How to predict the critical temperature of superconductors: An ab-initio perspective

E. K. U. Gross

Max Planck Institute of Microstructure Physics, Halle

CO-WORKERS:

HALLE

A. Sanna
C. Bersier
F. Essenberger
A. Linscheid
H. Glawe
A. Floris
S. Kurth
N. Lathiotakis
M. Lüders
M. Marques

CAGLIARI

S. Massidda
C. Franchini

L'AQUILA

A. Continenza
G. Profeta
P. Cudazzo

Outline

1. What do we want to describe?

2. Warm-up exercise: Density functional theory of magnetism

3. Density functional theory for superconductors

4. Results for
   - simple metals
   - MgB_2
   - Li, K, Al under pressure
   - Pb revisited
   - CaC_6
   - H under extreme pressure

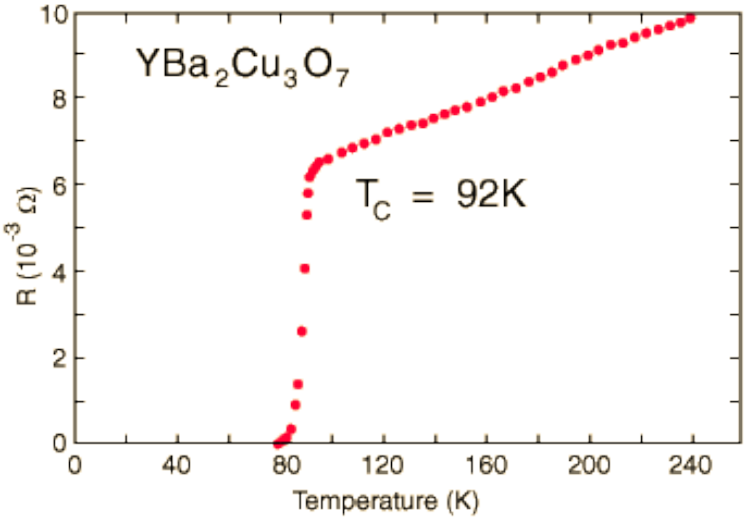
5. The superconducting order parameter in real space

6. Towards the description of pnictide superconductors

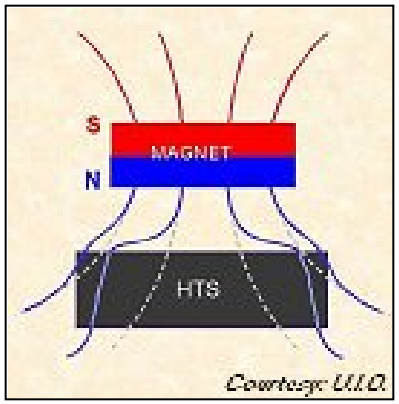
What do we want to describe: Phenomenology of the superconducting phase

