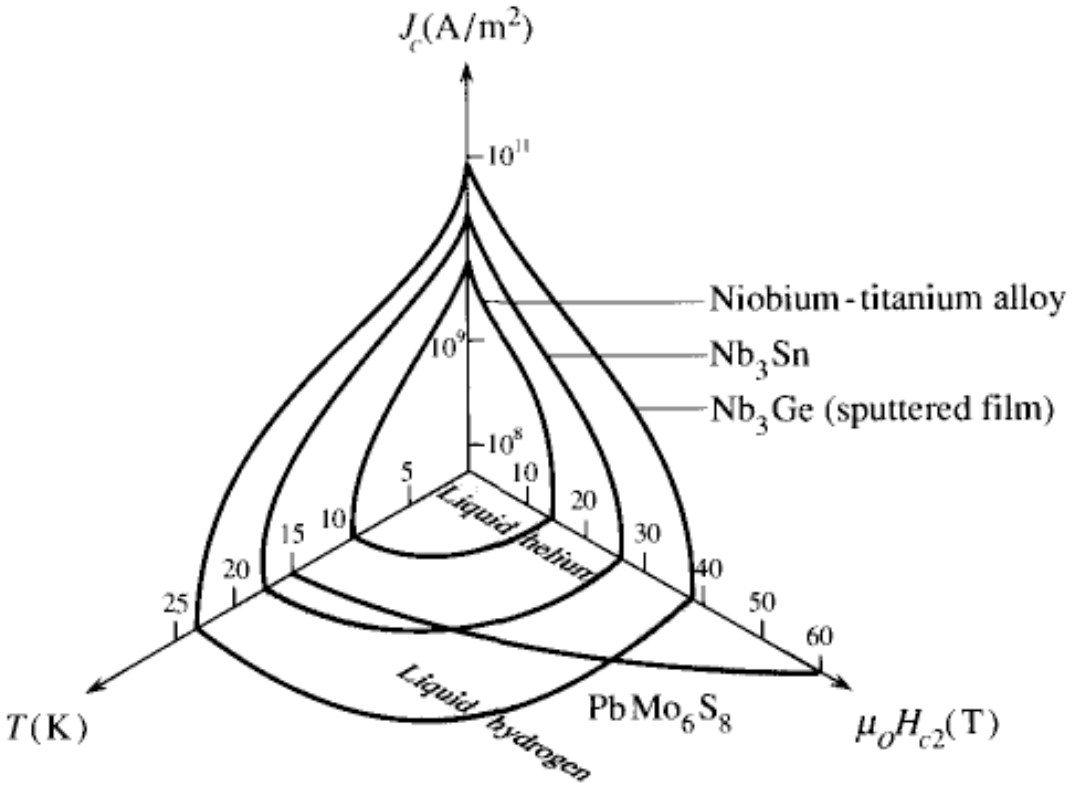
Zero resistivity below T_c

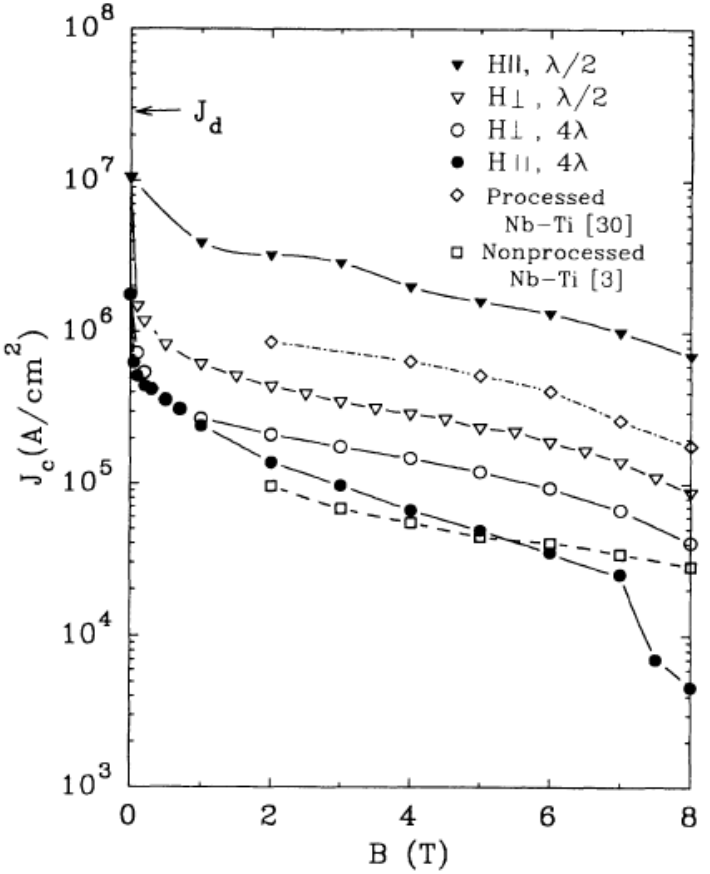


Expulsion of magnetic field

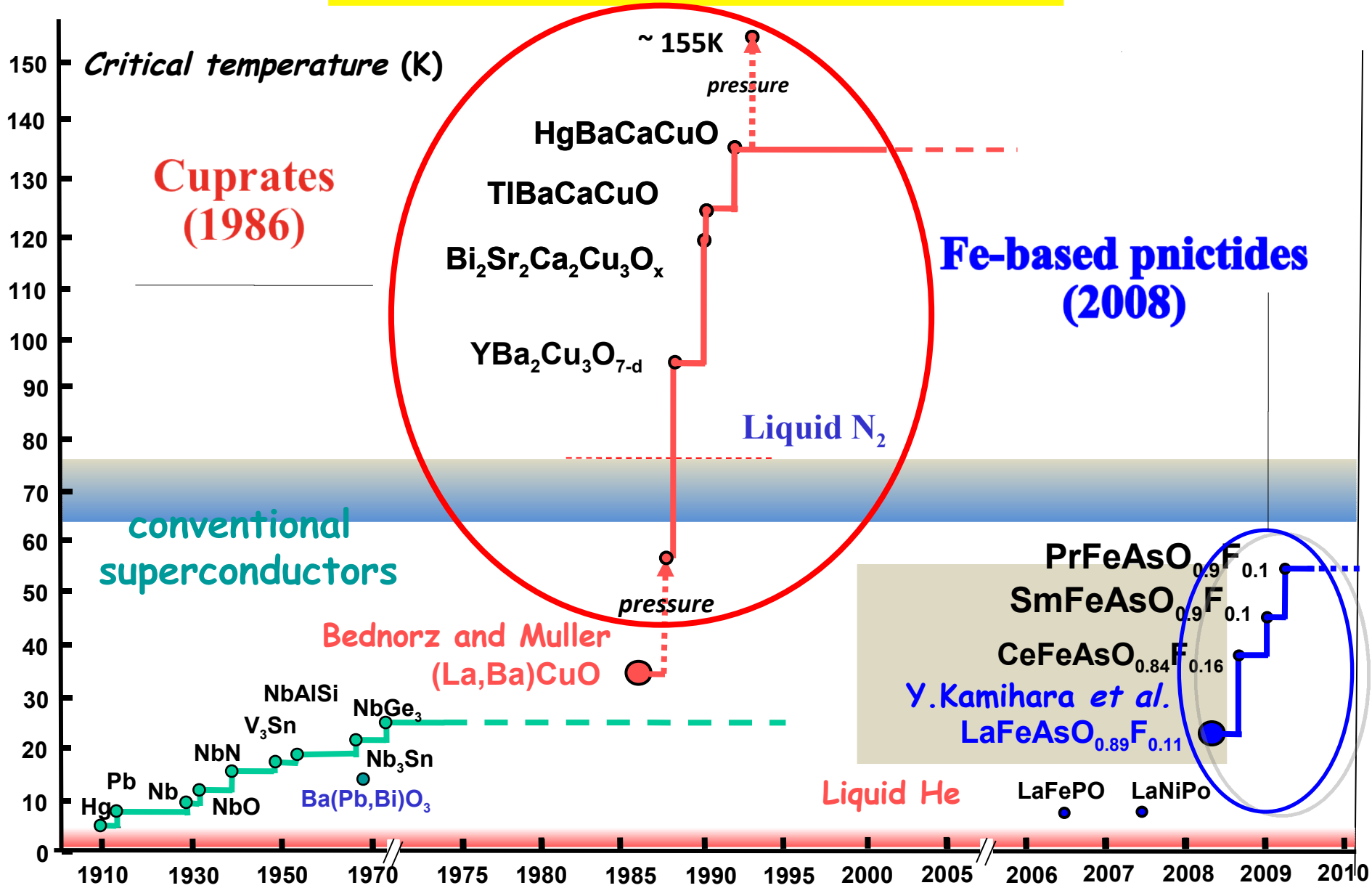
$$F_N - F_S = \frac{H_c^2}{8\pi} V$$

Application needs: high critical temperature, currents e fields



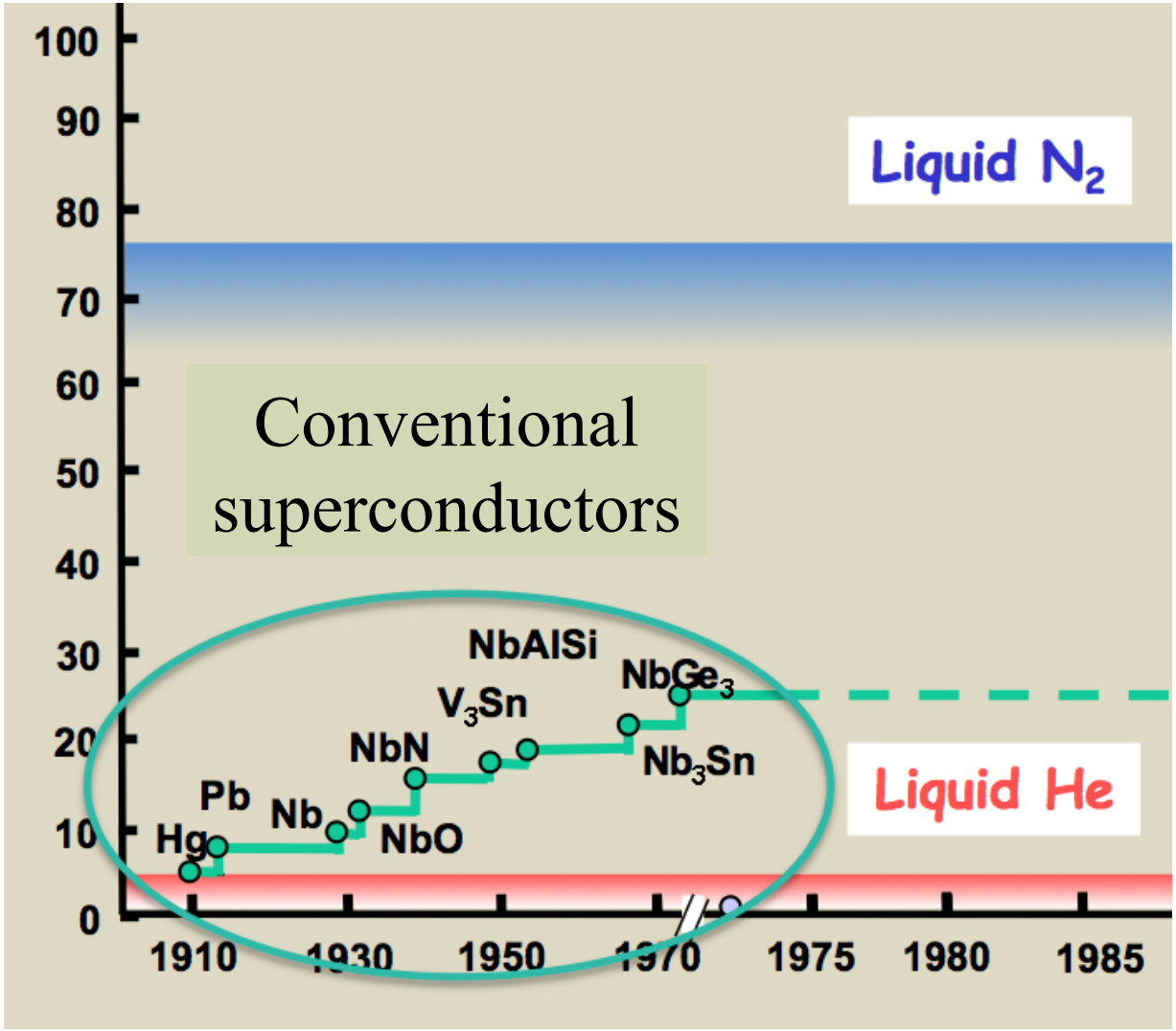


T_c as a function of time



Conventional superconductivity (year < 1986)

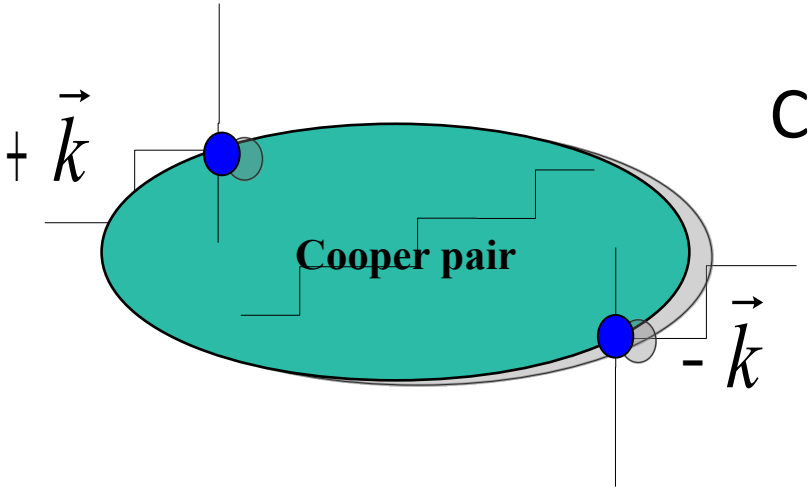
Elemental superconductors and alloys with $T_c \leq 25$ K



BCS: theory for conventional SC (1957)

J. Bardeen, L. Cooper, R. Schrieffer

Nobel prize in 1972



Cooper pairs

Cooper pairs form zero-spin (singlet) bosons who condense and transport electric current without dissipation

How can electrons possibly attract each other to form a pair?

Normal state: Fermi liquid (Landau)

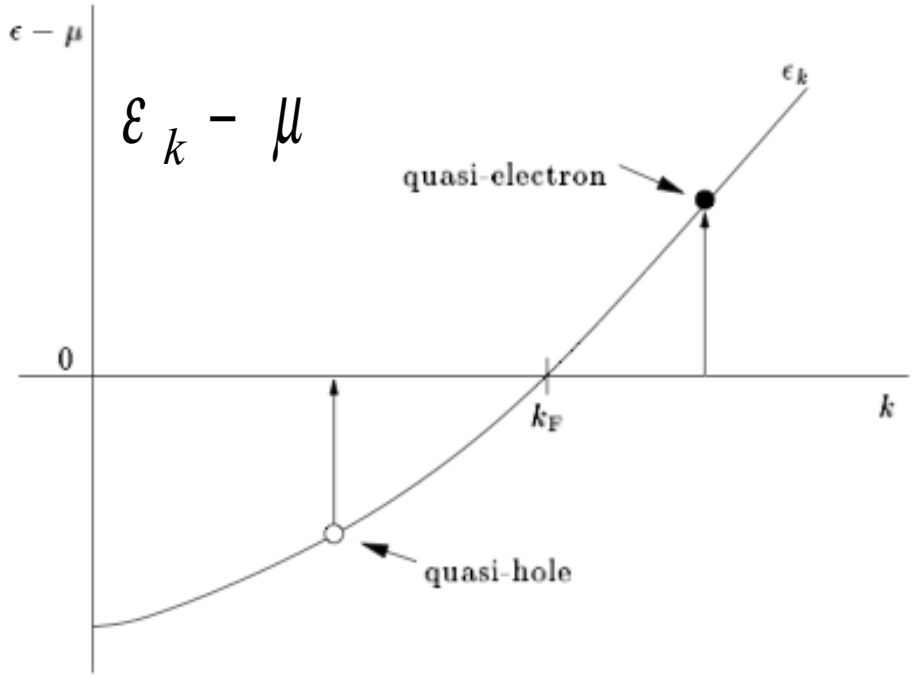


FIG. 33: Creation of an excited electron and of a hole, resp.

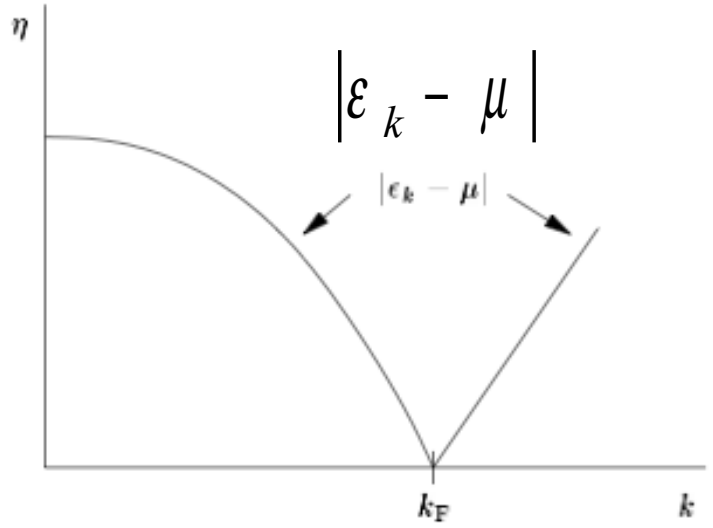
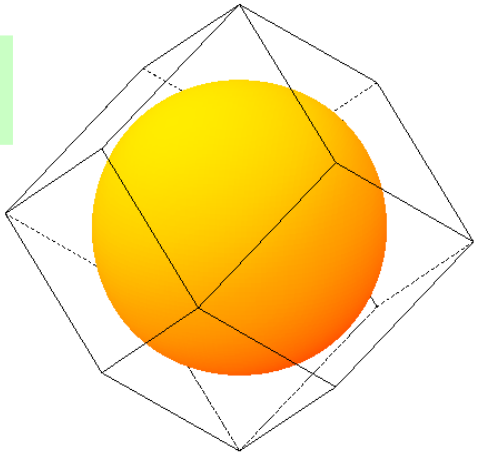


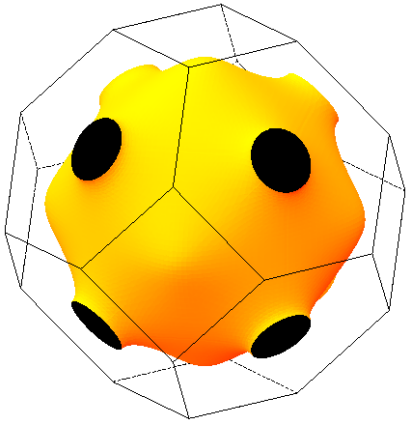
FIG. 34: Excitation spectrum of a Fermi gas.

- Holes and electrons: basis of elementary excitations
- *e* and *h* interaction is **screened by the *e*-gas**,
- *e* and *h* become **quasi-particles with a very long life-time close to E_F**

The electrons occupying low lying energy states appear to form a very stable system

Na





Cu

Cooper Problem: **The Fermi liquid is unstable towards any arbitrarily small attractive *e-e* interaction**

How can such a small attraction mess up an apparently very stable system?

1. Cooper problem

$$\left[-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + V(r_{12}) \right] \varphi(\mathbf{r}_1, \mathbf{r}_2) = E\varphi$$

$$\varphi(\mathbf{r_1}, \mathbf{r_2}) = \sum_{k > k_F} g_k \, e^{i\mathbf{k}\cdot\mathbf{r}_1} \, e^{-i\mathbf{k}\cdot\mathbf{r}_2} \, \chi(1,2)$$

$$g_{\mathbf{k}} = g_{-\mathbf{k}}$$

Singlet wavefunction:

$$\chi(1,2) = \alpha_1\beta_2 - \alpha_2\beta_1$$

$$\mathbf{k}\uparrow, -\mathbf{k}\downarrow$$

The two-*e* Schrödinger Equation yields to a bound state: $E < 2E_F$

Approximate interaction (BCS):

$$V_{kk'} = -V \text{ if } \varepsilon_k, \varepsilon_{k'} < \hbar\omega_{cut}$$
$$= 0 \quad \text{otherwise}$$

The solution of SE gives:

$$E - 2E_F = -2\hbar\omega_{cut} e^{-1/\lambda} \qquad \lambda = N(E_F)V$$

- A solution exists **independently** of the coupling strength λ
- It can not be developed in Taylor series (perturbation th.)
- **If ω_{cut} is a phonon frequency, the isotope effect is explained: ($\omega_{ph} \sim M^{-1/2}$)!**

2. Source of electron-electron attraction

REVIEWS OF MODERN PHYSICS VOLUME 23, NUMBER 3 JULY, 1951

Electron-Vibration Interactions and Superconductivity

J. BARDEEN*

Bell Telephone Laboratories, Murray Hill, New Jersey

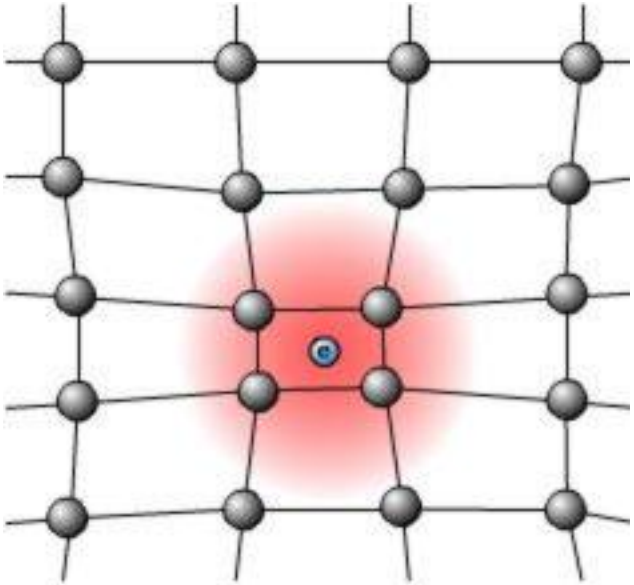
I. INTRODUCTION

THE isotope effect, discovered independently by E. Maxwell[1] of the National Bureau of Standards and by Reynolds, Serin, Wright, and Nesbitt[2] of Rutgers University, indicates that superconductivity arises from interactions between electrons and vibrations of the crystal lattice. Using separated isotopes, both groups

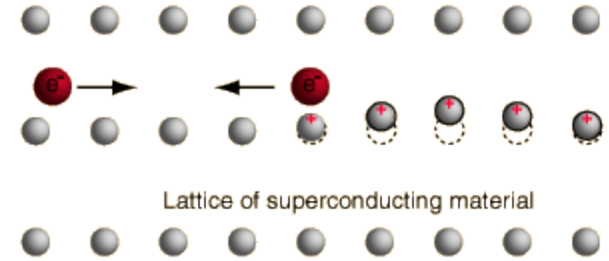
Independently, the writer[7] has also proposed a theory of superconductivity based on interactions between electrons and lattice vibrations. We have used a model based on energies of the individual electrons as affected by interactions with the vibrations. It was proposed that in the superconducting phase electrons with energies within $\sim\kappa T_c$ of the Fermi surface are lowered in energy by an amount also $\sim\kappa T_c$. This energy decrease,

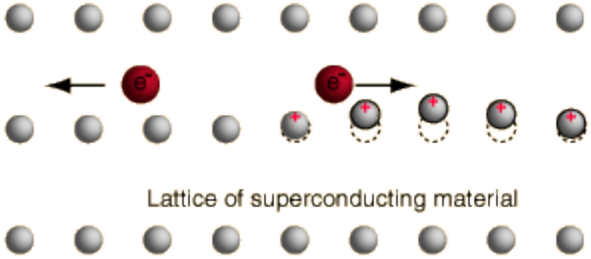
BCS theory in 1957!