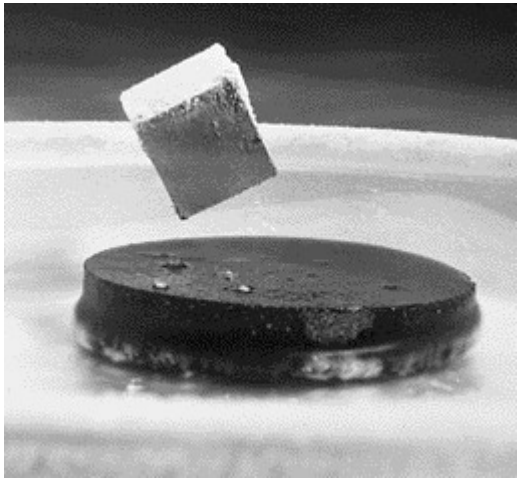
Two essential properties

- Resistance drops to zero at T_c



- Meissner-Ochsenfeld-Effect

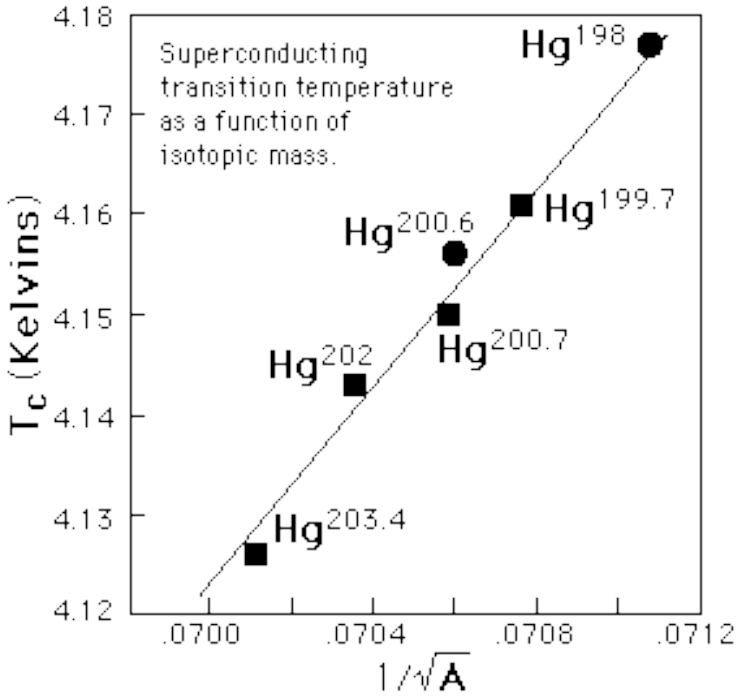




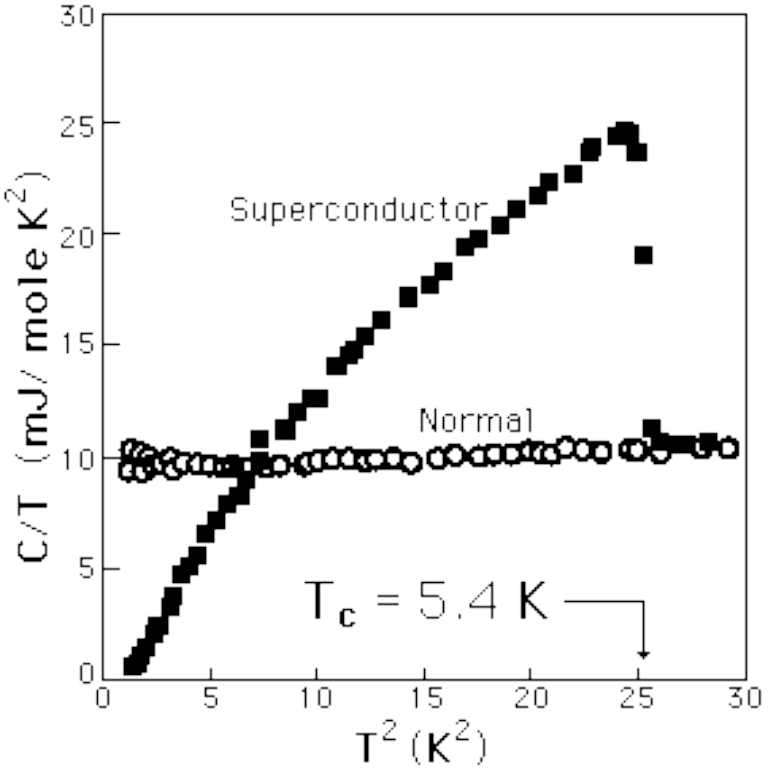
Secondary features

- Isotope effect

$$T_c \propto 1/\sqrt{A}$$

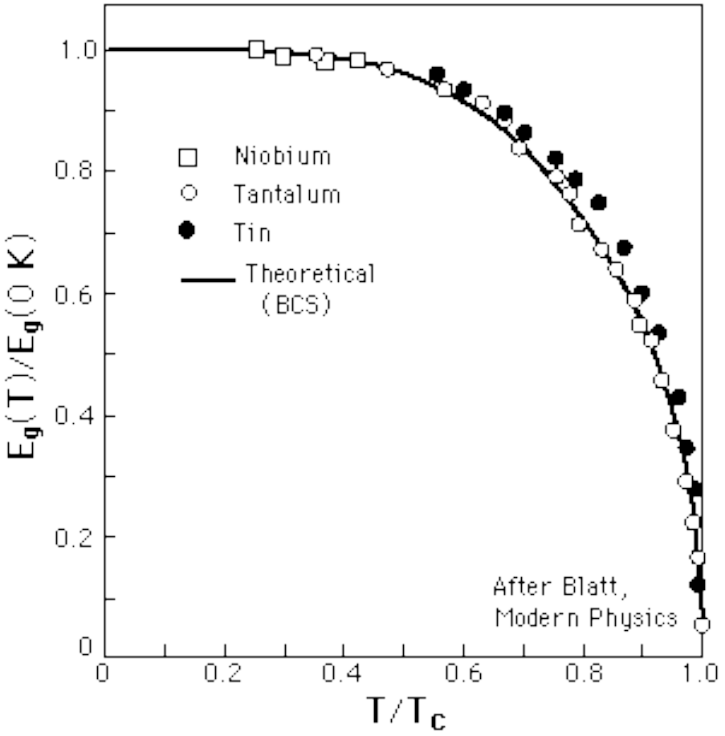


- Specific heat

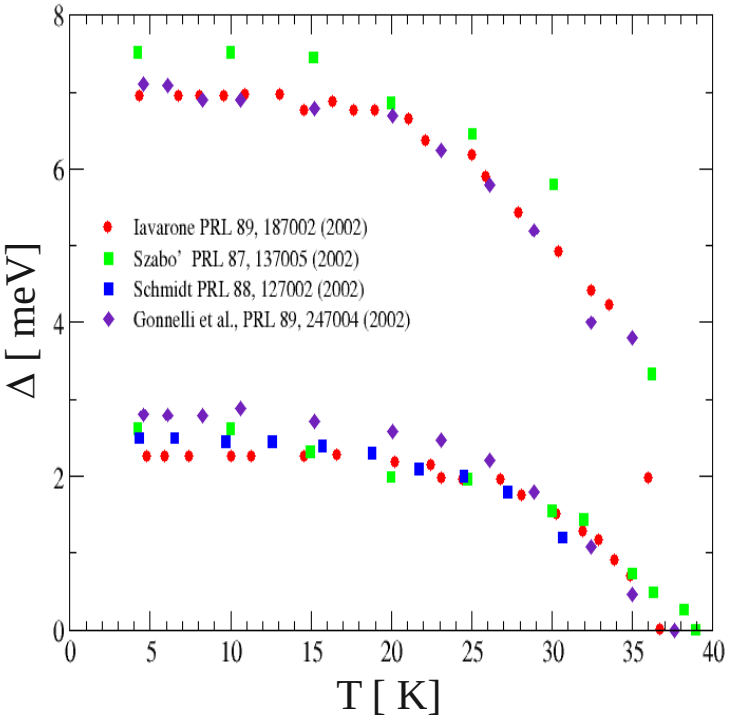


Secondary features

- Energy gap in excitation spectrum



MgB_2



Standard theory: Bardeen – Cooper – Schrieffer (BCS)

For inhomogeneous superconductors, BCS takes the form of the Bogoliubov- de Gennes equations:

$$\left(-\frac{\hbar^2\nabla^2}{2m}+v_{eff}(r)-\mu\right)u_k(r)+\int\Delta_{eff}(r,r')v_{eff}(r')d^3r'=\varepsilon_k u_k(r)$$

$$\int\Delta^*_{eff}(r,r')u_k(r')d^3r'-\left(-\frac{\hbar^2\nabla^2}{2m}+v_{eff}(r)-\mu\right)v_k(r)=\varepsilon_k v_k(r)$$

short-hand:

$$\begin{pmatrix}[\hat{h}_{eff}-\mu] & \hat{\Delta}_{eff}\\ \hat{\Delta}^+_{eff} & -[\hat{h}_{eff}-\mu]\end{pmatrix}\begin{pmatrix}u_k\\ v_k\end{pmatrix}=\varepsilon_k\begin{pmatrix}u_k\\ v_k\end{pmatrix}$$

Mean fields

$$v_{eff}(r) = v_{lattice}(r) + \int \frac{e^2}{|r - r'|} \rho(r') d^3 r'$$

Coulomb interaction

density

$$\rho(r) = \sum_{\sigma=\uparrow\downarrow} \left\langle \hat{\psi}^{+}_{\sigma}(r) \hat{\psi}_{\sigma}(r) \right\rangle$$

$$\Delta_{eff}(r_1, r_2) = \int W_{model}(r_1, r_2, r_1', r_2') \chi(r_1', r_2') d^3 r' d^3 r_2'$$

BCS model interaction (from Fröhlich)

order parameter
"anomalous density"

$$\chi(r_1, r_2) = \left\langle \psi_{\uparrow}(r_1) \psi_{\downarrow}(r_2) \right\rangle$$

General (model-independent) characterization of superconductors:
Off-diagonal long-range order of the 2-body density matrix:

$$\rho^{(2)}(xx', yy') = \left\langle \hat{\psi}^{+}_{\downarrow}(x')\hat{\psi}^{+}_{\uparrow}(x)\hat{\psi}_{\uparrow}(y)\hat{\psi}_{\downarrow}(y') \right\rangle$$

$$\xrightarrow[|X-Y|\to\infty]{} \underbrace{\left\langle \hat{\psi}^{+}_{\downarrow}(x')\hat{\psi}^{+}_{\uparrow}(x) \right\rangle}_{\chi^{*}(x,x')} \cdot \underbrace{\left\langle \hat{\psi}_{\uparrow}(y)\hat{\psi}_{\downarrow}(y') \right\rangle}_{\chi(y,y')}$$

$$X = \frac{x+x'}{2} \qquad Y = \frac{y+y'}{2}$$

$$\chi\ (r, r') = \left\langle \hat{\psi}_{\uparrow}(r)\hat{\psi}_{\downarrow}(r') \right\rangle$$

order parameter of the N-S phase transition

BCS theory describes the universal features that all (weakly coupled phonon-driven) superconductors have in common, e.g. universal ratio $\Delta_o / (k_B T_c)$.

BCS theory is not able to make predictions of material-specific properties such as T_c .

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Eliashberg theory includes phonon degrees of freedom perfectly through $\alpha^2 F(\omega)$.

Electron-electron interaction not treated on same footing: Adjustable parameter μ^*.

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Quotations:

"If I want to know T_c of a superconducting material I ask my experimental colleague next door to measure it." (M. Fisher)

"In any known theory of superconductivity, T_c is the first fudge factor entering the theory" (D. Rainer)

DENSITY-FUNTIONAL THEORY OF THE NORMAL-CONDUCTING STATE

ESSENCE OF DENSITY-FUNTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE (Hohenberg, Kohn, 1964).**

- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965).**

Kohn-Sham Theorem (1965)

The ground state density of the interacting system of interest can be calculated as ground state density of non-interacting particles moving in an effective potential $v_s(r)$:

$$\left(-\frac{\hbar^2\nabla^2}{2m} + v_s[\rho](r)\right)\varphi_i(r) = \varepsilon_i\varphi_i(r) \qquad \rho(r) = \sum_{\text{N lowest } \varepsilon_j} |\varphi_j(r)|^2$$

$$v_s[\rho](r) = v_0(r) + \int \frac{\rho(r')}{|r-r'|}\, d^3r' + v_{xc}[\rho](r)$$

Coulomb potential of nuclei

Hartree potential

exchange-correlation potential

W. Kohn: KS potential is "exactification" of Hartree MF

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$$

universal

DENSITY-FUNTIONAL THEORY OF MAGNETIC SYSTEMS

Quantity of interest: Spin magnetization m(r)

In principle, Hohenberg-Kohn theorem guarantees that m(r) is a functional of the density: $m(r) = m[\rho](r)$. In practice, $m[\rho]$ is not known.

Include m(r) as basic variable in the formalism, in addition to the density ρ(r).

DFT for spin-polarized systems

$$\hat{H}_{v,\vec{B}} = \hat{T} + \hat{W} + \int \hat{\rho}(r) v(r) d^3r - \int \hat{\vec{m}}(r) \cdot \vec{B}(r) d^3r$$

KS scheme

$$\left(-\frac{\nabla^2}{2m} + [v(\mathbf{r}) + v_H(\mathbf{r}) + \mathbf{v_{xc}(r)}] - \mu_o \sigma \cdot [B(\mathbf{r}) - \mathbf{B_{xc}(r)}] \right) \varphi_j(\mathbf{r}) = \in_j \varphi_j(\mathbf{r})$$

$B \longrightarrow 0$ limit

These equations do not reduce to the original KS equations for $B \to 0$ if, in this limit, the system has a finite m(r).