How can phonons produce an attraction among electrons? (classical view)



Lattice deformation

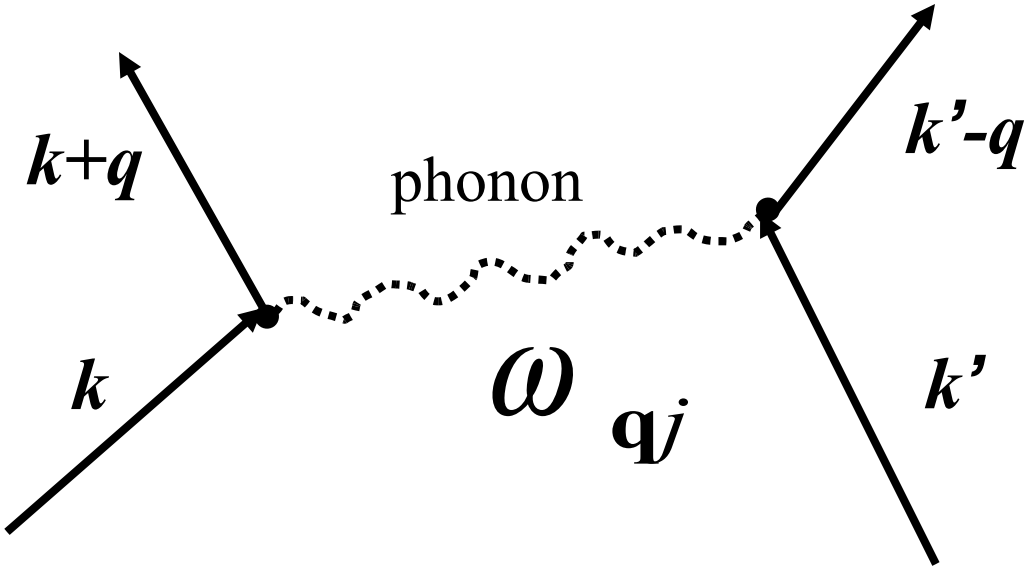




Overscreening of *e-e* repulsion by the lattice

The lattice deformation by the first electron attracts the second

Attractive phonon-mediated interaction



Exchange of virtual phonons produces an attraction for electrons close to E_F ($k = \mathbf{k},n$)

$$V_{k,k'} = \left|g_{\mathbf{q}j}\right|^2 \frac{2\hbar\omega_{\mathbf{q}j}}{\left(\varepsilon_k - \varepsilon_{k'}\right)^2 - \hbar^2\omega_{\mathbf{q}j}^2}$$

Bardeen-Pines, attraction when

$$\varepsilon_k - \varepsilon_{k'} < \hbar\omega_{qj}$$

BCS theory: language

$c^{\dagger}_{k\uparrow} \left|..0_k..\right\rangle = \left|..1_{k\uparrow}..\right\rangle$ creation of an e

$c_{k\uparrow} \left|..1_{k\uparrow}..\right\rangle = \left|..0_k..\right\rangle$ destruction of an e

$c^{\dagger}_{k\sigma} c_{k\sigma} \left|..n_k..\right\rangle = \hat{n}_{k\sigma} \left|..n_k..\right\rangle = n_{k\sigma} \left|..n_k..\right\rangle$ number of electrons

$c^{\dagger}_{k\uparrow} c^{\dagger}_{-k\downarrow} \left|..0_k..\right\rangle \equiv b^{\dagger}_k \left|..0_k..\right\rangle = \left|..1_{k\uparrow} 1_{-k\downarrow}..\right\rangle$ Cooper pair

BCS Hamiltonian: scattering of pairs only

$$\hat{H} = \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + \sum_{k,k'} V_{kk'} b^{\dagger}_{k'} b_k$$

Kinetic energy

Scattering of pairs from k to k'

BCS wavefunction:

$$|\Psi_{BCS}\rangle = \prod_k \left(u_k + v_k b_k^\dagger\right)|0\rangle \qquad u_k^2 + v_k^2 = 1$$

- **Linear combination of *e* and *h***
- No space left for singles (excitations of the system)
- Number of *e* fluctuates around N_0
- All pairs added with the same phase (coherence)

Coherence factors u_k, v_k: determine how much of an *e* or of a *h* is travelling as a quasi-particle in the superconductor

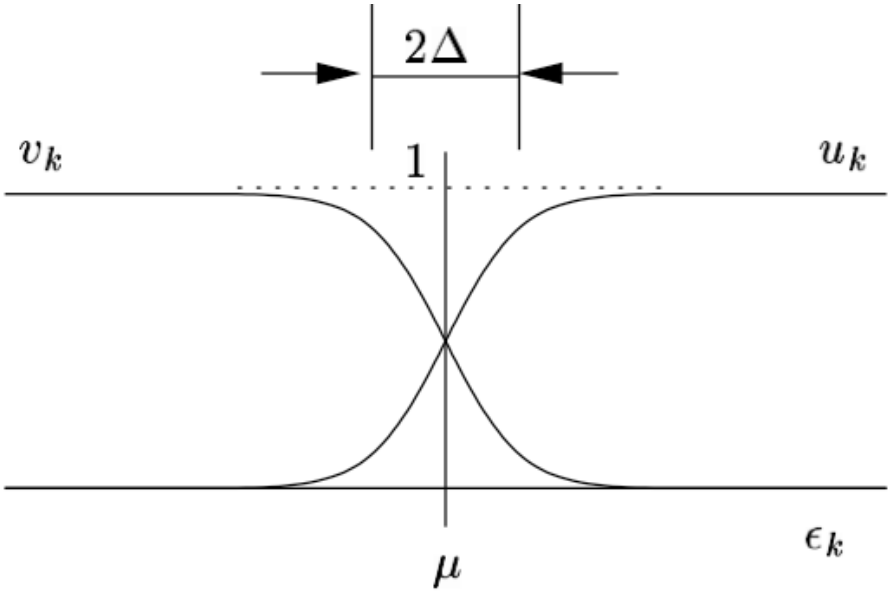
$$u_k = |u_k|$$

$$v_k = |v_k| e^{i\phi}$$

Solution:

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta_k^2}}\right) \qquad \xi_k = \varepsilon_k - \mu$$

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\xi_k}{\sqrt{\xi_k^2 + \Delta_k^2}}\right)$$



$u_k v_k \neq 0$ close to E_F in the SC

$u_k v_k = 0$ in the normal state

Conservation of electron number

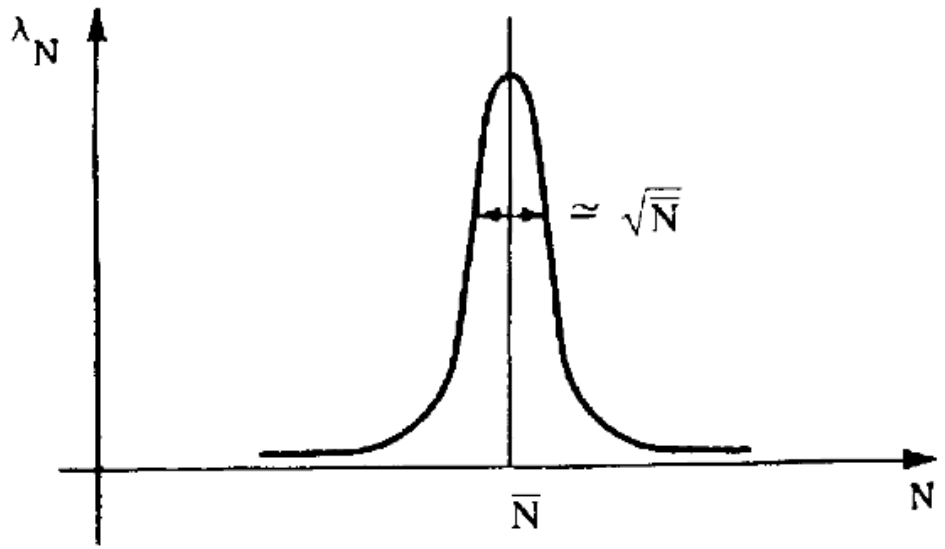


Figure 26.1 The probability amplitude λ_N of finding a configuration with N particles in the BCS wavefunction. Note λ_N is strongly peaked around $\bar{N}$.

- The number of particles is not fixed, but the relative fluctuation is proportional to $N_0^{-1/2}$
- Phase coherence implies release of number conservation

What is Δ_k? BCS gap equation

$$\Delta_k = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2\sqrt{\xi_{k'}^2 + \Delta_{k'}^2}}$$

$$E_k = \sqrt{\xi_k^2 + \Delta_k^2}$$ excitation energies

Solution of gap equation, within the BCS approximation

$$\Delta = 2\hbar\omega_D e^{-1/\lambda}$$

$$\lambda = N(E_F) \langle V_{kk'} \rangle_{E_F}$$

$V_{kk'}$, pairing potential results from competition of phonon attraction and Coulomb repulsion

Meaning of Δ_k

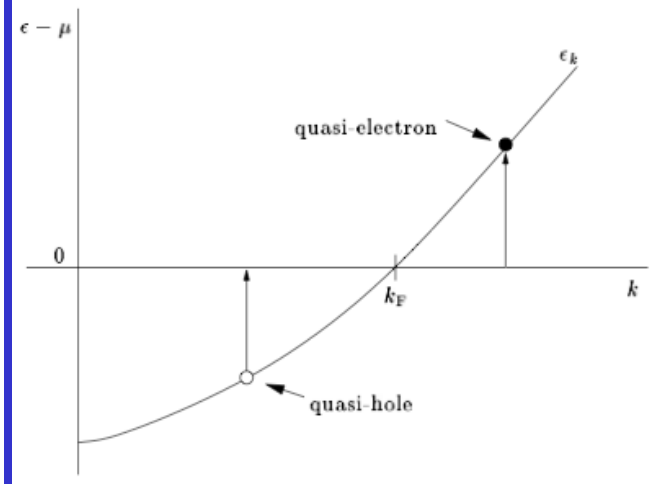


FIG. 33: Creation of an excited electron and of a hole, resp.

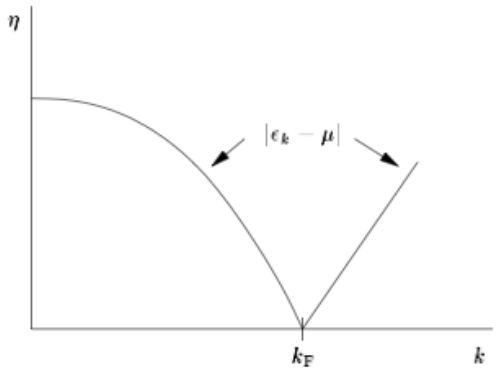


FIG. 34: Excitation spectrum of a Fermi gas.

Normal state

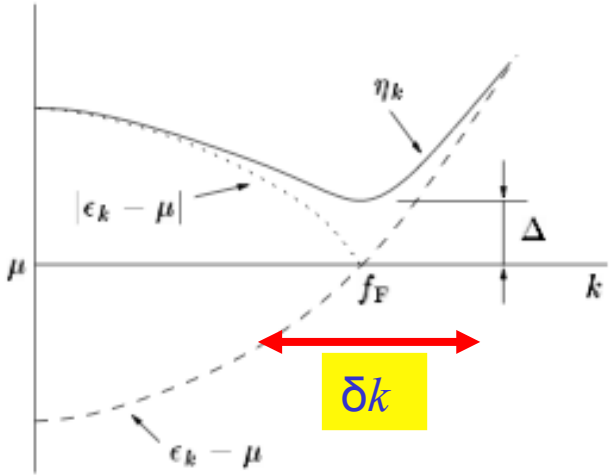


Figure 37: Quasi-particle dispersion relation in the superconducting state.

Superconducting state: minimum energy Δ_k to add a quasi-particle

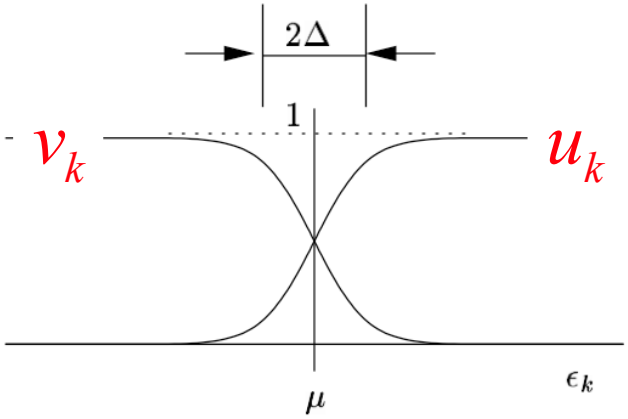
$E_k \approx |\varepsilon_k - \mu|$ far from FS

$\xi_0 \approx 2\pi/\delta k$ coherence length

Elementary excitations: Bogoliubov-Valatin transformations

$$\gamma^{\dagger}_{k\uparrow} = u_k c^{\dagger}_{k\uparrow} - v_k c_{-k\downarrow}$$

$$\gamma^{\dagger}_{-k\downarrow} = u_k c^{\dagger}_{-k\downarrow} + v_k c_{k\uparrow}$$



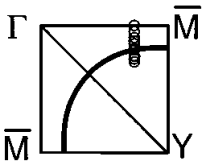
Quasi-particles have an energy E_k and correspond to:

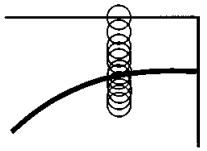
- **pure *h* or pure *e* far from E_F**
- **a combination of them close to E_F**

$$E_k = \sqrt{\xi^2_k + \Delta^2_k}$$

Spectral function $A(\mathbf{k},\omega)$

$$\pi A(\mathbf{k},\omega) = \frac{\Gamma u_{\mathbf{k}}^2}{(\omega - E_{\mathbf{k}})^2 + \Gamma^2} + \frac{\Gamma v_{\mathbf{k}}^2}{(\omega + E_{\mathbf{k}})^2 + \Gamma^2}$$





Campuzano et al, PRB 53, R14737 (1996)

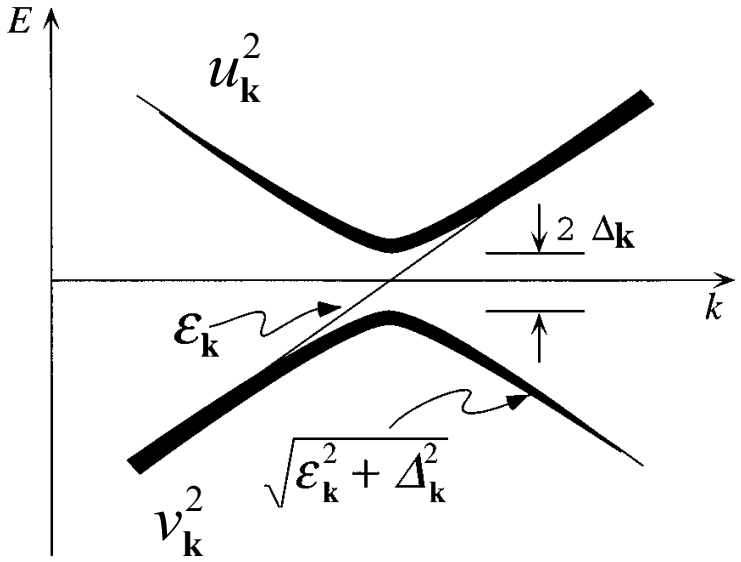


FIG. 1. Schematic dispersion in the normal (thin line) and superconducting (thick lines) states following BCS theory. The thickness of the superconducting state lines indicate the spectral weight given by the BCS coherence factors (v^2 below E_F and u^2 above).

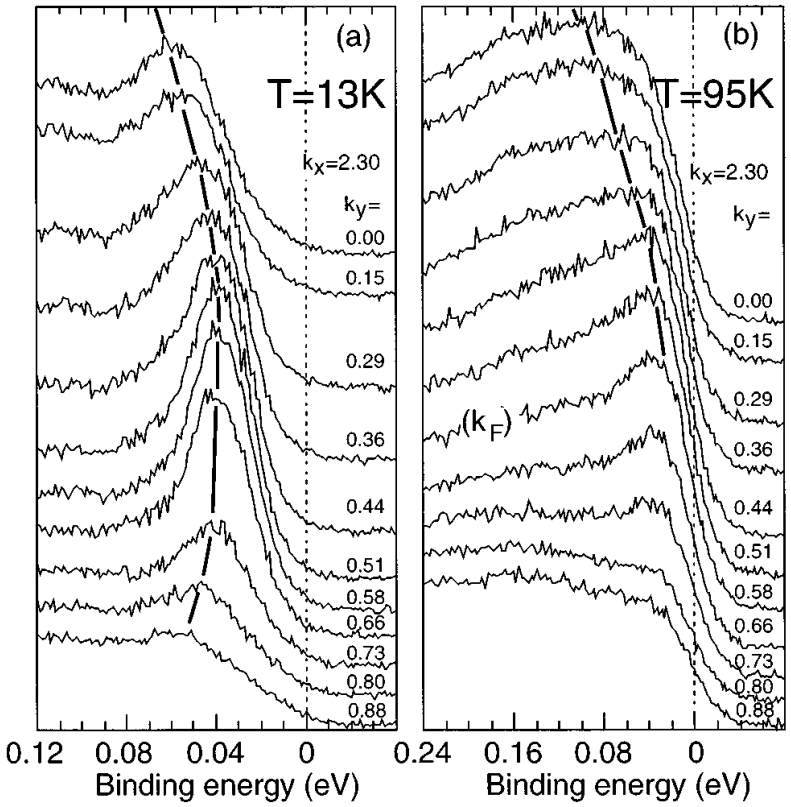
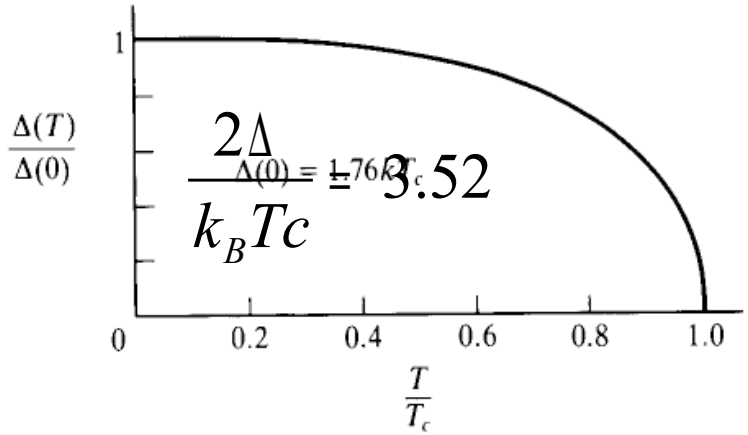


FIG. 2. Superconducting state (a) and normal state (b) EDC's for the same Bi2212 sample for the set of **k** values (1/*a* units) which are shown at the top. Note the different energy ranges.

T≠0 properties: the gap

$$\Delta_k = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2\sqrt{\xi_{k'}^2 + \Delta_{k'}^2}} \tanh \frac{\sqrt{\xi_{k'}^2 + \Delta_{k'}^2}}{2k_B T} \rightarrow 1 - f(E_k) - f(E_{k'})$$



T_c as the max T allowing a non-trivial solution

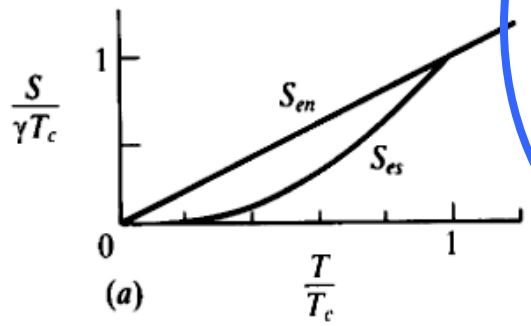
$$T_c = 1.14\,\Theta\, e^{-1/\lambda}$$

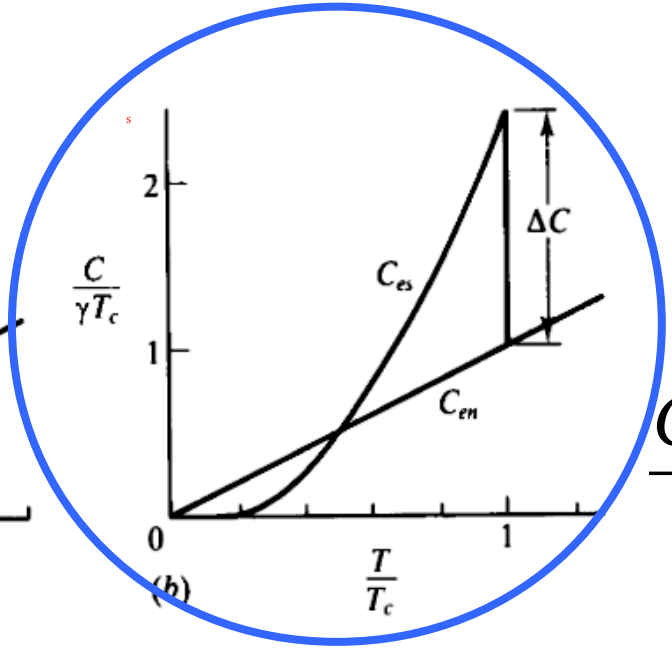
The nuclear-mass dependence of Debye temperature Θ implies an isotopic effect $\alpha \approx 0.5$

$$T_c \propto M^{-\alpha}$$

Thermodinamic properties

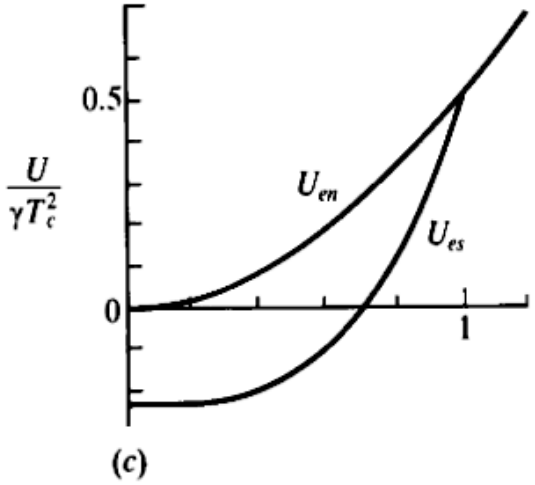
Entropy

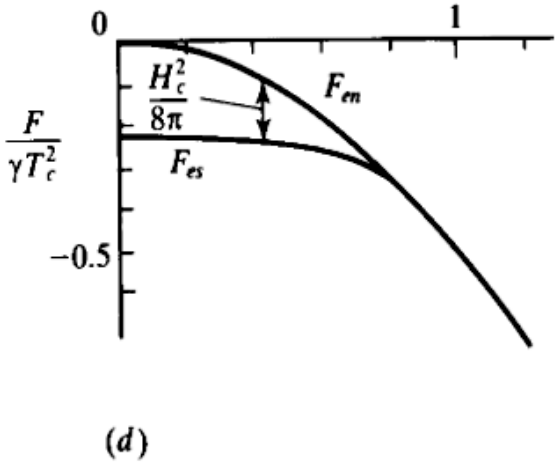




Specific heat jump at Tc

$$\frac{C_{es} - C_{en}}{C_{en}} = 1.43$$





Free energy (per unit volume)

$$F_s - F_n = -\frac{H_c^2}{8\pi}$$

Existence of an energy gap : photoemission, tunneling

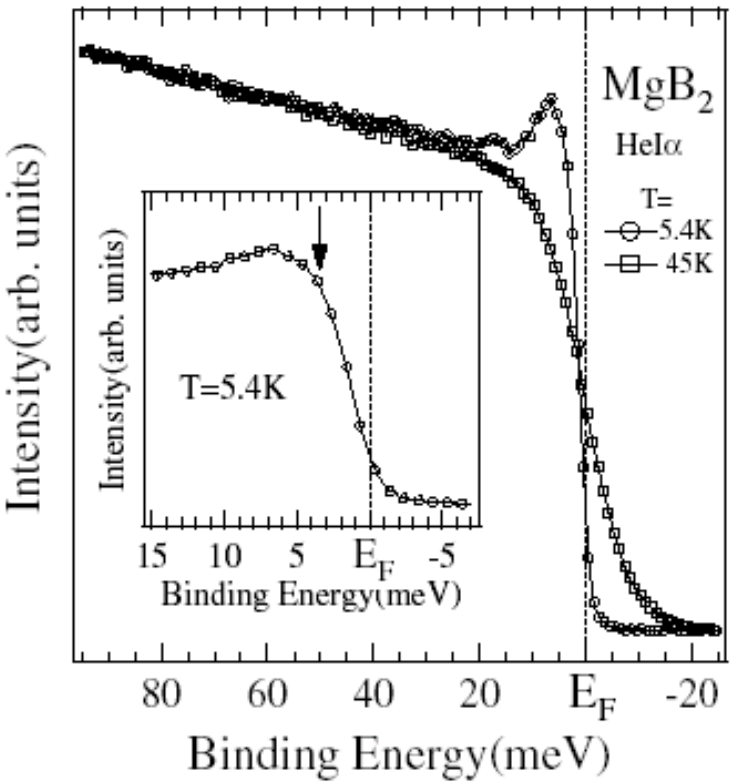


FIG. 1. High-resolution photoemission spectra of MgB_2 measured at 5.4 K (open circles connected with a solid line) and 45 K (open squares connected with a solid line) with a He Iα resonance line (21.2182 eV). The inset shows an expanded spectrum at 5.4 K in the vicinity of E_F. Please note that the spectrum has a peak with a shoulder structure as is emphasized with an arrow, which indicates a nonsimple isotropic gap.

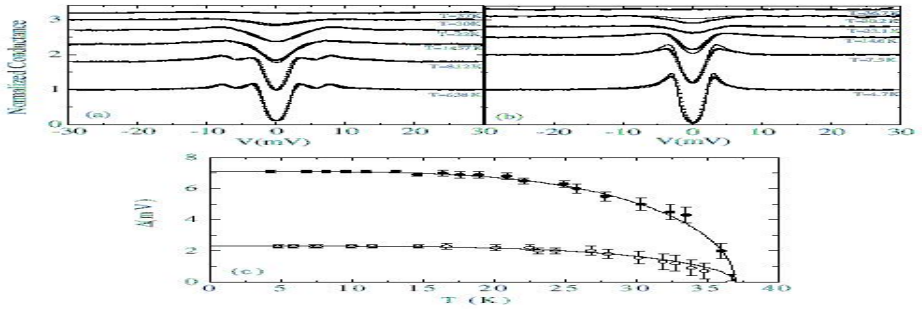
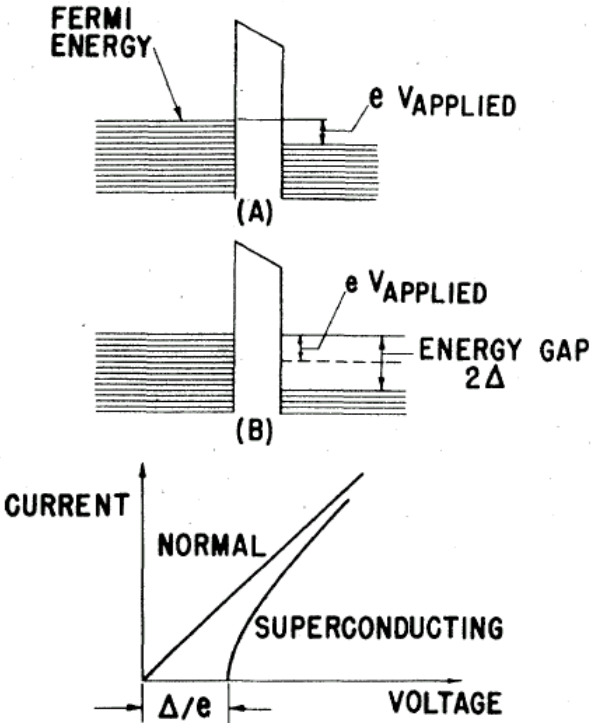


FIG. 3. Temperature evolution of the two tunneling spectra together with the theoretical curves. For all the curves $\Gamma_{12} = 0.1$ mV, $\Gamma_{21} = 0.14$ mV, and $\Gamma = 0.11$ mV (values optimized to the experimental curves at 4.2 K). In (a) the curves are reproduced using $\alpha = 0.87$, $\beta = 0.13$. In (b) $\alpha = 1$, $\beta = 0$. In (c) the gap values are extracted from the theoretical curves and are plotted as a function of the temperature together with the BCS $\Delta(T)$.



MgB_2

Problems of BCS theory

- It is a weak coupling theory ($\lambda \ll 1$)
- It neglects:

1. electron-electron Coulomb interaction
2. *e-ph* retardation effects

- Complete lack of predictive power

$$T_c = 1.14\,\Theta_D\, e^{-1/\lambda}$$

Example: Nb (λ=1.18)

T_c exp 9.5 K, BCS 134 K

Despite these problems, B, C & S largely deserved their Nobel prize: the qualitative behavior of most physical quantities is correctly described!

Repulsive electron-electron interaction

$$V(\mathbf{r},\mathbf{r}') = \int \varepsilon^{-1}(\mathbf{r},\mathbf{r}'',\omega)\,\frac{1}{|\mathbf{r}''-\mathbf{r}'|}\,d^3\mathbf{r}''$$

where ε^{-1} is the frequency dependent dielectric function

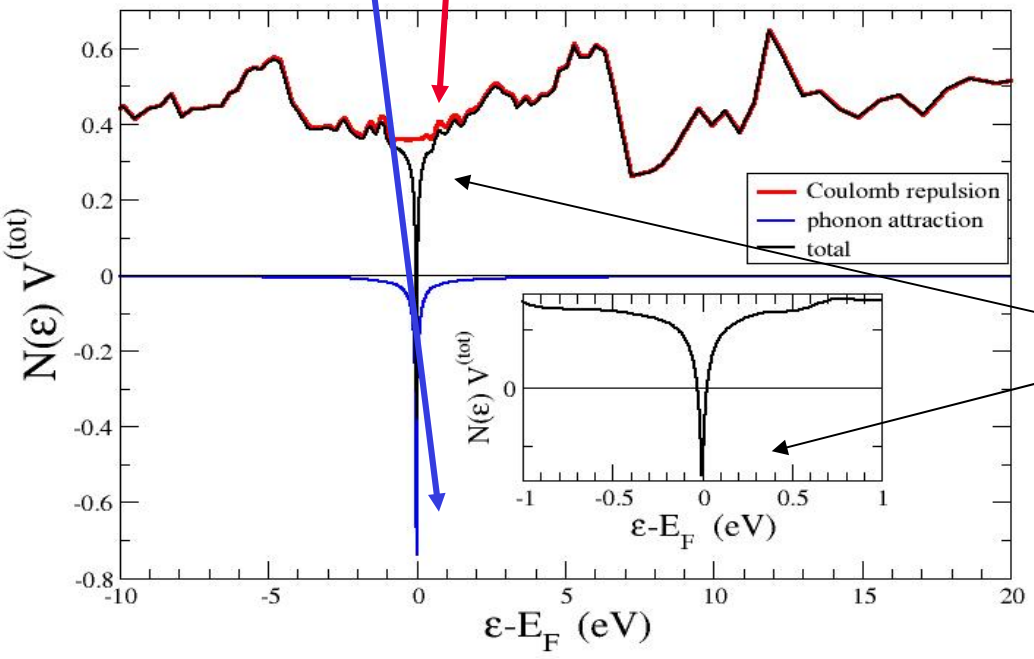
$$\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(q,\omega) = \delta_{\mathbf{G},\mathbf{G}'} + v_{\mathbf{q}+\mathbf{G}}\,\chi_{\mathbf{G},\mathbf{G}'}(q,\omega)$$

- Bare Coulomb potential: instantaneous
- Screened Coulomb potential: plasma frequency, few eV
- Phonon-mediated attraction: phonon frequencies ~100 meV

Different time scales allow superconductivity to occur

Interaction potential $V=V^{(ph)}+V^{(el)}$ includes:

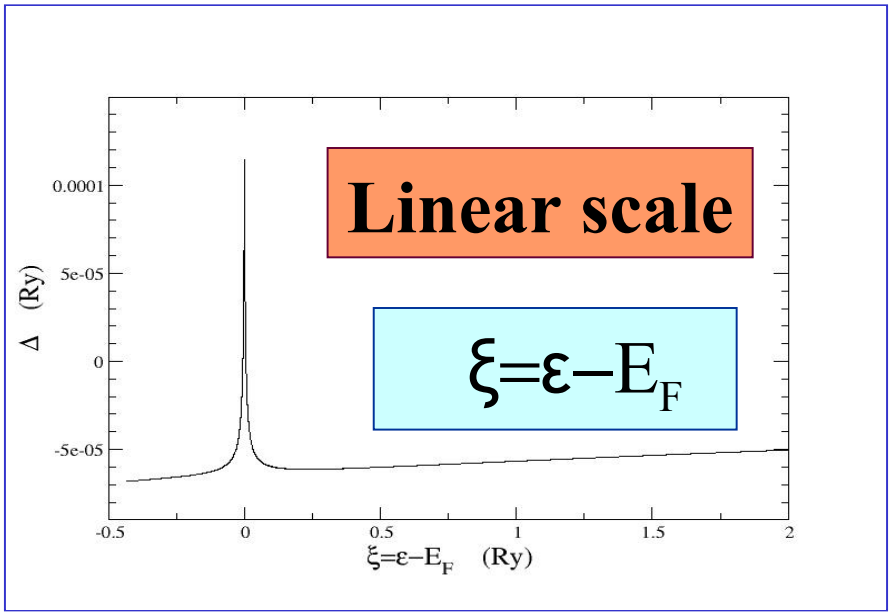
- Phonon-mediated attraction
- Direct electron-electron repulsion

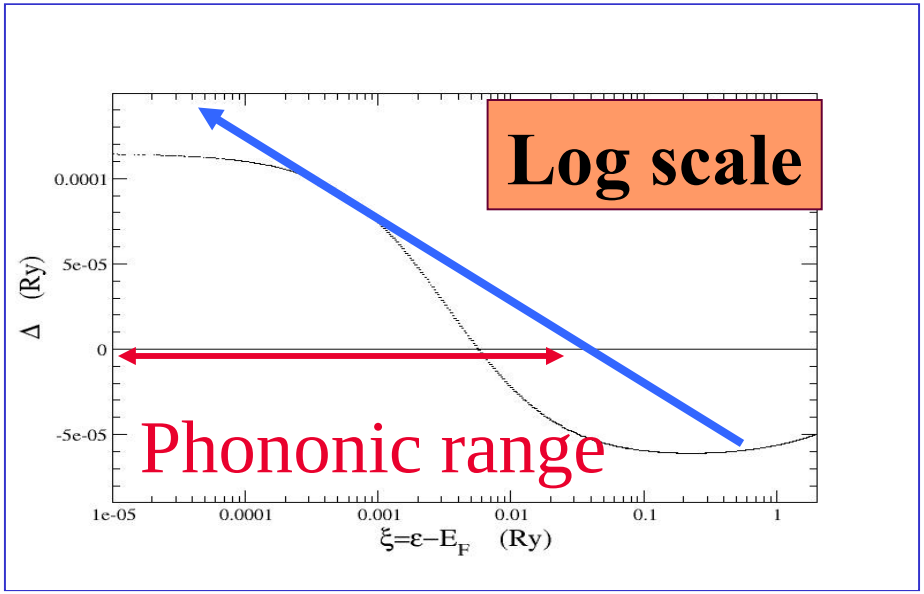


The total interaction is attractive only in a narrow region around E_F

To get superconductivity, David needs to defeat Goliath

Retardation effects: Nb





$$\Delta_{n\mathbf{k}} = -\sum_{n',\mathbf{k}'} V_{n\mathbf{k},n'\mathbf{k}'} \frac{\Delta_{n',\mathbf{k}'}}{2E_{n',\mathbf{k}'}} \tanh\left(\frac{E_{n'k'}}{2k_BT}\right)$$

Constructive interference from a repulsive interaction with states far from E_F

In ELIASHBERG theory:

- **repulsive Coulomb interaction (Morel Anderson):**

$$\mu = \langle V_{el-el} \rangle_{FS} \qquad \mu^* = \frac{\mu}{1 + \mu \ln \frac{E_F}{\hbar \omega_D}}$$

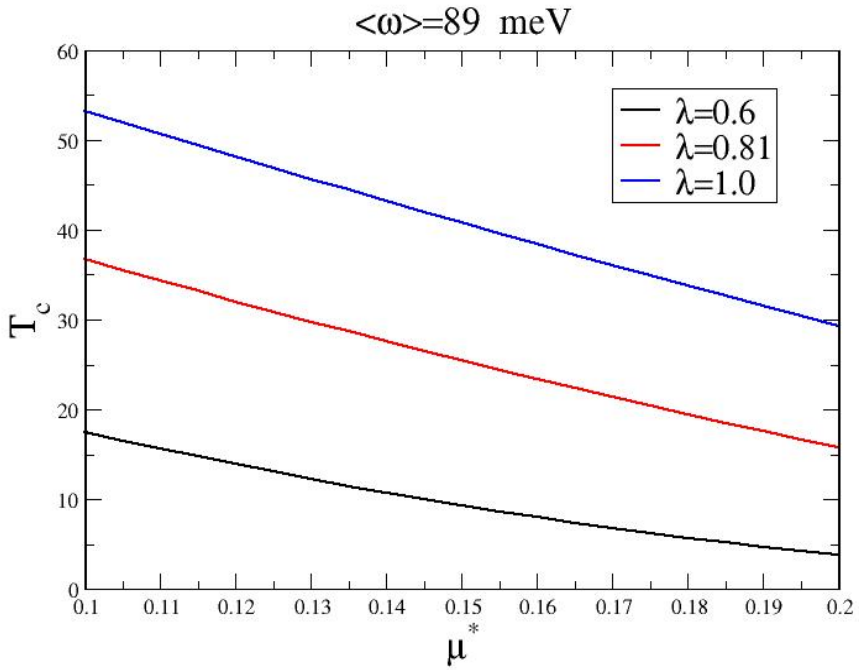
The difference between electron (h/E_F) and nuclear ($2\pi/\omega_{ph}$) time scales reduces the coulomb repulsion (retardation)

Superconductivity results from the competition of opposite effects: $\lambda - \mu^*$

Condensed Eliashberg:

McMillan Equation

$$T_c = \frac{\langle \omega \rangle}{1.2} e^{-1.04 \frac{1+\lambda}{\lambda - \mu^* (1+0.62\lambda)}}$$



μ^* is normally fitted to experimental T_c

e-ph coupling: ELIASHBERG spectral function

$$F(\omega) = \sum_{q,j} \delta\left(\omega - \omega_{qj}\right)$$

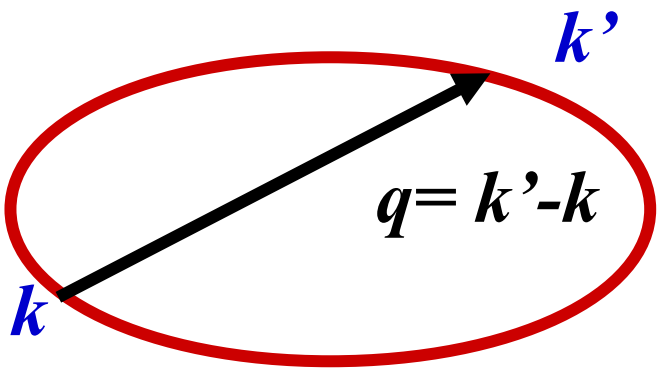
Phonon density of states

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_{\mathbf{q},j} \delta\left(\omega - \omega_{qj}\right) \sum_{n\mathbf{k},n'\mathbf{k}'} \left| g^{qj}_{nk,n'k'} \right|^2 \delta_{k+q,k'} \delta\left(\varepsilon_{nk}\right) \delta\left(\varepsilon_{n'k'}\right)$$

Phonon density of states weighted by the coupling with electrons at E_F

$$g^{qj}_{nk,n'k'} = \left\langle \psi_{n'k'} \left| \hat{\varepsilon}^{qj} \cdot \frac{\delta V_{eff}}{\delta \mathbf{u}(\mathbf{q}j)} \right| \psi_{nk} \right\rangle$$

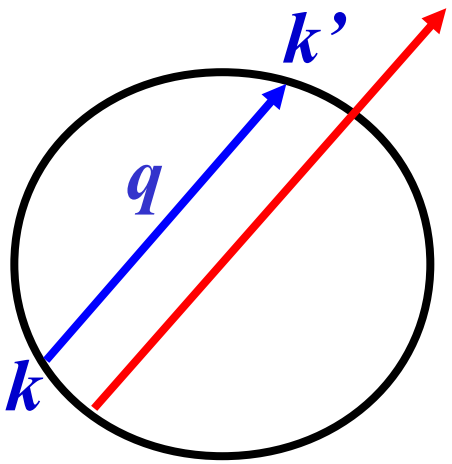
Material specific *e-ph* coupling



$$\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega$$

Kohn anomaly

The electronic screening is discontinuous at $2k_F$
(log singularity in the derivative of the response)



For $q>2k_F$ it is not possible to create excitations at zero energy

$$\left.\frac{d\chi(q)}{dq}\right|_{q\to 2k_F} \to -\infty$$

$$\chi(q) = -e^2 \frac{mk_F^2}{\hbar^2\pi^2}\left[\frac{1}{2} + \frac{1-x^2}{4x} ln\left|\frac{1+x}{1-x}\right|\right] \qquad x = q/2k_F$$

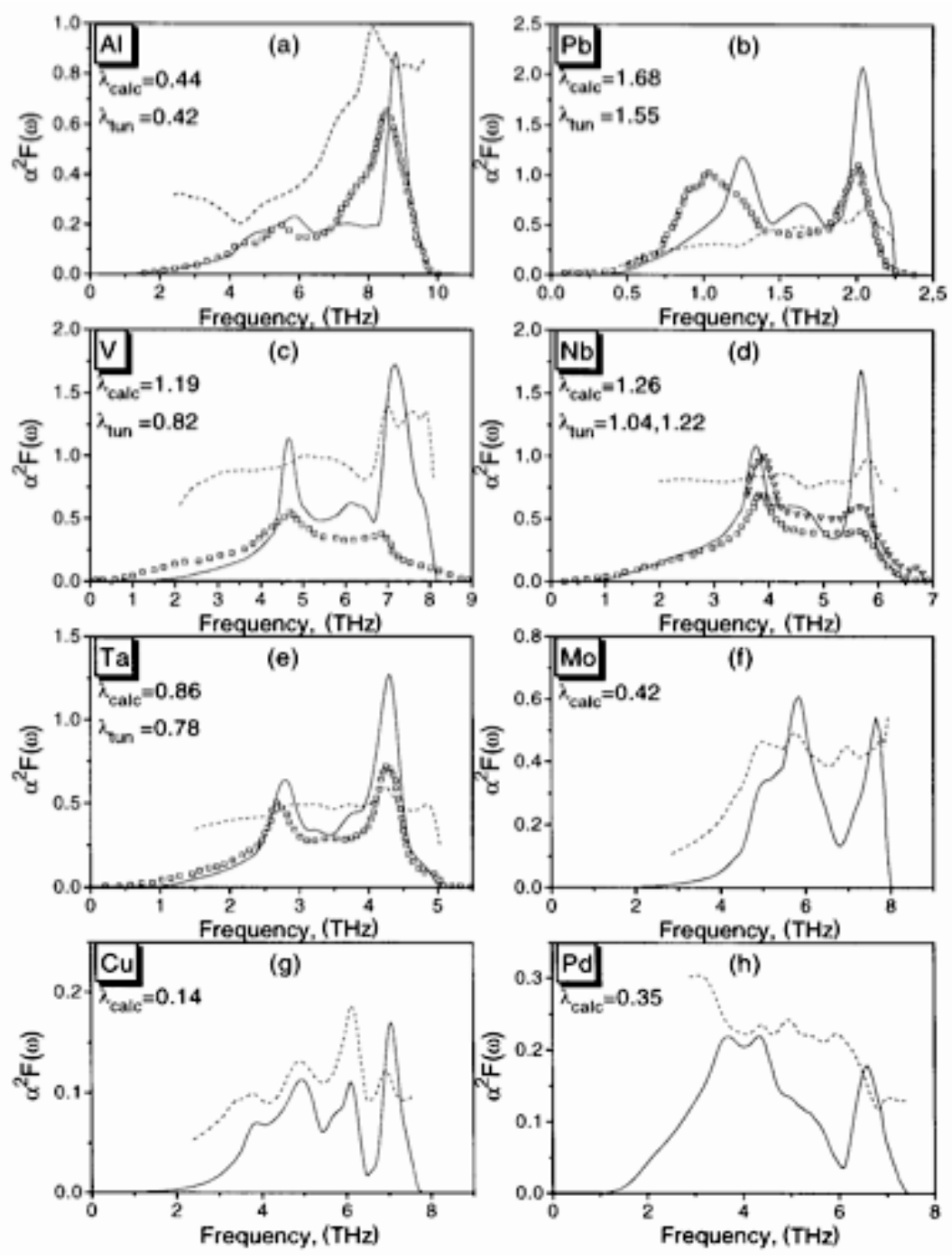
phonons

Baroni et al. Rev. Mod. Phys. 73, 515 (2001)

$$C^{\alpha\alpha'}_{ss',elettr}(\mathbf{q}) = \frac{1}{N_c}\int\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\partial V_{ion}(\mathbf{r}')}{\partial u^{\alpha}_{s}(\mathbf{q})}\,\chi(\mathbf{r},\mathbf{r}')\,\frac{\partial V_{ion}(\mathbf{r})}{\partial u^{\alpha}_{s'}(\mathbf{q})} +$$

$$\frac{1}{N_c}\int d\mathbf{r}\; n(\mathbf{r})\,\frac{\partial^2 V_{ion}(\mathbf{r})}{\partial u^{\alpha}_{s}(\mathbf{q})\,\partial u^{\alpha}_{s'}(\mathbf{q})}$$

The response of the electrons to ion displacement is a fundamental ingredient

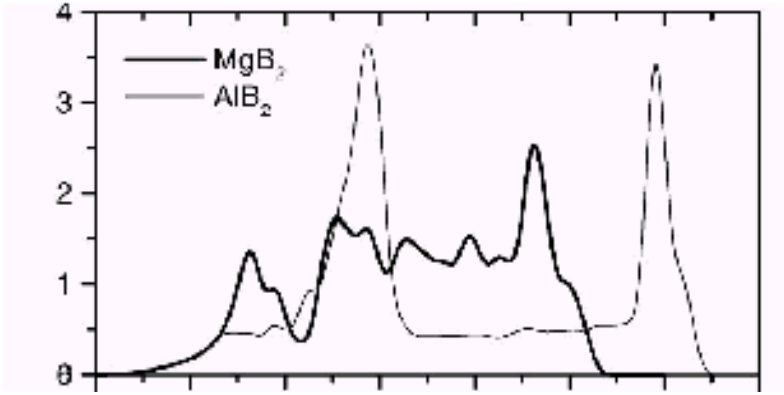


Electron-phonon spectral function $\alpha^2F(\omega)$

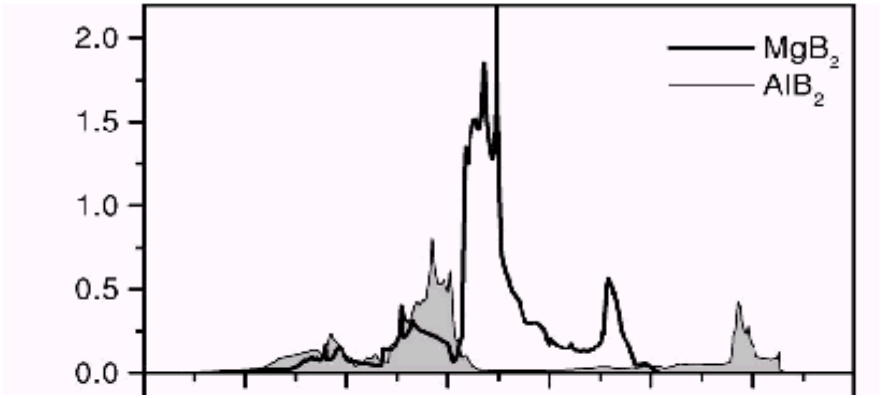
FIG. 2. (a)–(h) Calculated spectral functions $\alpha^2F(\omega)$ of the electron-phonon interaction (full lines) for the eight elemental metals considered in this work. The behavior of the electron-phonon prefactor $\alpha^2(\omega)$ [defined simply as the ratio $\alpha^2F(\omega)/F(\omega)$] is shown by dashed lines. Symbol plots present the results of available tunneling experiments (Refs. 3, 35, and 39).