3 generations of approximations for E_{xc}

1. Local Density Approximation (LDA):

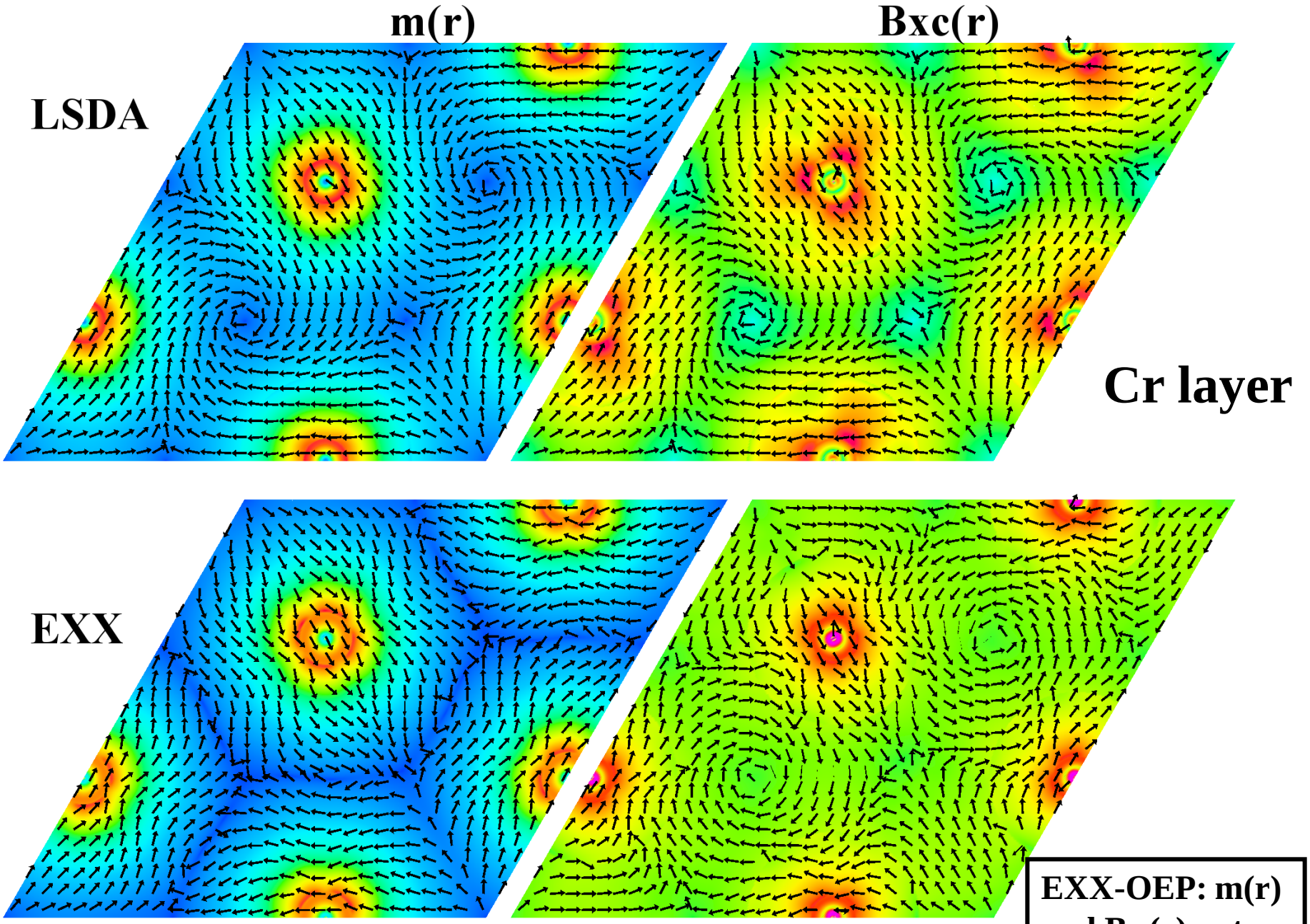
$$E_{xc}[\rho] = \int d^3r\, e_{xc}^{hom}(\rho(r), m(r))$$