MgB_2 is a superconductor, AlB_2 is not

Phonon density of states



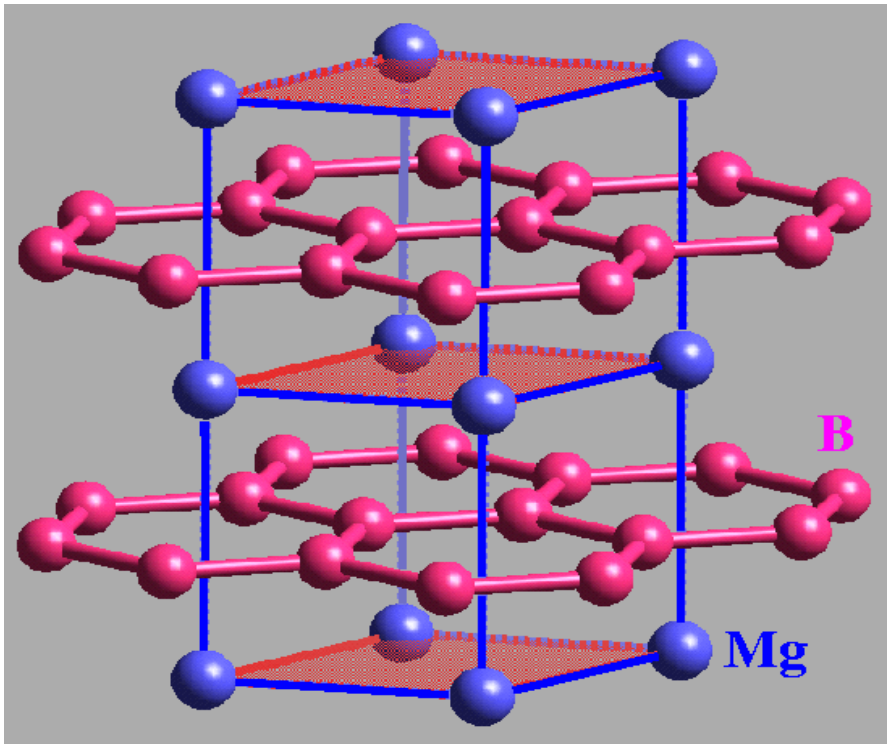
Spectral function $\alpha^2F(\omega)$



$$\lambda = 2\int \frac{\alpha^2 F(\omega)}{\omega} d\omega$$

Example: MgB_2

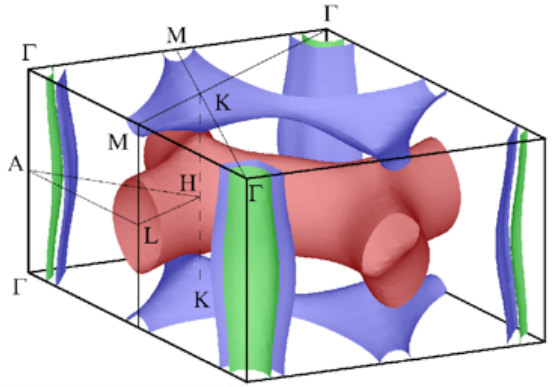
Superconductor, T_c=39.5 K

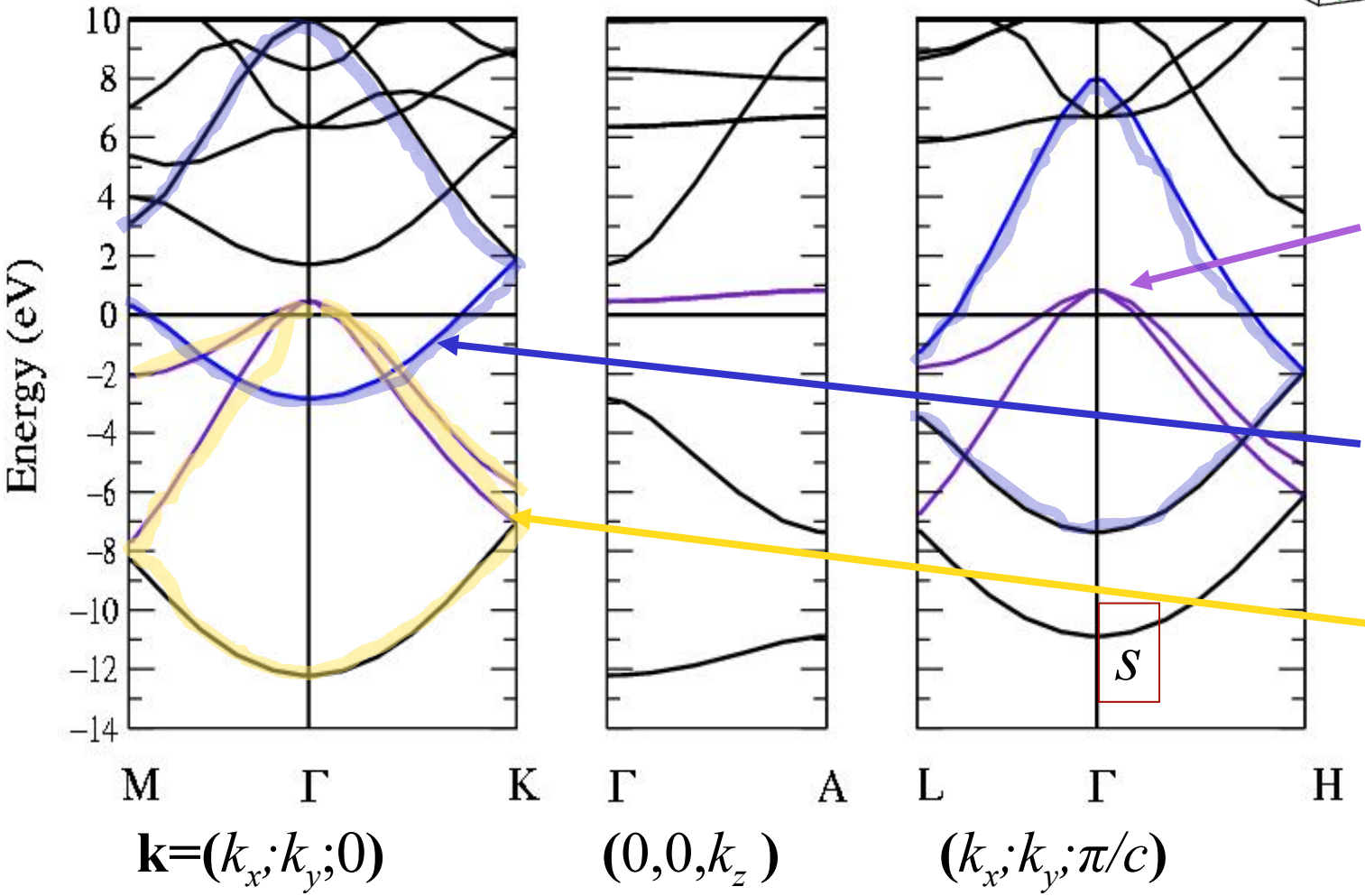


Energy bands of MgB2

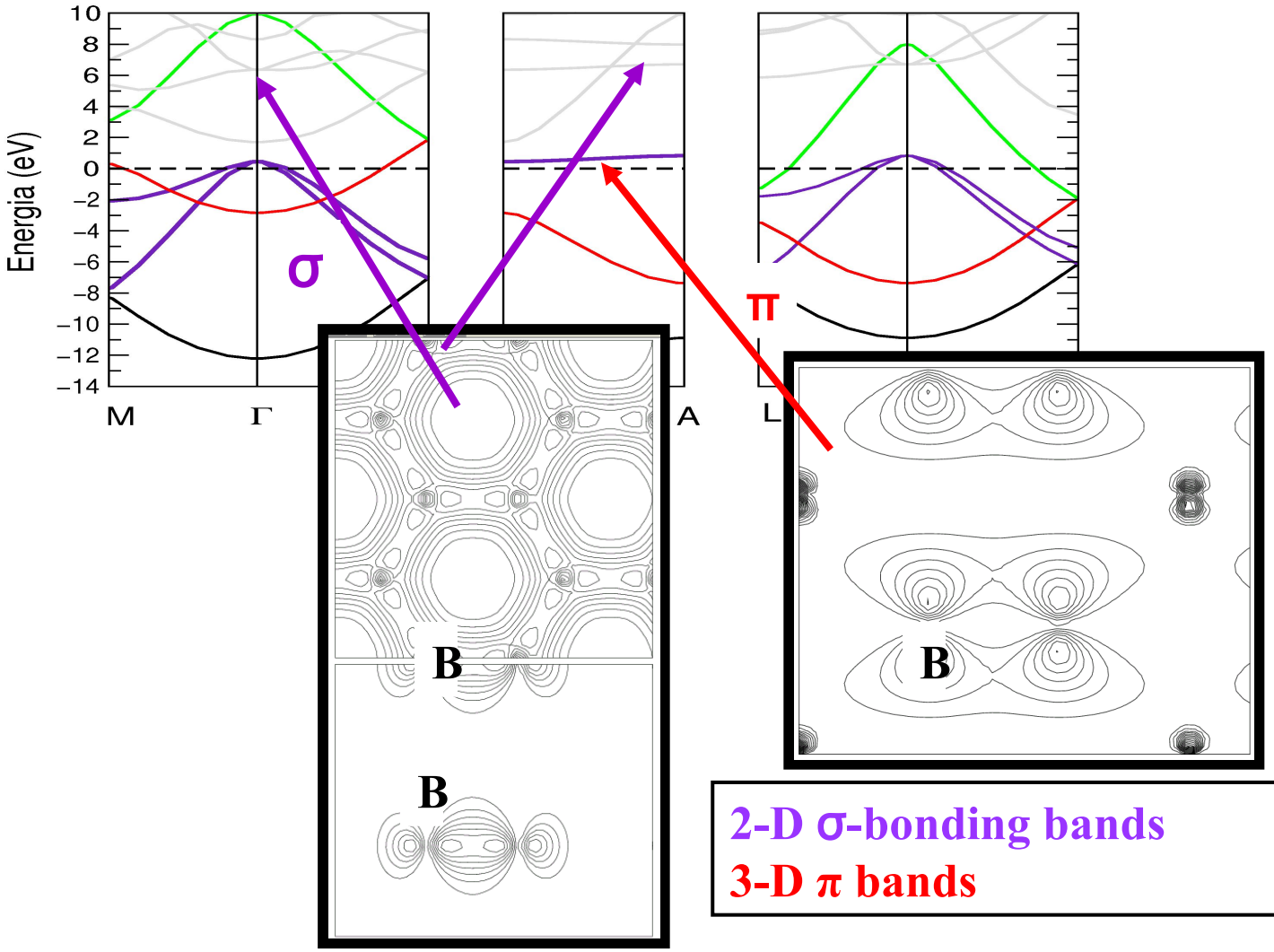
3D π bands (strongly dispersed along Γ-A (k_z))

2D σ bands (weakly dispersed along Γ-A)





Electronic properties of MgB_2



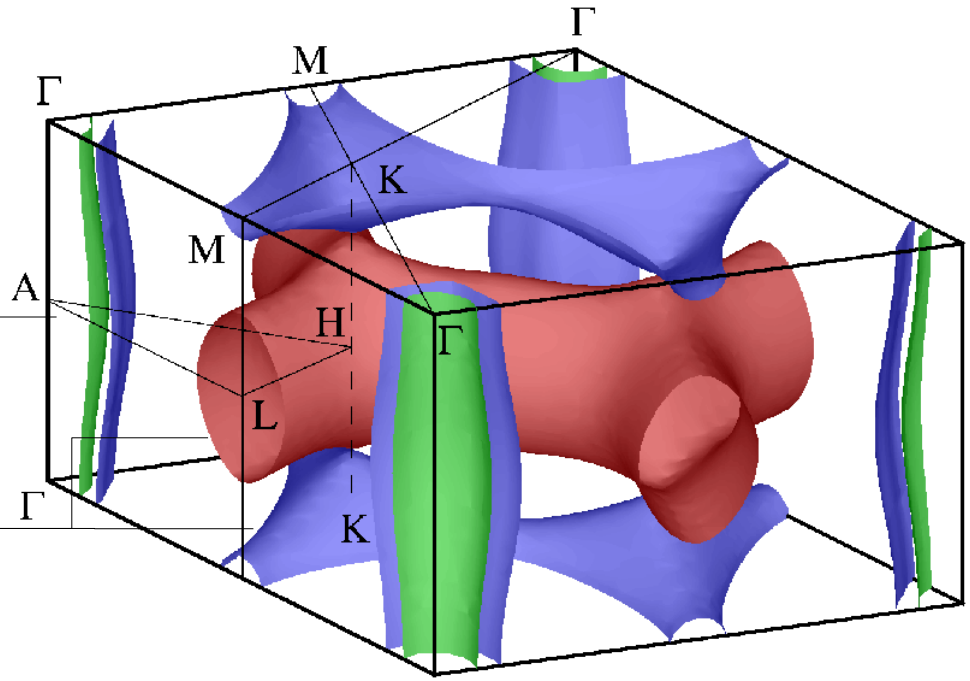
2-D σ-bonding bands

3-D π bands

Fermi surface of MgB_2

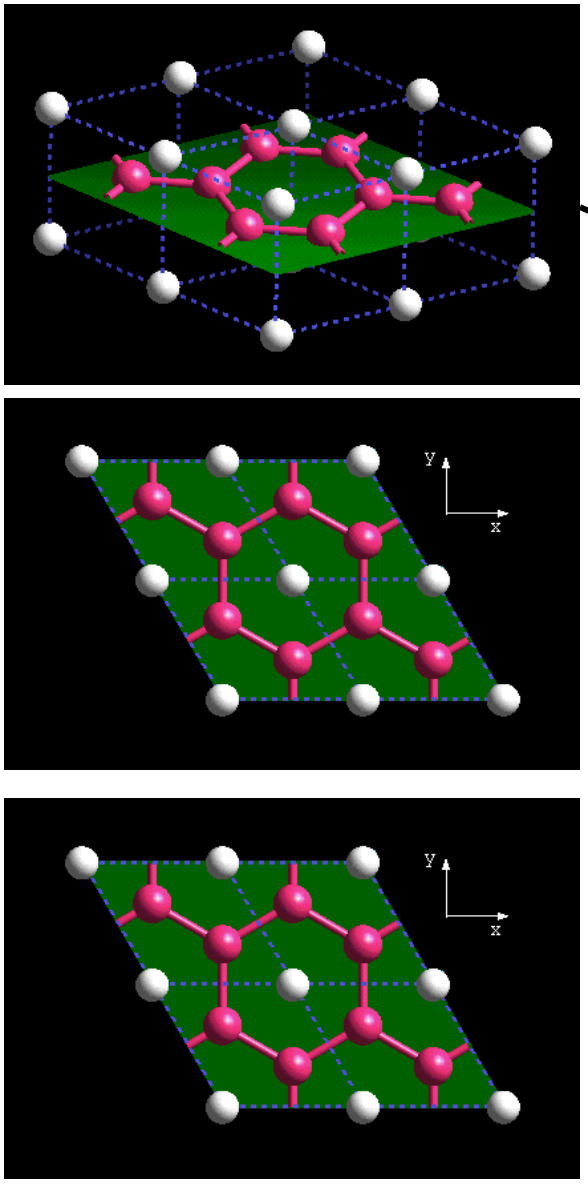
Blue and green warped cylinders derive from p_x and p_y orbitals (σ bonds)

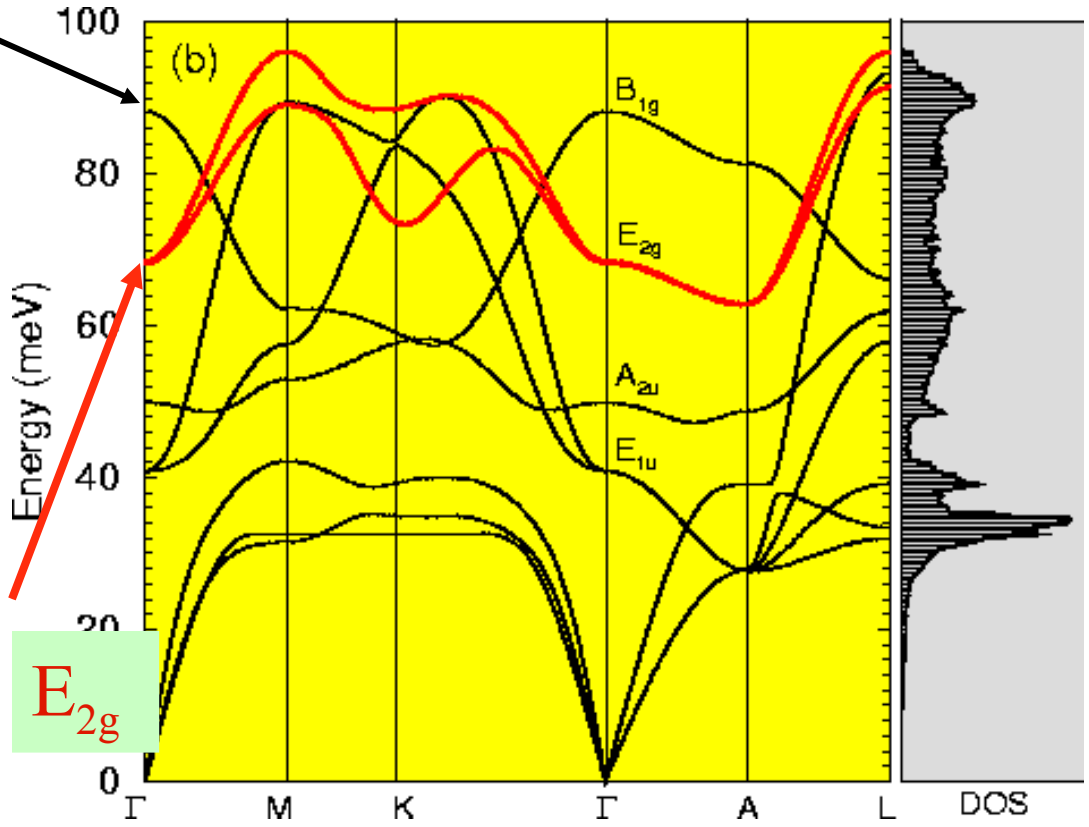
Blue and red "nets" come from p_z orbitals (π bonding and antibonding respectively)



Phonons in MgB_2

B_{1g}

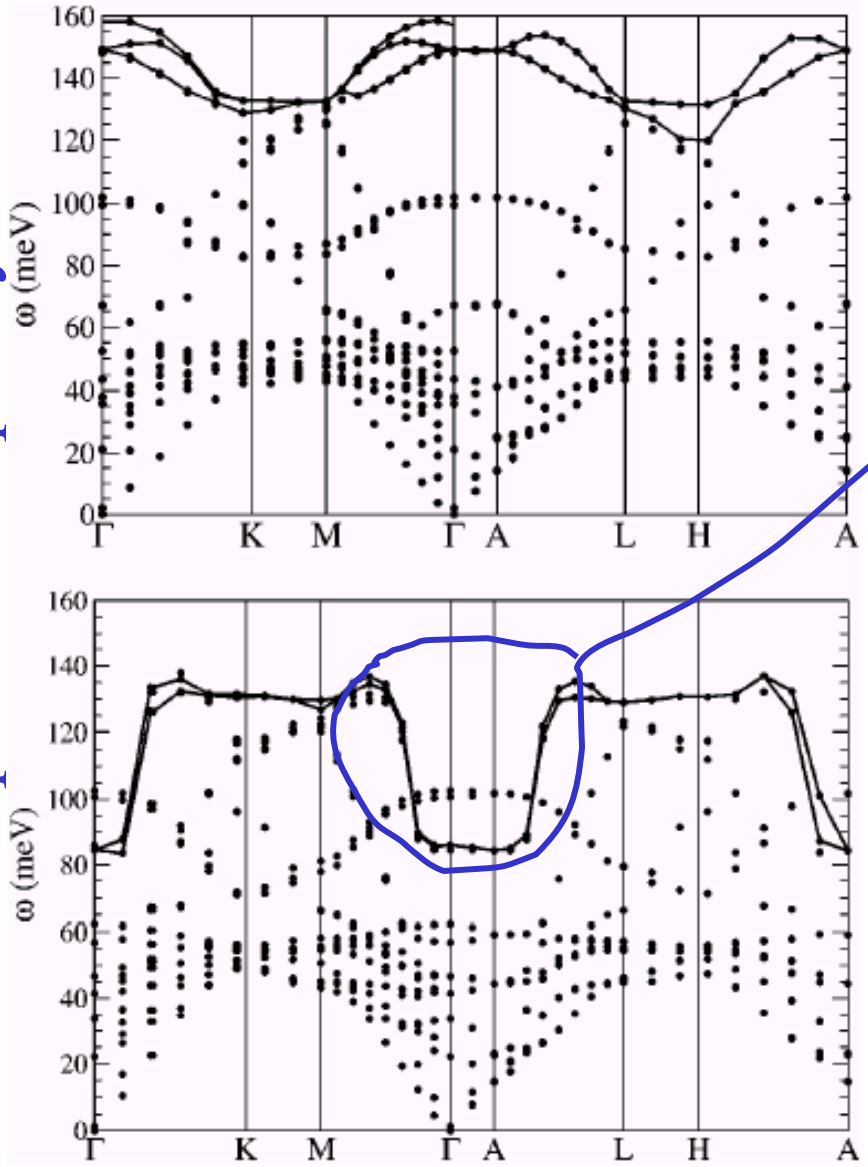




E_{2g}

Anomalously low frequency E_{2g} branch (B-B bond stretching) – Kohn anomaly

Kohn anomaly: LiBC, isoelettronic to MgB_2 (Pickett)



Stoichiometric compound
is a semiconductor

Strong renormalization
of phonon frequencies

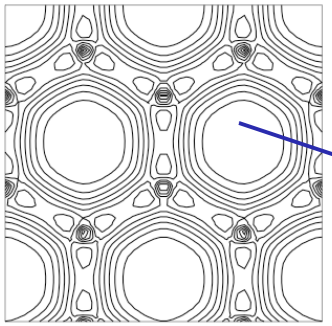
Metallic upon doping

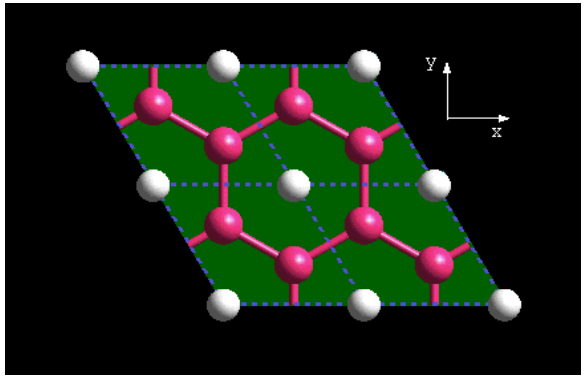
Kohn anomaly

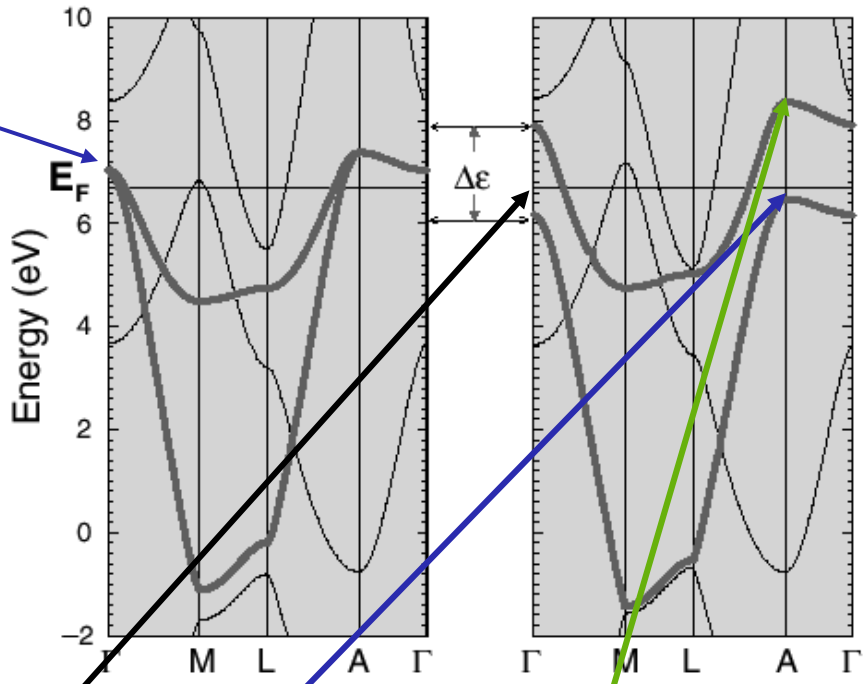
High T_c predicted

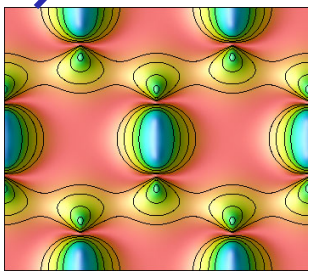
Unfortunately not found experimentally

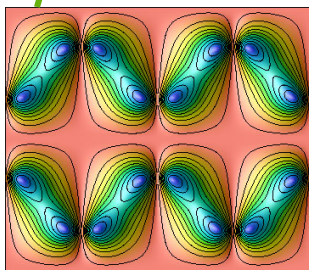
Large coupling of the E_{2g} phonon mode with σ hole pockets (band splitting)







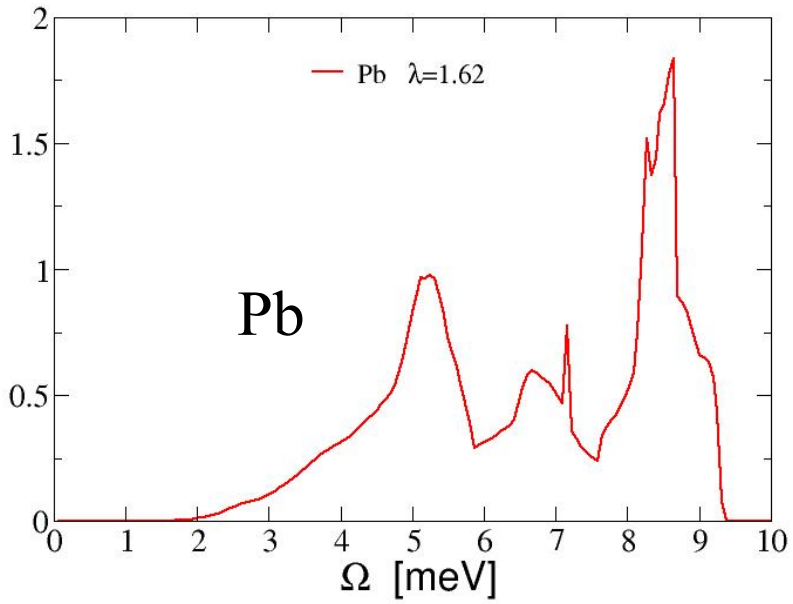




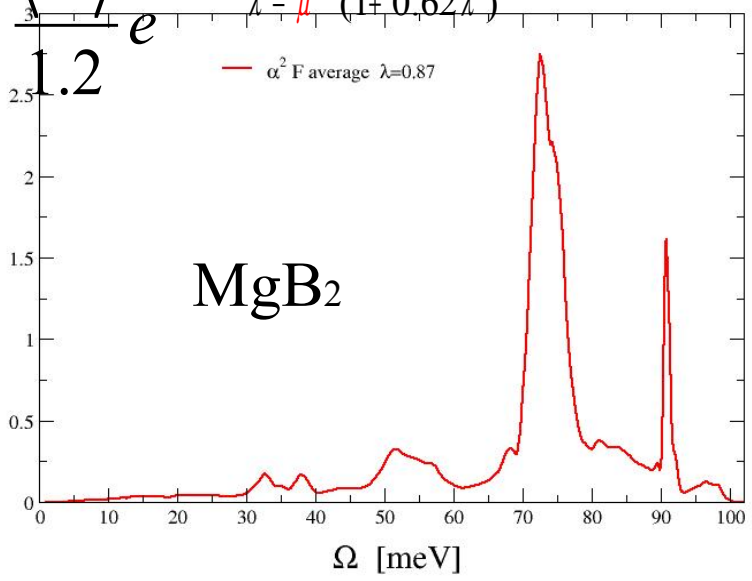
ω_{E2g}=0.075 eV

Δε~1-2 eV !!!

Pb and MgB2 Eliashberg functions



$$T_c = \frac{\langle \omega \rangle}{1.2} e^{-1.04\frac{1+\lambda}{\lambda - \mu^*(1+0.62\lambda)}}$$



λ=1.62

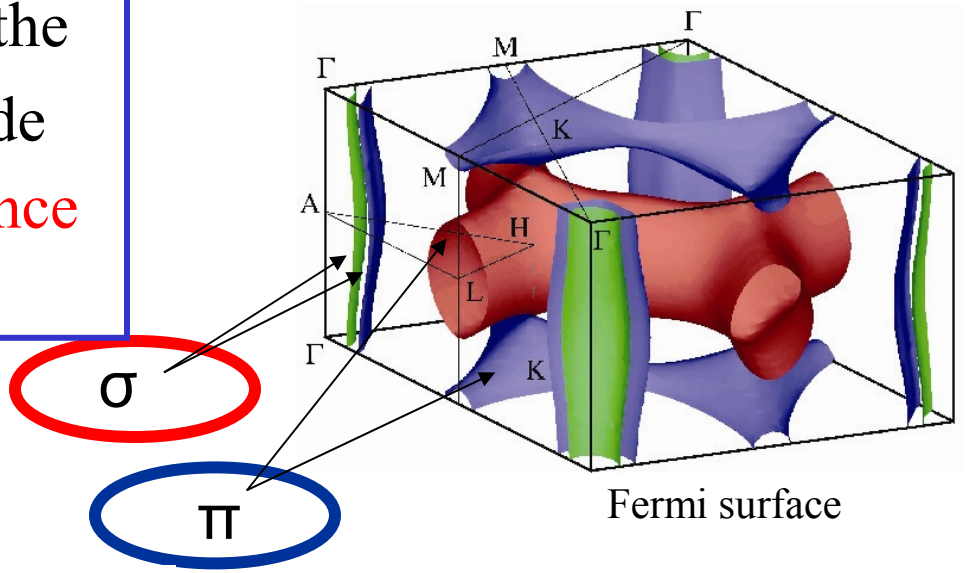
T_c=7.2 K

λ=0.87

T_c=39.5 K

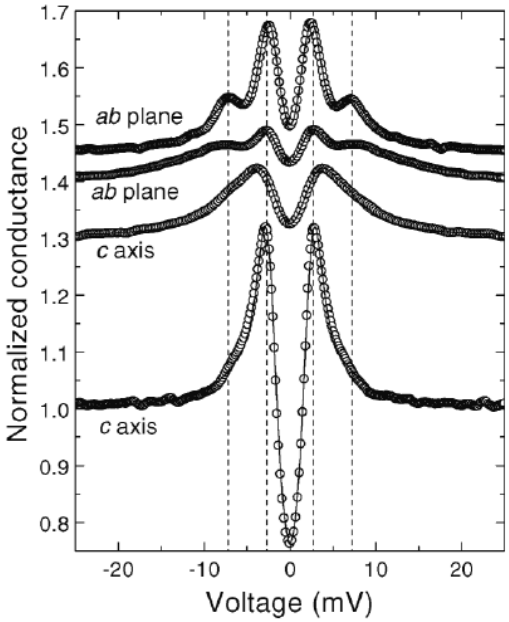
Two band model for the electron phonon coupling (EPC)

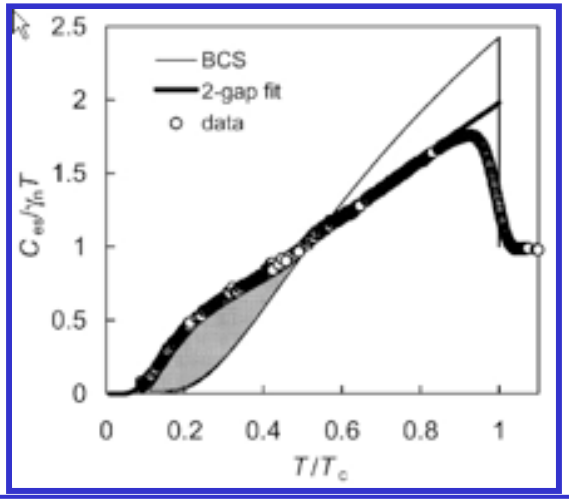
- λ stronger in σ bands due to the coupling with E_{2g} phonon mode
- Experiments show the existence of two gaps: Δ_σ and Δ_π.



Fermi surface

Two band model: experimental evidence
R. S. Gonnelli, PRL **89**, 247004 (2002)





Specific heat evidence of 2 gaps

Two-gap structure associated with σ and π bands

Tunnelling experiments

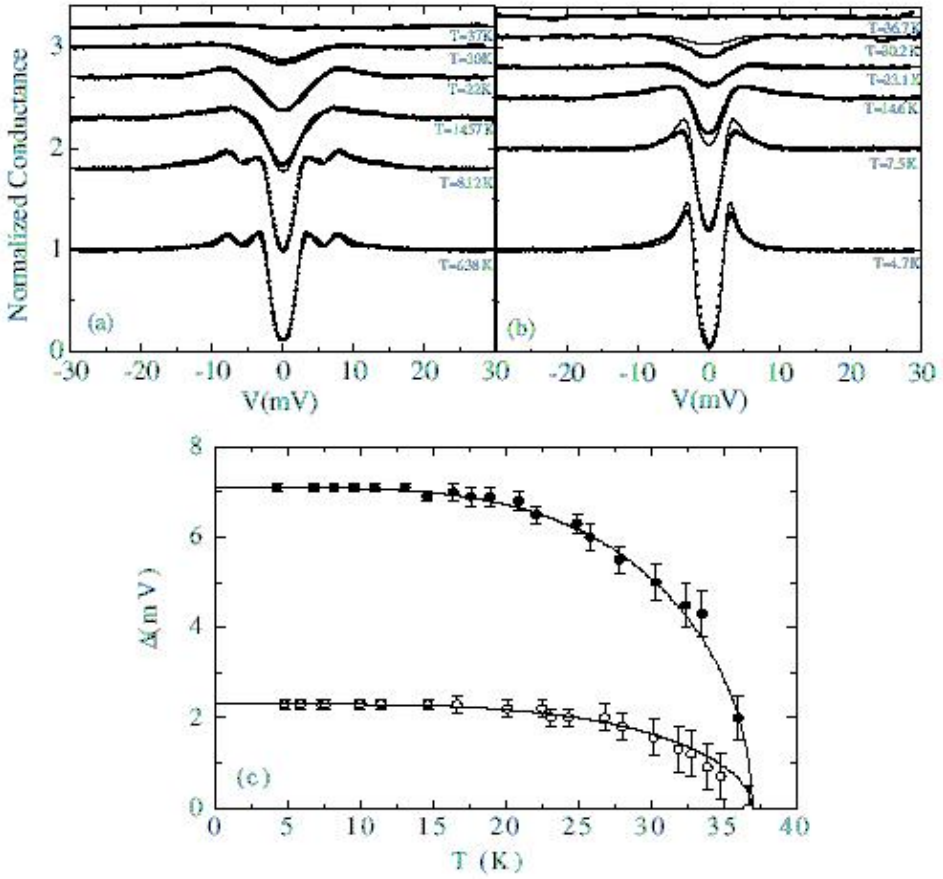


FIG. 3. Temperature evolution of the two tunneling spectra together with the theoretical curves. For all the curves $\Gamma_{12} = 0.1$ mV, $\Gamma_{21} = 0.14$ mV, and $\Gamma = 0.11$ mV (values optimized to the experimental curves at 4.2 K). In (a) the curves are reproduced using $\alpha = 0.87$, $\beta = 0.13$. In (b) $\alpha = 1$, $\beta = 0$. In (c) the gap values are extracted from the theoretical curves and are plotted as a function of the temperature together with the BCS $\Delta(T)$.

Two band superconductivity

VOLUME 3, NUMBER 12 PHYSICAL REVIEW LETTERS DECEMBER 15, 1959

BARDEEN-COOPER-SCHRIEFFER THEORY OF SUPERCONDUCTIVITY IN THE CASE OF OVERLAPPING BANDS

H. Suhl, B. T. Matthias, and L. R. Walker
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received November 16, 1959)

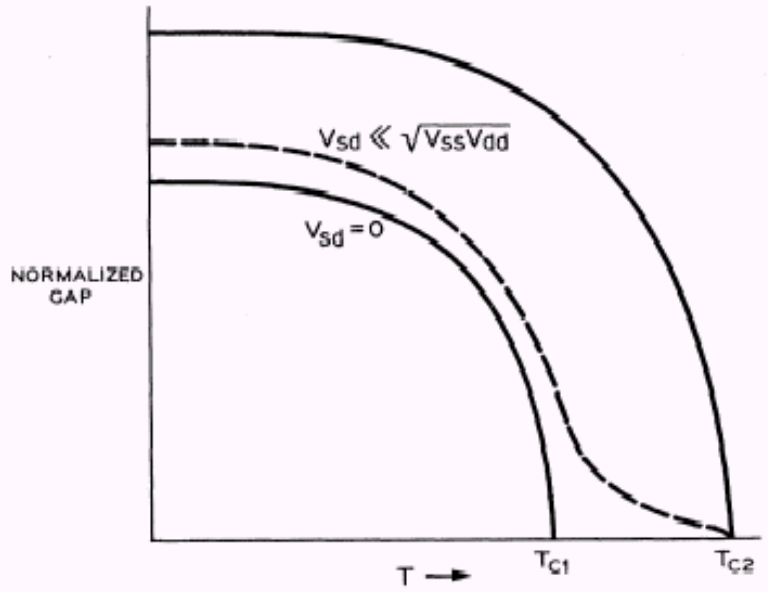


FIG. 2. When $V_{sd} = 0$, there are two transition temperatures. When V_{sd}^2 is finite but much less than $V_{ss}V_{dd}$, the lower transition temperature disappears in the manner shown.

T_c depends on the largest eigenvalue of the inter- and intra-band coupling constants, λ_{nm} in place of the average λ

Newest developments:
EXTENSION OF **DFT** TO THE SUPERCONDUCTING STATE (**SCDFT**)

Order parameter

$$\chi\left(\mathbf{r},\mathbf{r}'\right) = \left\langle \psi_{\uparrow}\left(\mathbf{r}\right)\psi_{\downarrow}\left(\mathbf{r}'\right)\right\rangle \neq 0$$

In the SC state

SCDFT Oliveira Gross Kohn, PRL **60**, 2430 (1988)

S. Kurth, M. Lüders, M. Marques, PhD thesis

The anomalous density χ represents the order parameter

Normal $\rho(\mathbf{r}) = \sum_{\sigma} \langle \psi^{\dagger}(\mathbf{r}) \psi(\mathbf{r}) \rangle$

Anomalous $\chi(\mathbf{r},\mathbf{r}') = \langle \psi_{\uparrow}(\mathbf{r}) \psi_{\downarrow}(\mathbf{r}') \rangle$

Nuclear $\Gamma(\underline{\underline{R}}) = \langle \hat{\phi}^{+}(R_1) \cdots \hat{\phi}^{+}(R_{N_n}) \hat{\phi}(R_{N_n}) \cdots \hat{\phi}(R_1) \rangle$

Hohenberg-Kohn Theorem: $\rho, \chi, \Gamma \leftrightarrow V^e_{ext}, \Delta_{ext}, V^n_{ext}$

$$\Omega = F[\rho, \chi, \Gamma] + \int dr\, \rho\, (V^e_{ext} - \mu) - \iint drdr' [\chi\, \Delta^*_{ext} + h.c.] + \int dR\, \Gamma\, V^n_{ext}$$

PRB B 72, 24545 (2005), *ibid* 72, 24546 (2005)

Universal exchange-correlation functional F_{xc}

$$V_{xc}(\mathbf{r}) = \frac{\delta F_{xc}}{\delta \rho(\mathbf{r})} \qquad \Delta_{xc}(\mathbf{r},\mathbf{r}') = -\frac{\delta F_{xc}}{\delta \chi^{*}(\mathbf{r},\mathbf{r}')} \qquad V_{cn}(\mathbf{R}) = \frac{\delta F_{xc}}{\delta \Gamma(\mathbf{R})}$$

Variational eqs.: Bogoliubov-De Gennes-type + nuclear eq

$$\left[-\frac{\nabla^2}{2} + V_s(\mathrm{r}) - \mu\right] u_{kn}(\mathrm{r}) + \int d^3r' \Delta_s(\mathrm{r},\mathrm{r}') v_{kn}(\mathrm{r}') = E_{kn} u_{kn}(\mathrm{r}')$$

$$\int d^3r' \Delta_s^{*}(\mathbf{r},\mathrm{r}') u_{kn}(\mathrm{r}') - \left[-\frac{\nabla^2}{2} + V_s(\mathrm{r}) - \mu\right] v_{kn}(\mathrm{r}) = E_{kn} v_{kn}(\mathrm{r}')$$

SCDFT

physical ρ,χ,Γ minimize the grand-canonical potential

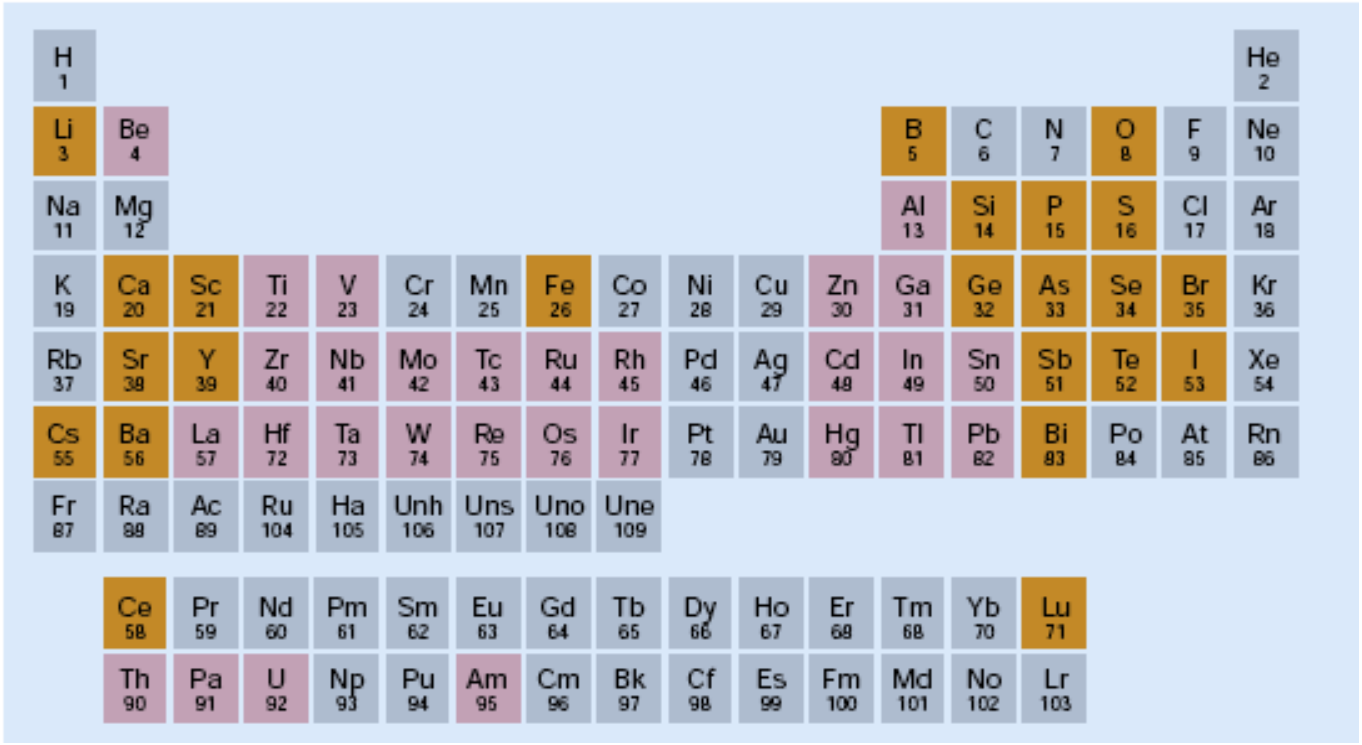
- BCS-like gap equation, with an interaction potential coming from *first-principles*: no μ^*

$$\Delta_{n,\mathbf{k}} = -\sum_{n',\mathbf{k}'} w_{n\mathbf{k},n'\mathbf{k}'} \frac{\Delta_{n',\mathbf{k}'}}{2E_{n',\mathbf{k}'}} \tanh\left(\frac{\beta E_{n'k'}}{2}\right)$$

We solve self-consistently for Δ_{nk}

Static-looking potential, but dynamical effects are build-in in the spirit of DFT

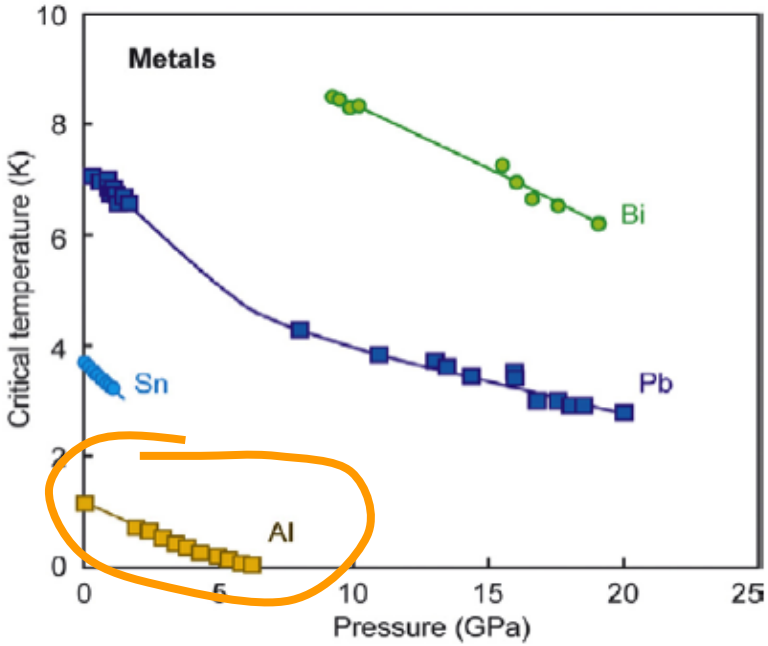
Superconductivity under pressure

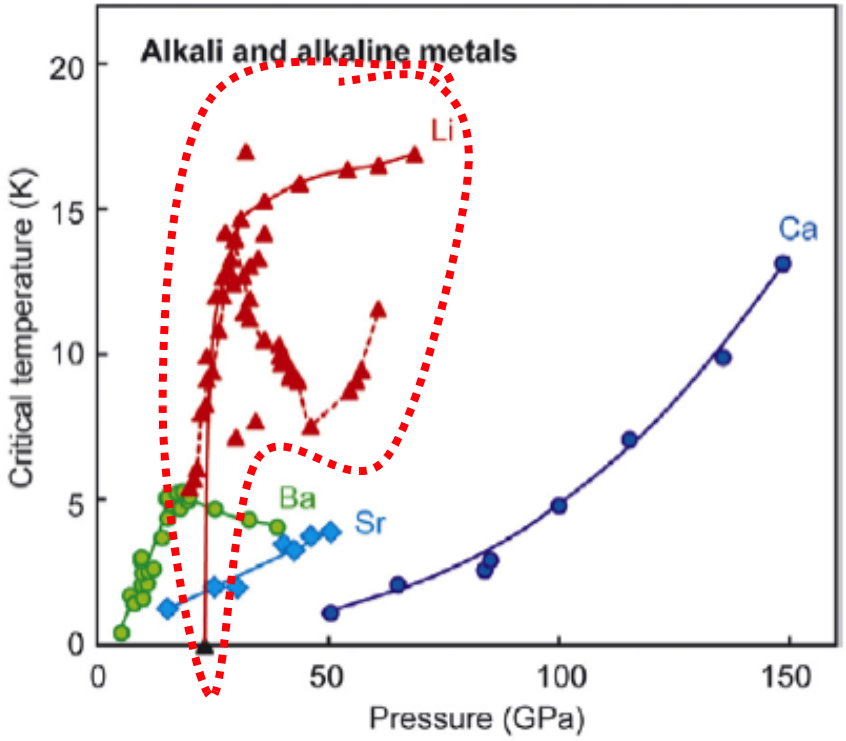


29 elements superconducts under normal conditions

23 only under pressure: Lithium is the last discovered

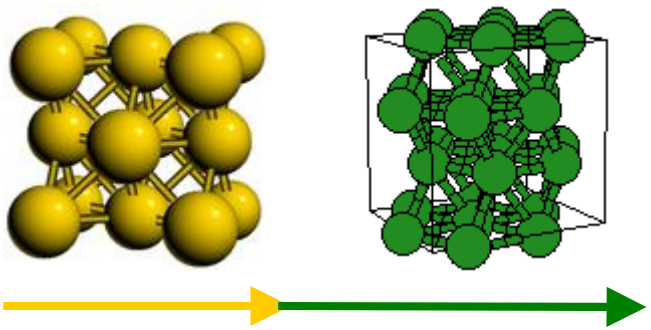
$T_c(P)$ is a strongly material-dependent function*



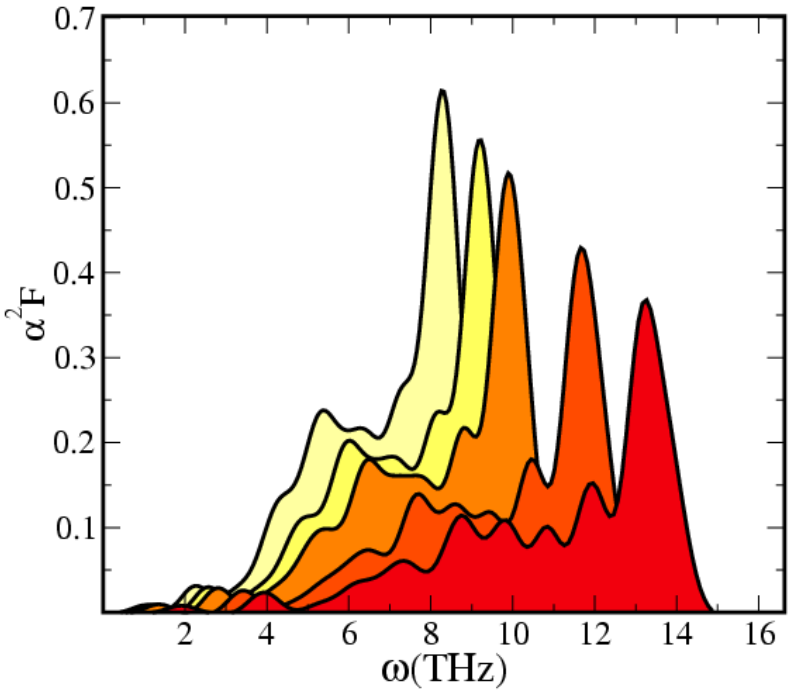


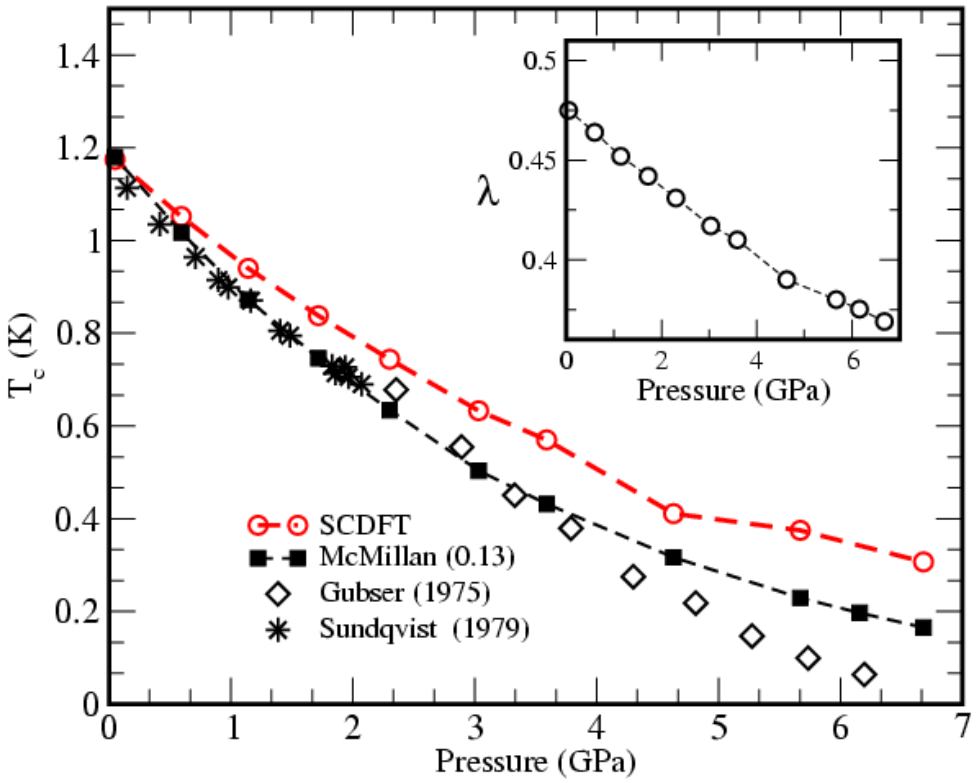
* C. Buzea and K. Robbie
Supercond. Sci. Technol. **18** (2005) R1–R8

Aluminium under pressure……



270 GPa



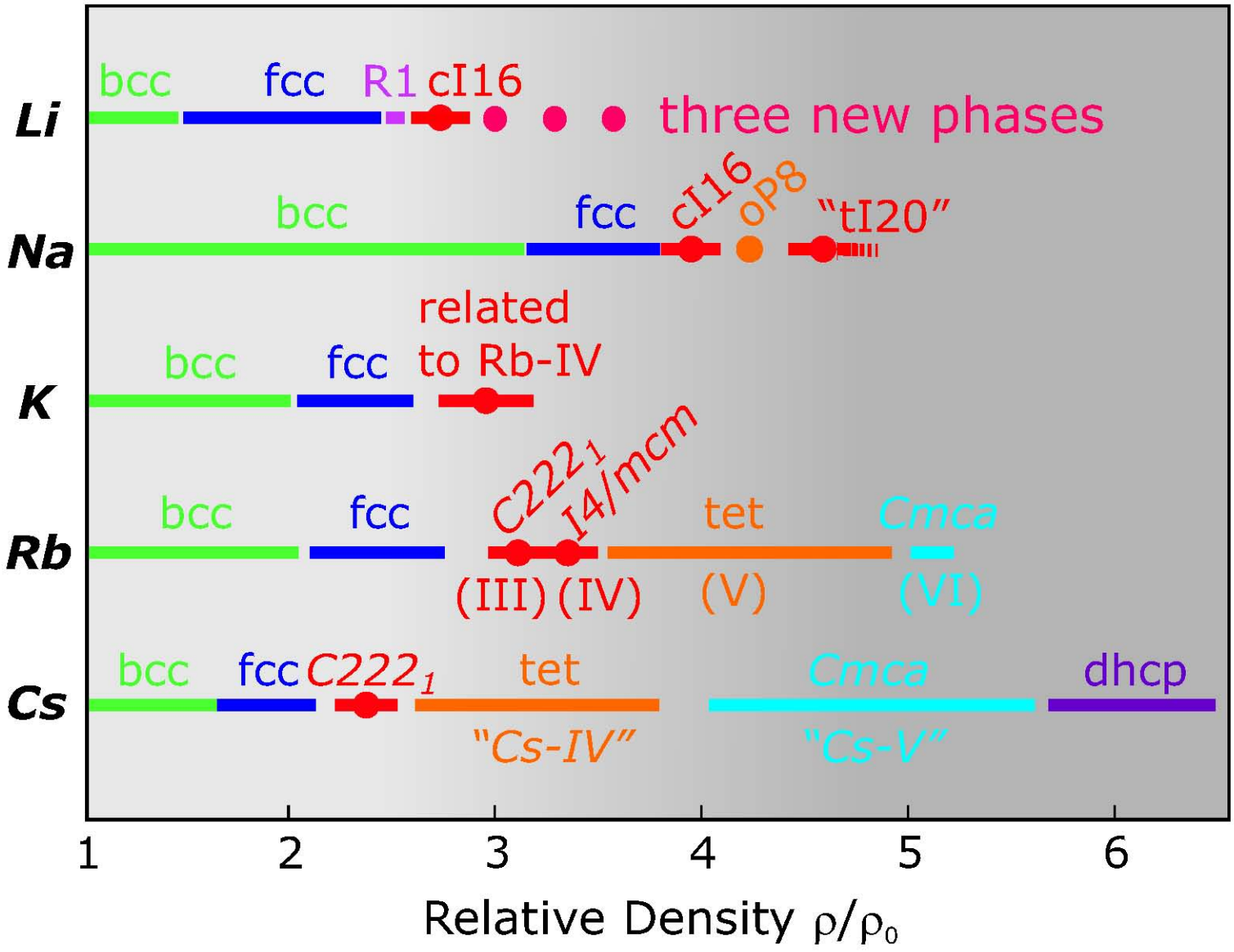


Bonds get stiffer, frequencies higer

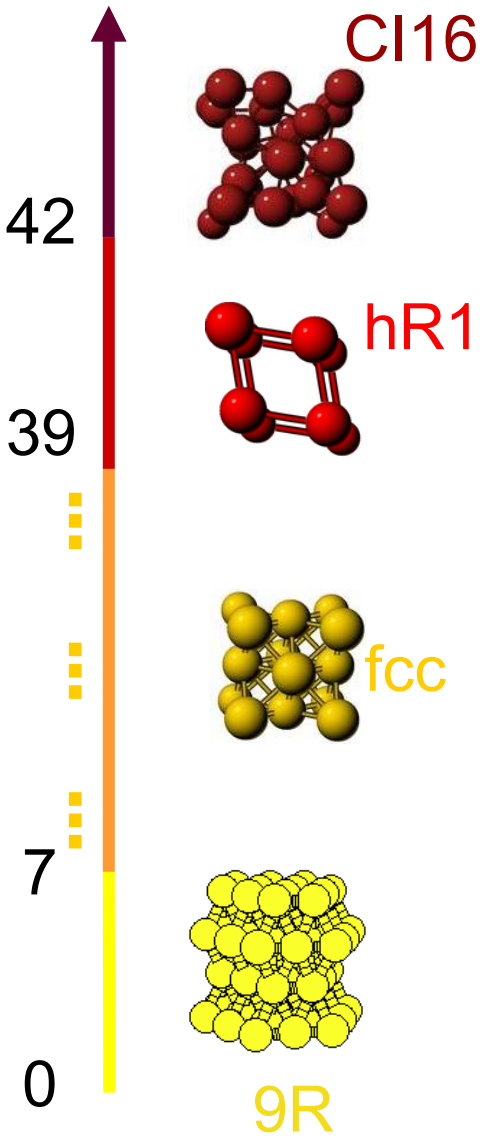
…Al becomes a normal metal

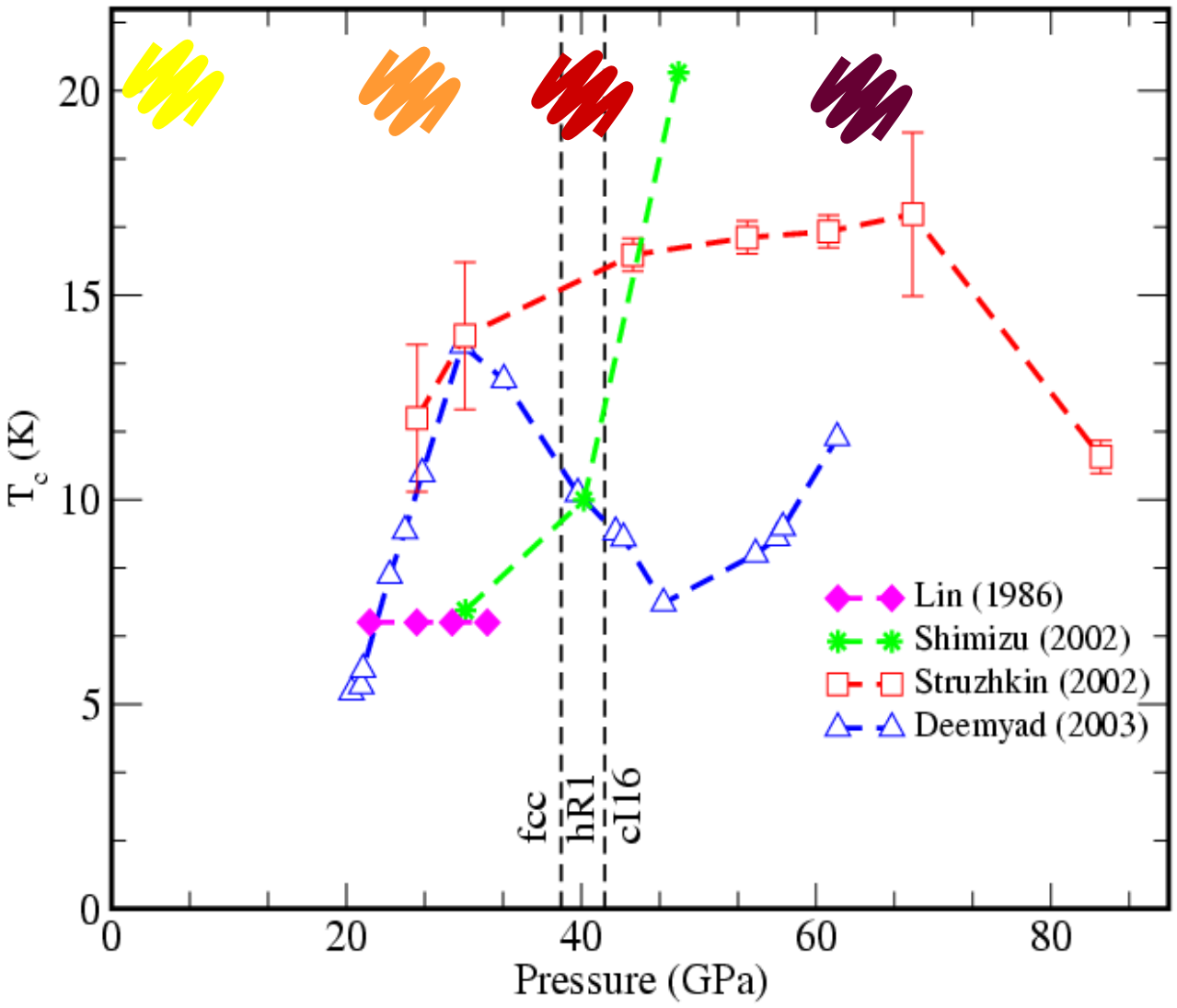
$$\lambda = \frac{N(E_F)I^2}{M\omega_{ph}^2}$$

Alkali metal under high pressure

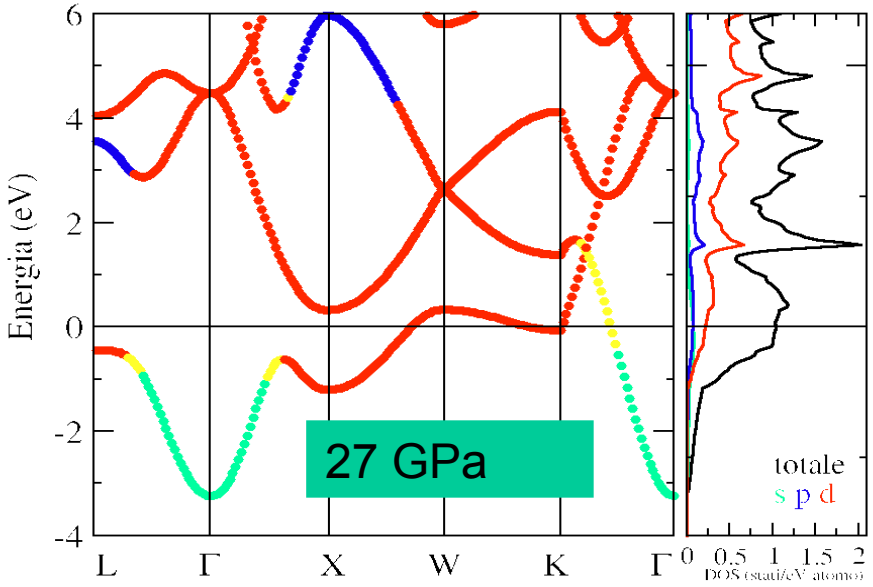


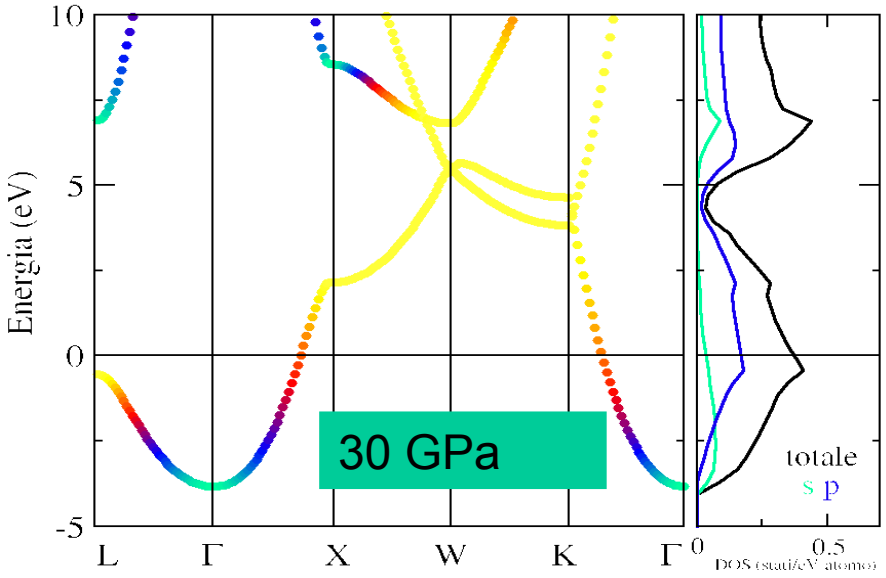
Lithium is a superconductor under pressure



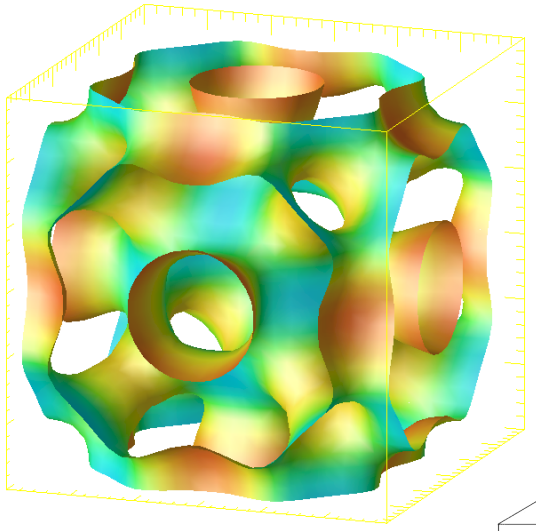


Electron states of Li and K under pressure

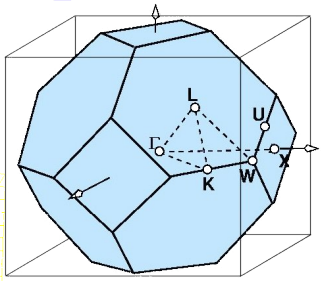




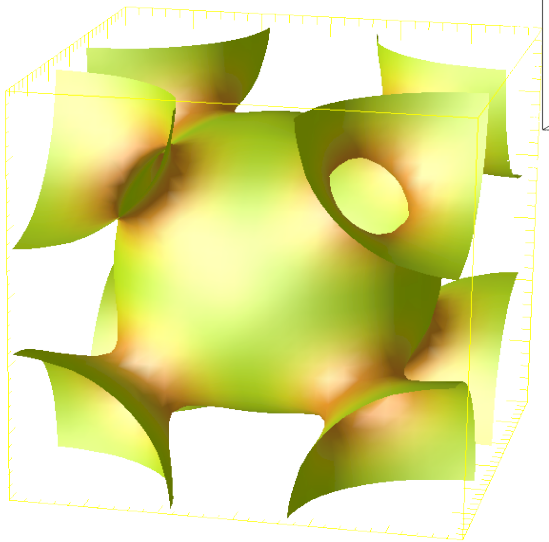
K



Charge on d states



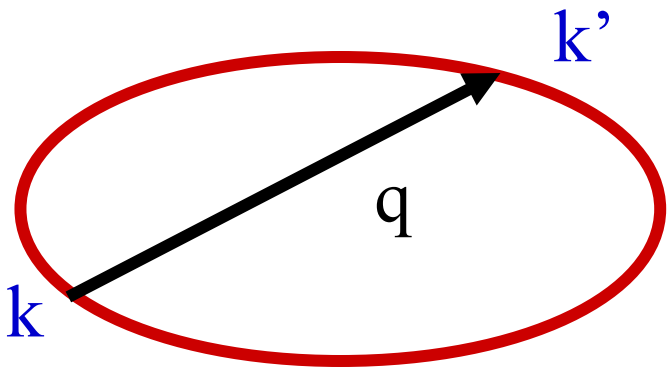
Li

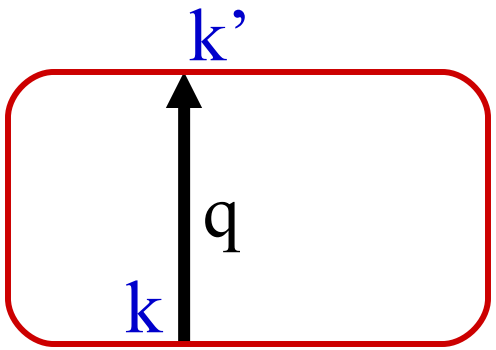


Charge on p states

Spectral Function $\alpha^2F(\omega)$

$$\alpha^2F(\omega) = \frac{1}{N(E_F)} \sum_{\mathbf{q},j} \sum_{n\mathbf{k},n'\mathbf{k}'} \left| g^{qj}_{nk,n'k'} \right|^2 \delta_{k+q,k'} \delta(\varepsilon_{nk}) \delta(\varepsilon_{n'k'}) \delta(\omega - \omega_{qj})$$

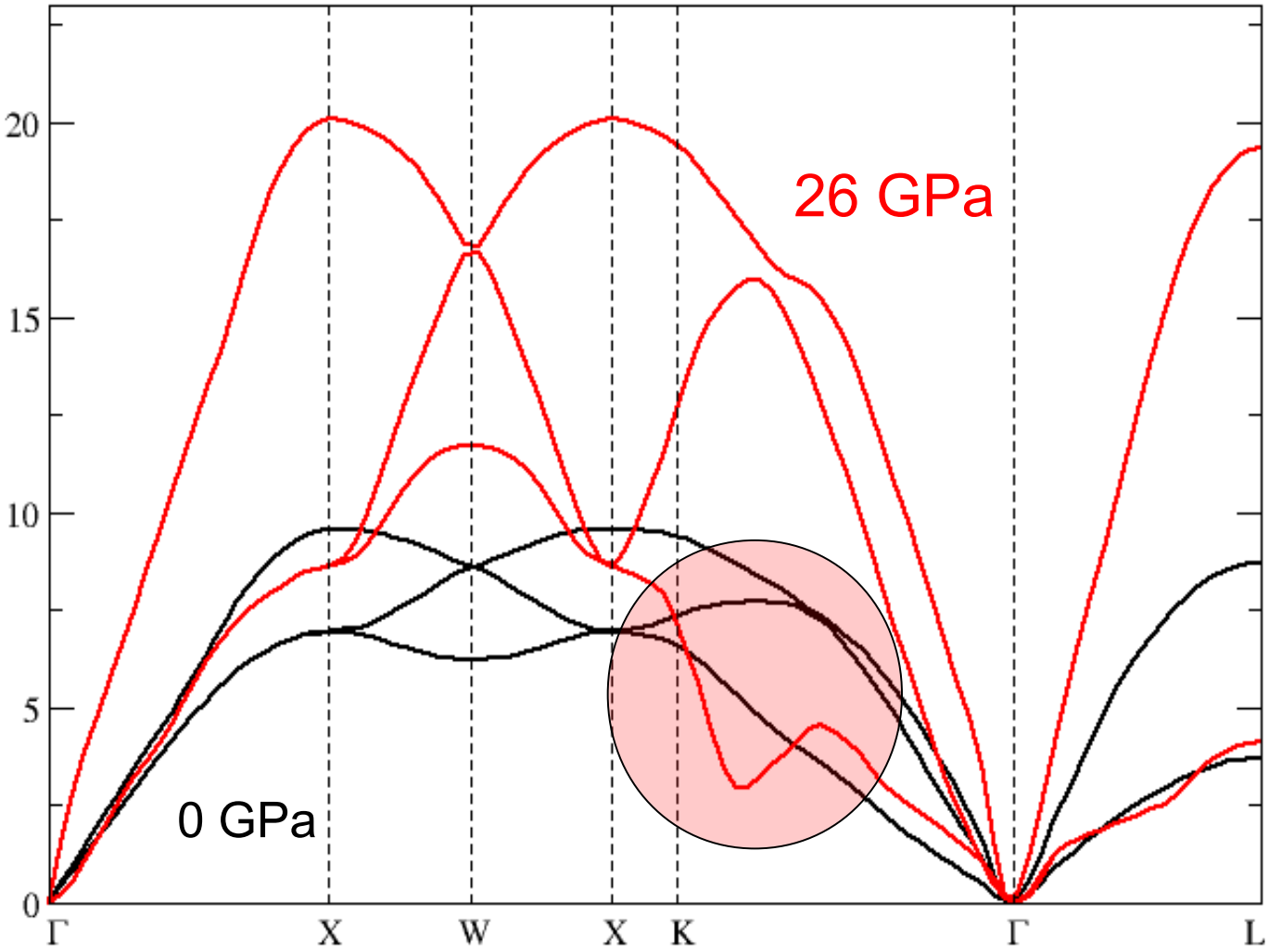




λ comes from a complex integration over the Fermi surface

parallel pieces of the Fermi surface enhance the coupling (NESTING)

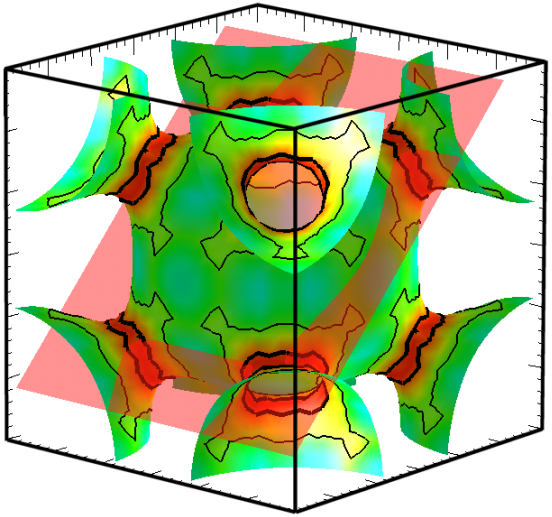
Phonon dispersion in Li: softening

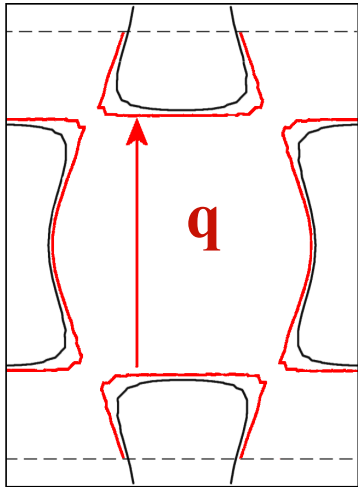


Why?

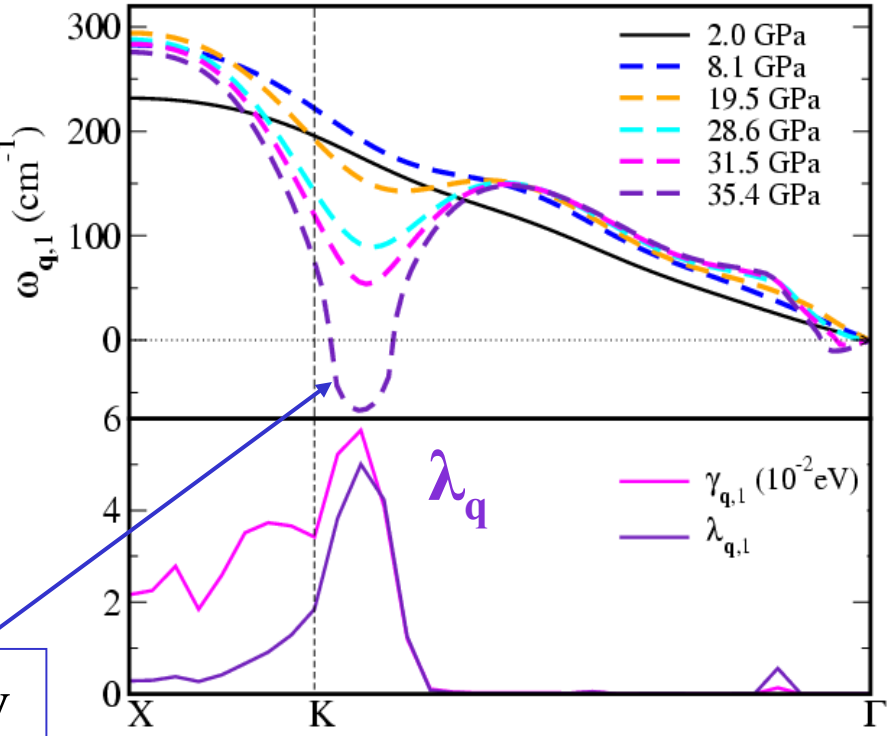
Increasing the pressure a lattice instability drive by the Fermi surface nesting increases the electron-phonon coupling

Pieces of Fermi surface connected by the same wave-vector **q**



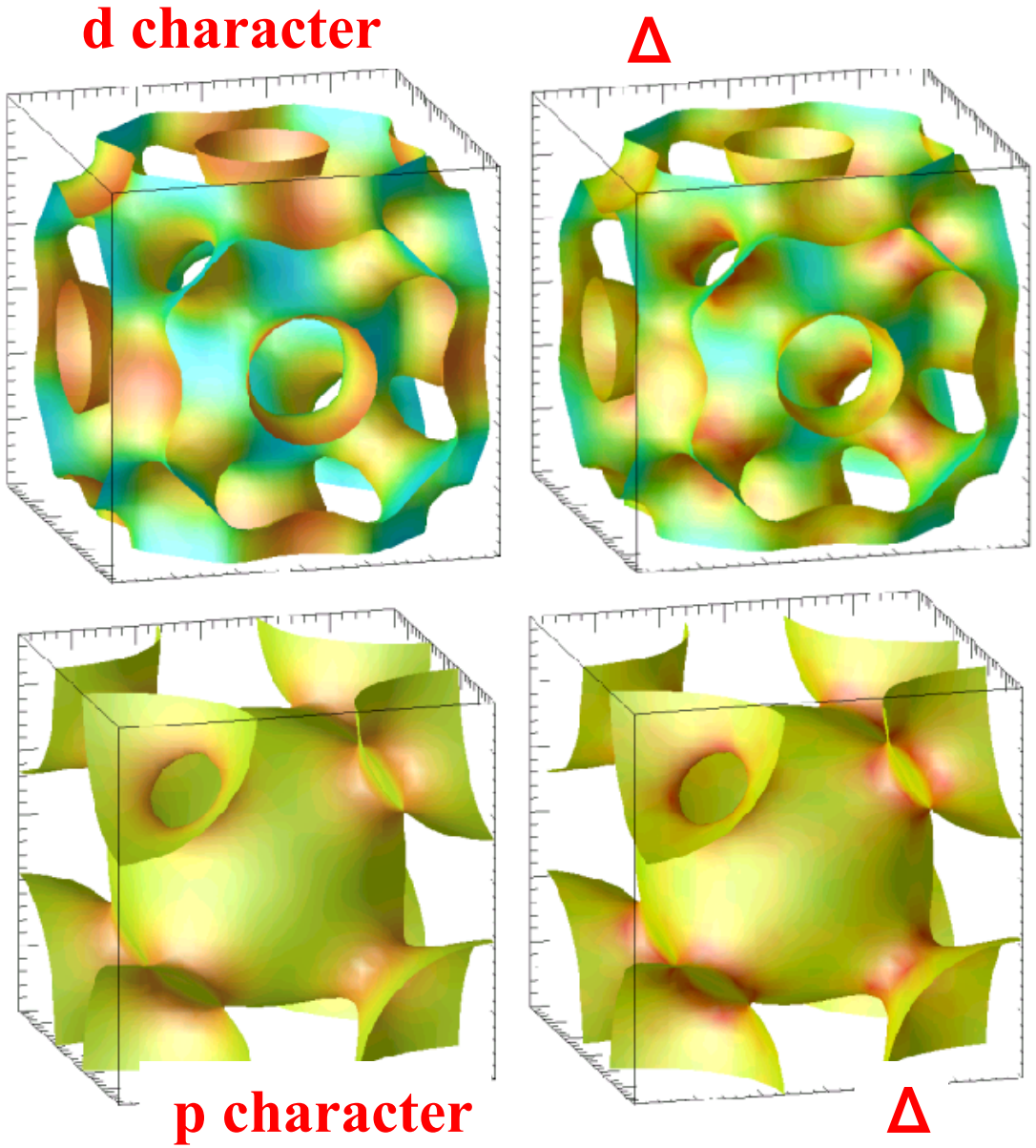


Phonon softening and lattice instability



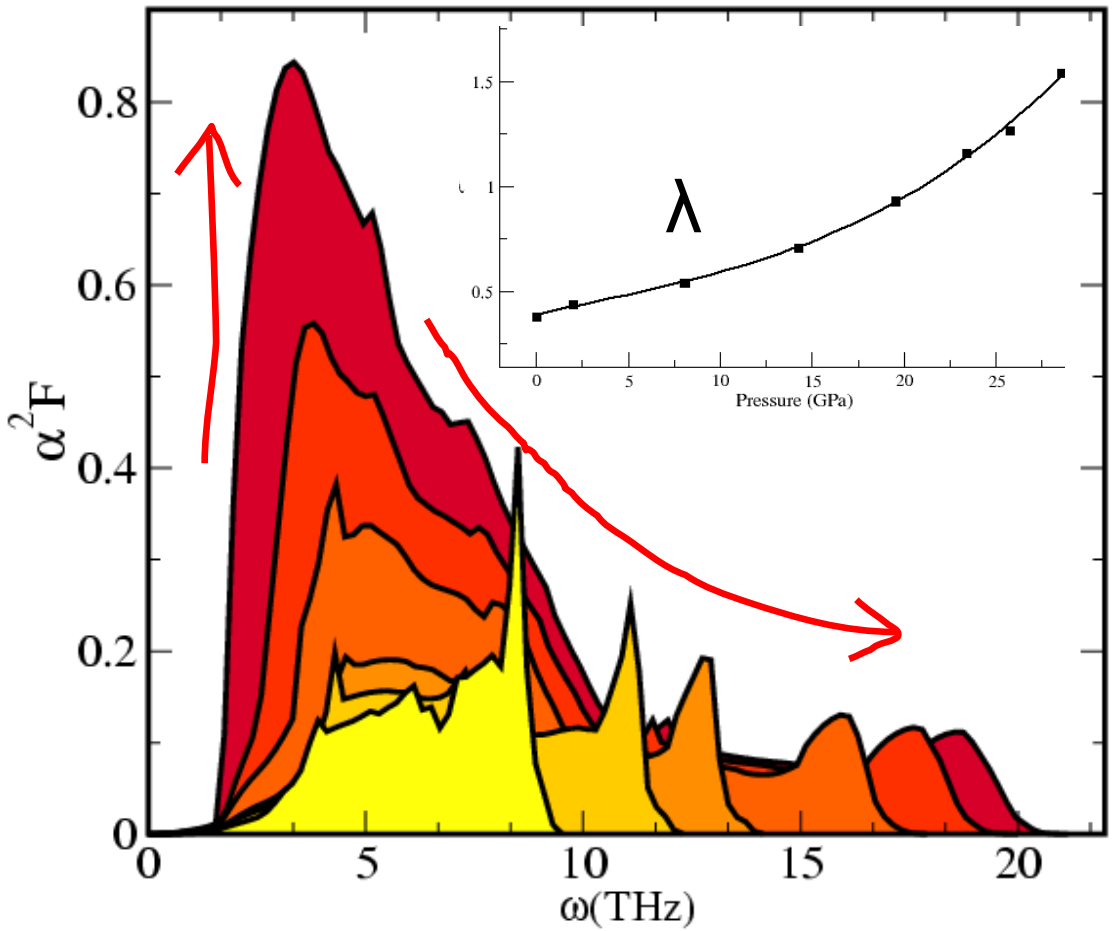
Imaginary frequency: instablility

Orbital character at E_F and superconductivity



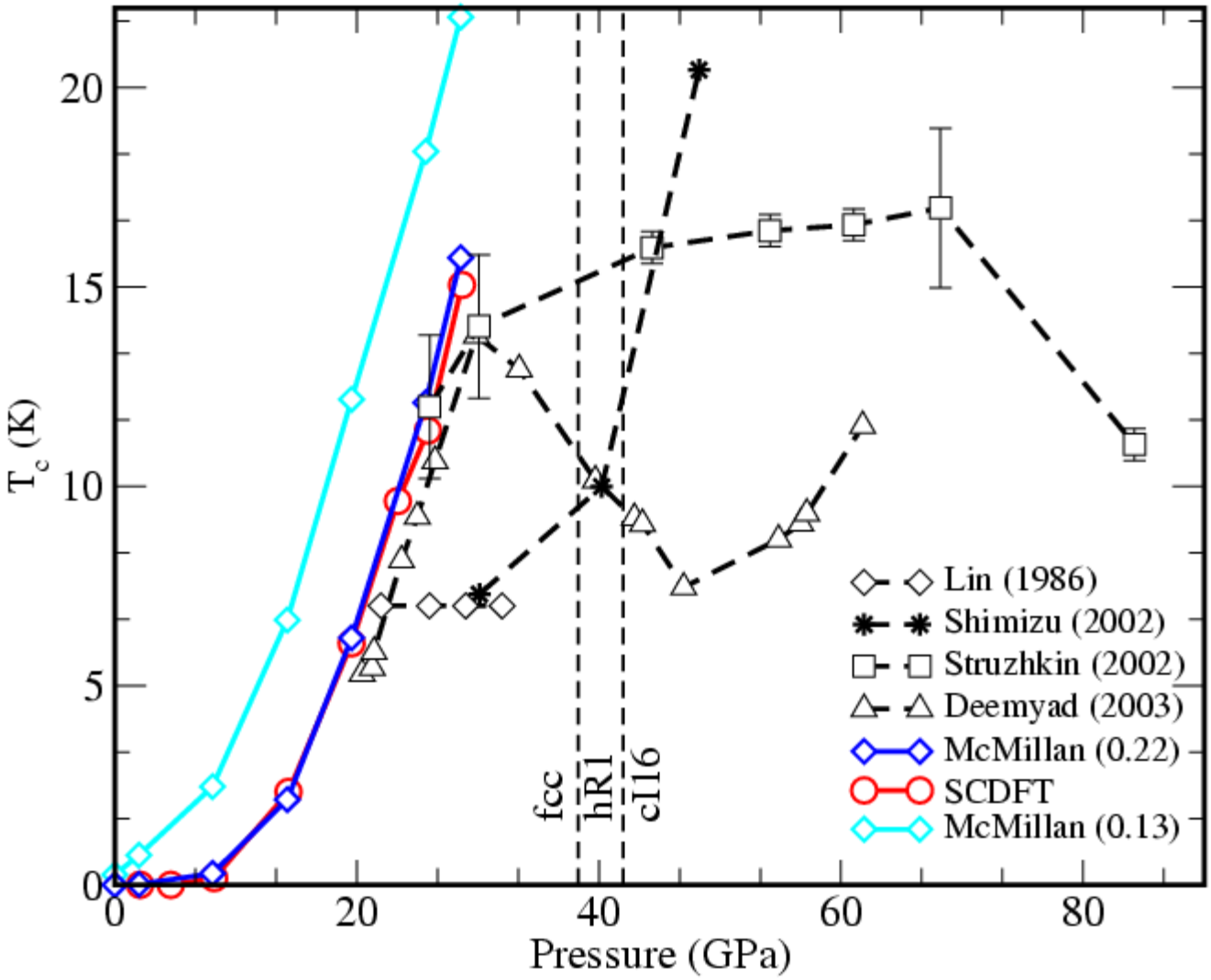
Electron-Phonon Coupling

Pressure



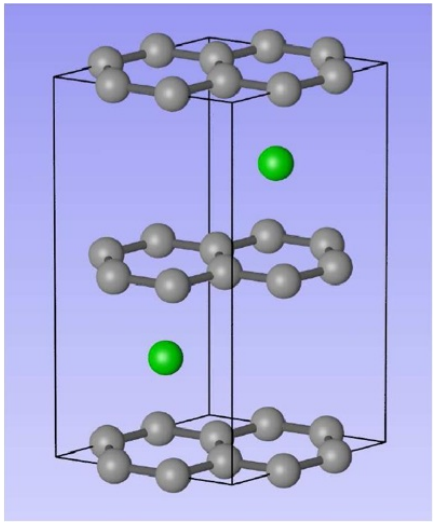
Stiffer bonds (higher ω's) but higher coupling at low ω

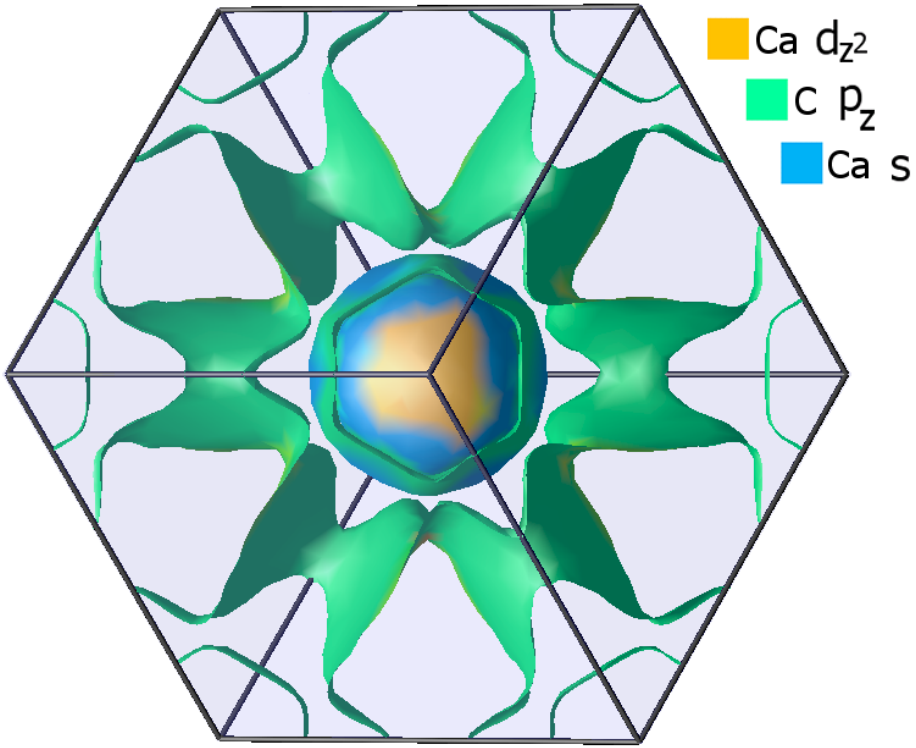
Theoretical predictions



Intercalated graphite: CaC_6 Tc=11.5 K

N. Emery *et al.* Phys. Rev Lett.
95, 087003 (2005)





Fermi surface of CaC_6

CaC_6

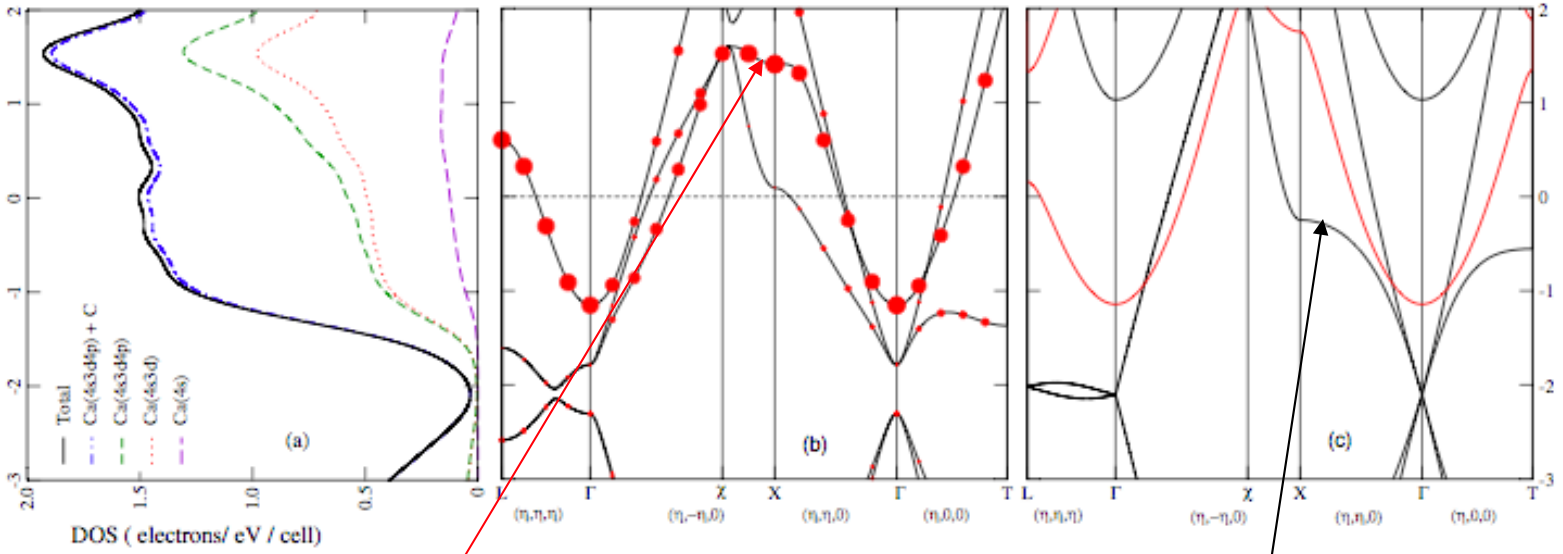
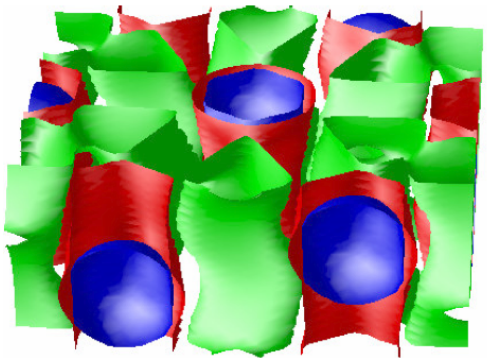


FIG. 1 (color online). (a) Total DOS and DOS projected on selected atomic wave functions in C_6Ca. (b) Band structure of C_6Ca. The size of the dots represents the percentage of Ca component. As a reference, the dot at ≈ 0.6 eV at the L point represents the 0.95 Ca component. (c) Band structure of $^*Ca$ (red) and C_6^* (black). The bands have been shifted to compare with the C_6Ca band structure. The directions are given in terms of the rhombohedral reciprocal lattice vectors. χ is the interception between the $(\eta, -\eta, 0)$ line with the border of the first Brillouin zone ($\eta = 0.3581$). The points L, Γ, X, T have $\eta = 0.5$.

Amount of Ca contribution

FS



Bands similar to graphite

Phonons in CaC_6

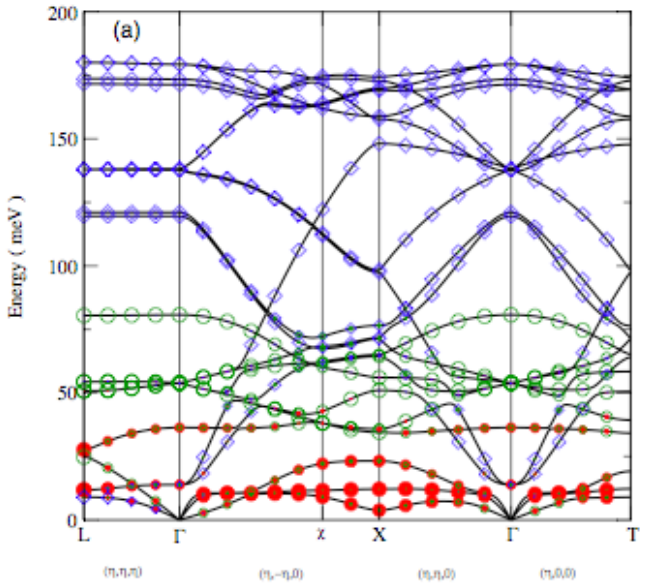


FIG. 2 (color online). (a) and (b) C_6Ca phonon dispersion. The amount of Ca vibration is indicated by the size of the ●, of C_z by the size of ○, of C_{xy} by the size of ◇, of Ca_{xy} by the size of ▲, and of Ca_z by the size of ▼.

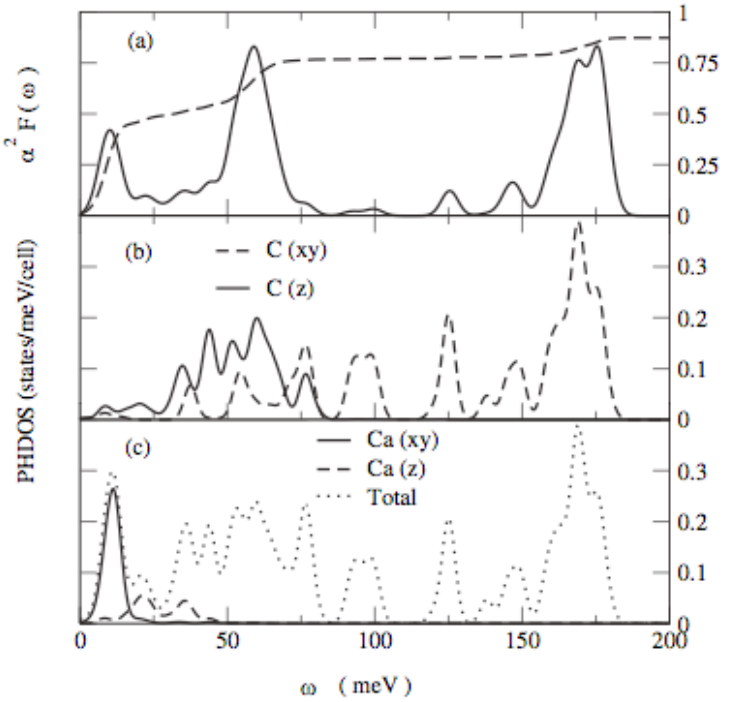
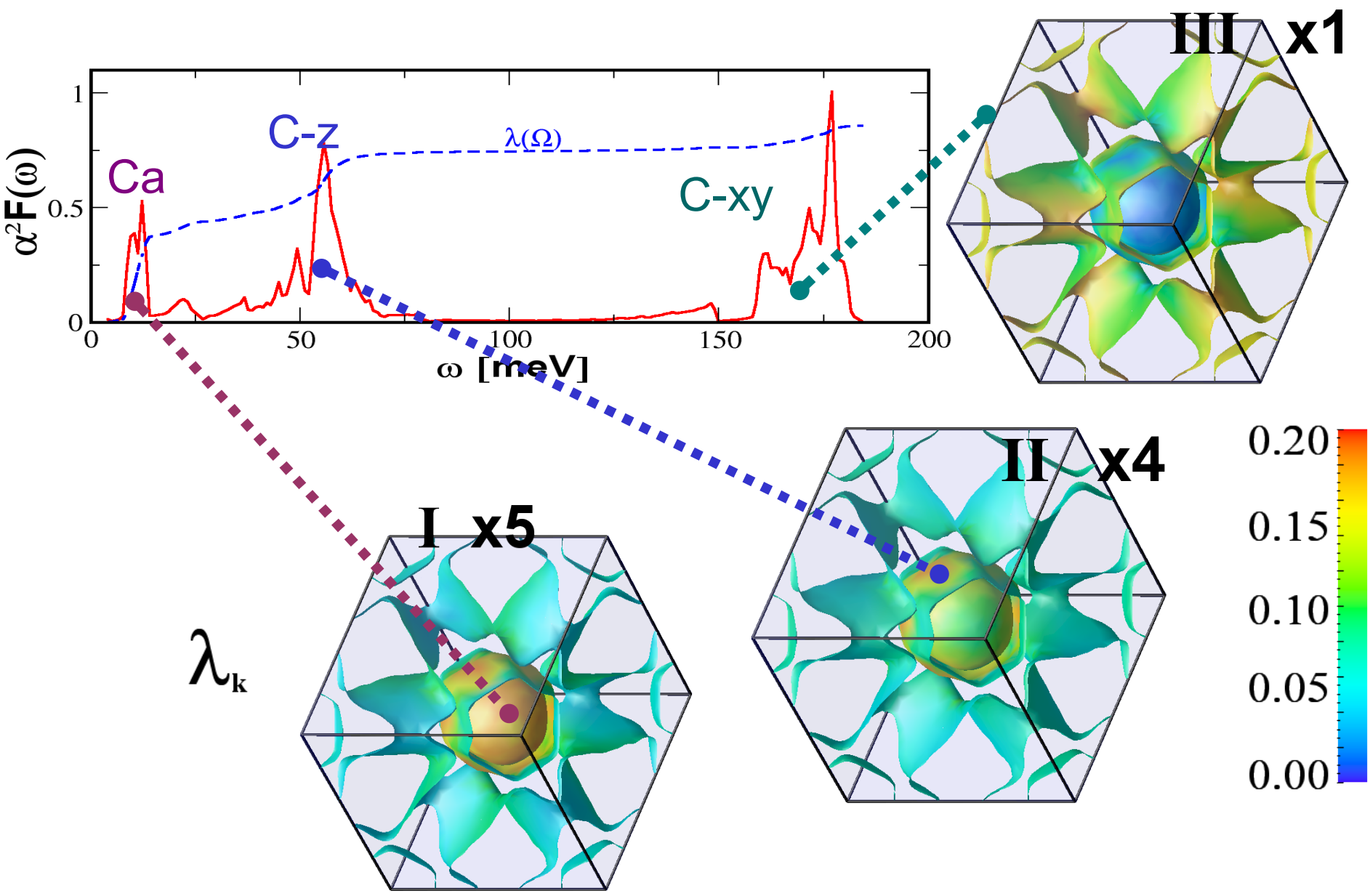


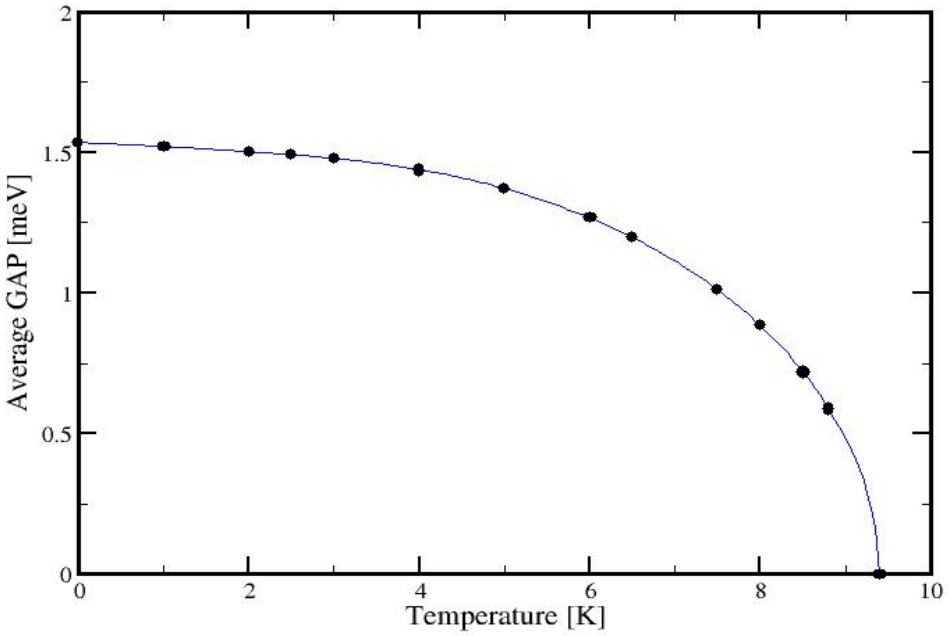
FIG. 3. (a) Eliashberg function $\alpha^2F(\omega)$ (continuous line) and integrated coupling $\lambda(\omega)$ (dashed line). (b) and (c) PHDOS projected on selected vibrations and total PHDOS.

Electron-phonon coupling



CaC_6

Calculated T_c=9.5 K Experiment T_c=11.5 K

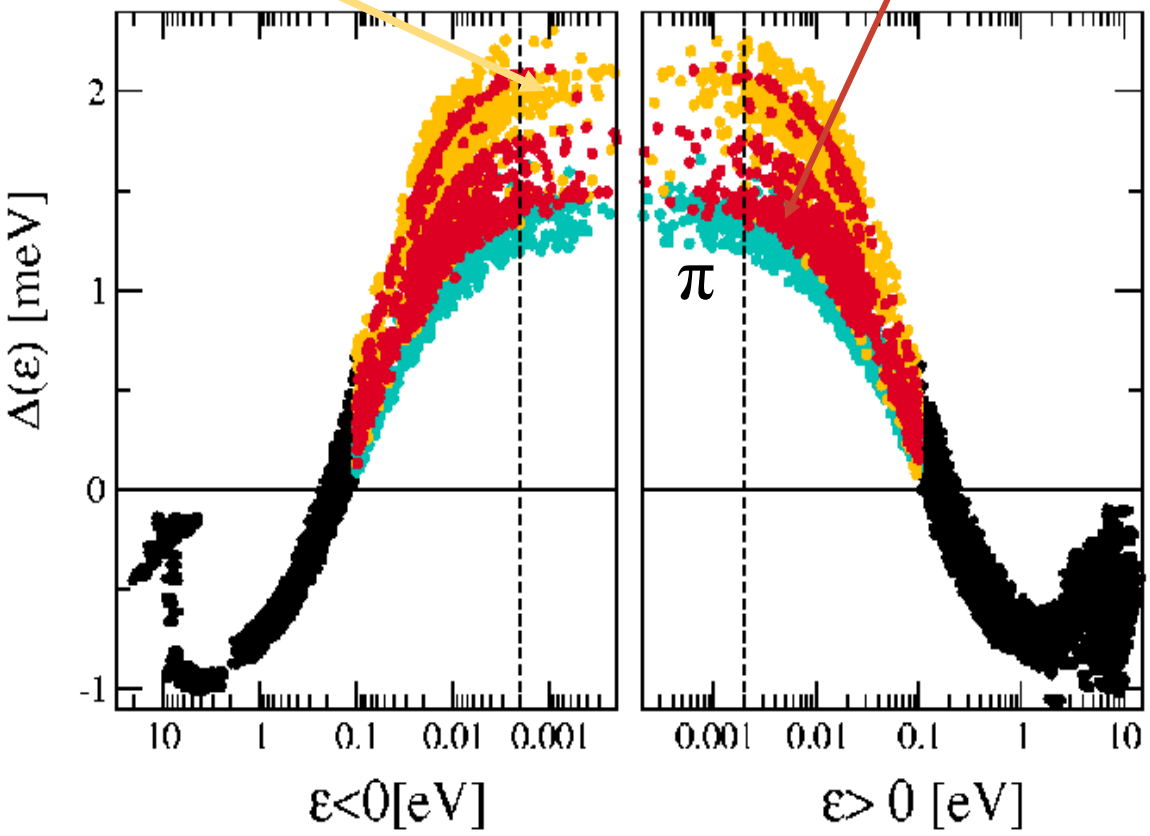


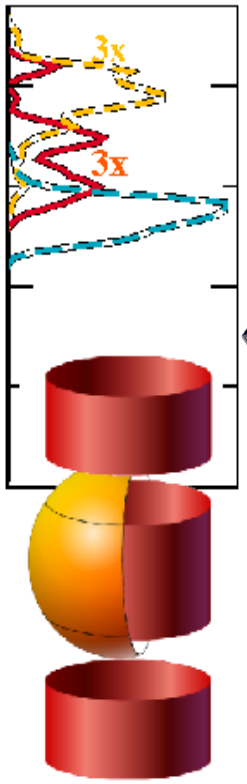
A. Sanna et al. PRB 75, 20511(R) (2007)

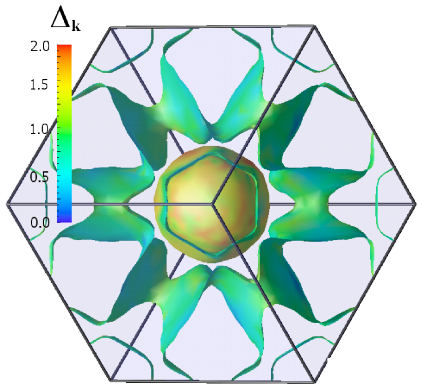
CaC_6 gap anisotropy

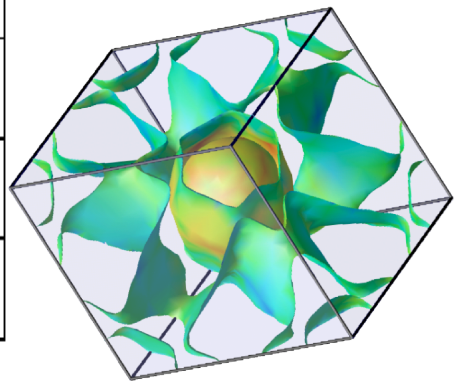
Spherical (intercalant) FS

Tubular FS









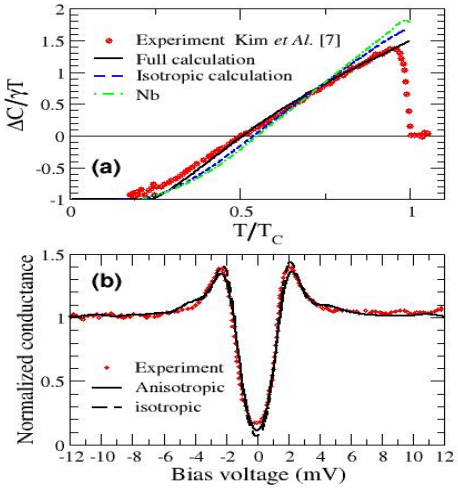
Large anisotropy but with a continuous gap distribution

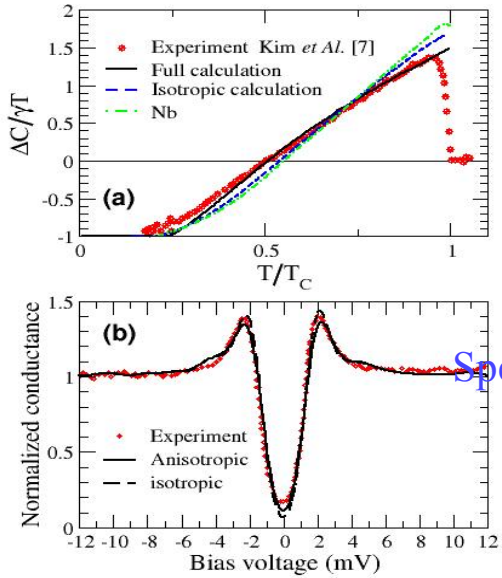
Anisotropy confirmed by experiments (tunneling)

CaC_6 comparison with experiments

STM experiments Begeal et al PRL 97, 77003 (2006) on samples with a slightly reduced T_c (accidentally very similar to ours)

Comparison with STM





Specific heat

Specific heat by Kim et al. PRL 96, 217002 (2006)

The agreement improves by considering gap anisotropy

CaC_6 comparison with experiments at 0.4 K; to be published on PRL

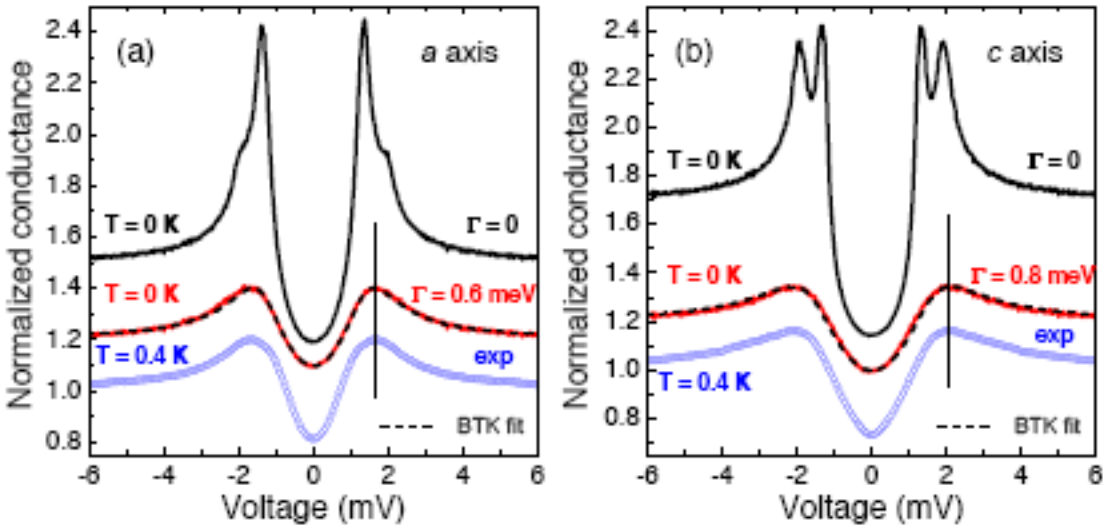
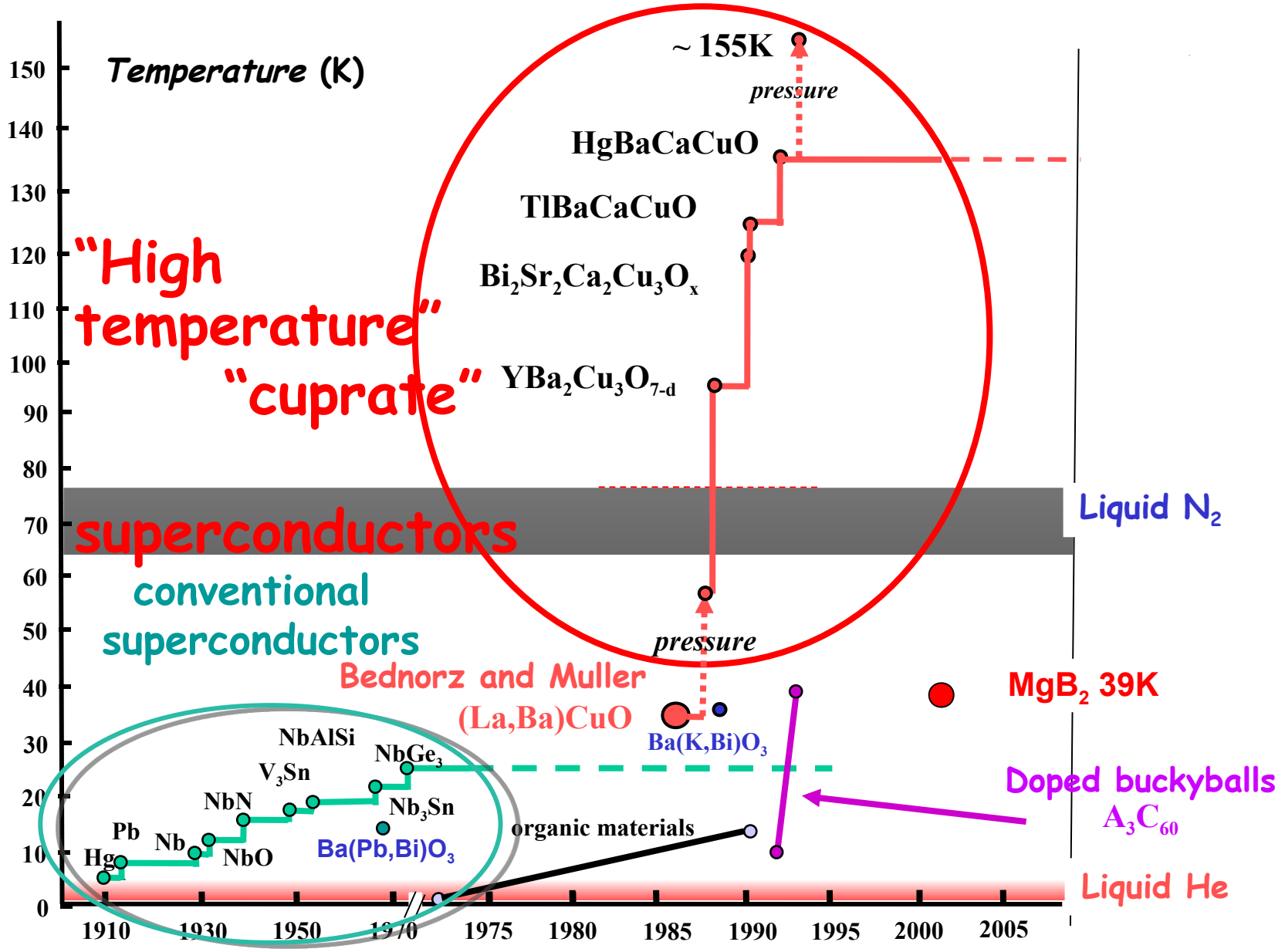


FIG. 4: (Color online) Theoretical AR conductances calculated at $T = 0$ by Eq. (1). (a) Current injected along the a axis with $Z = 0.75$ and $\Gamma = 0$ (black) and $\Gamma = 0.6$ (red); (b) current injected along the c axis with $Z = 1$ and $\Gamma = 0$ (black) and $\Gamma = 0.8$ (red). Experimental curves at 400 mK are shown for comparison (blue circles).

non conventional superconductivity : cuprates, pnictides



Summary

- I gave a brief description of BCS theory of superconductivity

- I tried to give an essential overview of the state of the art in electronic structure calculations

- I presented an essential description of the properties and SC mechanisms in a few important materials

- Each real material has plenty of interesting physics