2. Generalized Gradient Approximation (GGA):

$$E_{xc}[\rho] = \int d^3r\, g_{xc}(\rho, m, \nabla\rho, \nabla m \ldots)$$

3. Orbital functionals (exact exchange, hybrids, meta-GGAs)

$$E_{xc}[\rho] = E_{xc}[\varphi_1 \ldots \varphi_N]$$



S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, S. Kurth, N. Helbig, S. Pittalis, S. Shallcross, L. Nordstroem E.K.U.G., Phys. Rev. Lett. 98, 196405 (2007)

EXX-OEP: m(r) and $B_{xc}(r)$ not locally collinear

DENSITY-FUNTIONAL THEORY OF THE SUPERCONDUCTING STATE

BASIC IDEA:

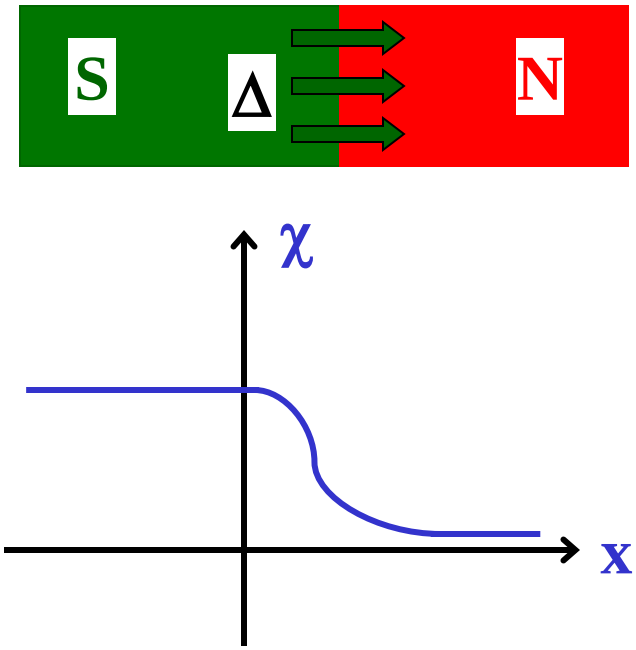
- **Include order parameter, χ , characterising superconductivity as additional "density"**
  L.N. Oliveira, E.K.U.G., W. Kohn, PRL **60**, 2430 (1988)

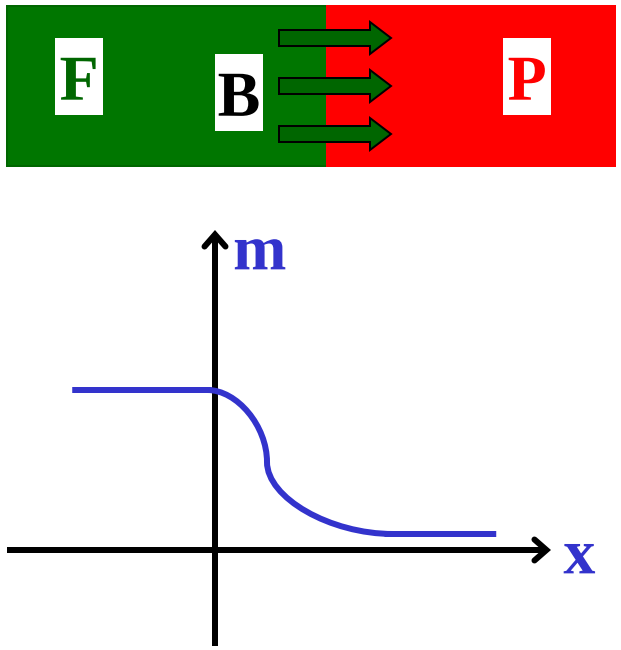
- **Include N-body density matrix, Γ, of the nuclei as additional "density"**
  T. Kreibich, E.K.U.G., PRL **86**, 2984 (2001)

Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho}(r)\, v(\mathbf{r})\, d^3r - \int d^3r \int d^3r' \left(\hat{\chi}(r, r')\, \Delta^*(r, r') + \text{H.c.} \right)$$

ANALOGY





“proximity effect”

Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho}(r)\, v(\mathbf{r})\, d^3r - \int d^3r \int d^3r' \left(\hat{\chi}(r, r')\, \Delta^*(r, r') + \text{H.c.} \right)$$

Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho}(r)\, v(\mathbf{r})\, d^3r - \int d^3r \int d^3r' \left(\hat{\chi}(r,r')\, \Delta^*(r,r') + \text{H.c.} \right)$$

$$\hat{H}_n = \hat{T}_n + \int d^{N_n} R\, \hat{\Gamma}(\underline{\underline{R}}) W(\underline{\underline{R}})$$

$$\hat{H} = \hat{H}_e + \hat{H}_n + \hat{U}_{en}$$

3 densities:

$$\rho(r) = \left\langle \sum_{\sigma=\uparrow\downarrow} \hat{\psi}^+_\sigma(r) \hat{\psi}_\sigma(r) \right\rangle$$ electron density

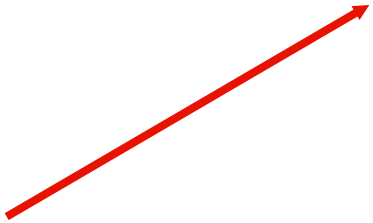
$$\chi(r,r') = \left\langle \hat{\psi}_\uparrow(r) \hat{\psi}_\downarrow(r') \right\rangle$$ order parameter

$$\Gamma(\underline{\underline{R}}) = \left\langle \hat{\phi}^+(R_1) \hat{\phi}^+(R_2) \cdots \hat{\phi}(R_1) \hat{\phi}(R_2) \cdots \right\rangle$$

diagonal of nuclear N_n-body density matrix

Hohenberg-Kohn theorem for superconductors

$$[v(r),\Delta(r,r'),W(\underline{\underline{R}})] \xleftrightarrow{\text{1-1}} [\rho(r),\chi(r,r'),\Gamma(\underline{\underline{R}})]$$



Densities in thermal equilibrium at finite temperature

Electronic KS equation

$$\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](r)\right)u(\boldsymbol{r})+\int \Delta_s[\rho,\chi,\Gamma](r,r')\,v(\boldsymbol{r}')d^3\boldsymbol{r}'=Eu(\boldsymbol{r})$$

$$\int \Delta_s{}^*[\rho,\chi,\Gamma](\mathbf{r},\mathbf{r}')\,u(\boldsymbol{r}')d^3\boldsymbol{r}'-\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](\mathbf{r})\right)v(\boldsymbol{r})=Ev(\boldsymbol{r})$$

Nuclear KS equation

$$\left(\sum_{\alpha=1}^{N_n}-\frac{\nabla_\alpha^2}{2M_\alpha}+W_s[\rho,\chi,\Gamma](\underline{\underline{R}})\right)\psi(\underline{\underline{R}})=E\psi(\underline{\underline{R}})$$

3 KS potentials: v_s Δ_s W_s

No approximation yet!

"Exactification" of BdG mean-field eqs.

KS theorem: There exist functionals $v_s[\rho,\chi,\Gamma]$, $\Delta_s[\rho,\chi,\Gamma]$, $W_s[\rho,\chi,\Gamma]$, such that the above equations reproduce the exact densities of the interacting system

In a solid, the ions remain close to their equilibrium positions:

$$W_s\left(\underline{\underline{R}}\right) = W_s\left(\underline{\underline{R}}_0 + \underline{\underline{U}}\right)$$

$$= W_s\left(\underline{\underline{R}}_0\right) + \underbrace{\left(\underline{\underline{\nabla}}\, W_s\right)\Big|_{\underline{\underline{R}}_0} \cdot \underline{\underline{U}}}_{0}$$

0 (because forces vanish at equilibrium positions)

$$+ \frac{1}{2}\sum_{ij}^{3}\sum_{\mu\nu}^{N_n}\left(\partial_i^{\mu}\partial_j^{\nu} W_s(\underline{\underline{R}})\right)\Big|_{\underline{\underline{R}}_o} U_i^{\mu} U_j^{\nu} + \cdots$$

$$\Rightarrow \quad \hat{H}_{n,KS} = \cdots = \sum_q \Omega_q \hat{b}_q^{+}\hat{b}_q + O\left(U^3\right)$$

$$v_s = v_{ext} + v_{en}^H + v_{ee}^H + v_{xc}$$
$$= o - Z\int d^3R \frac{N(R)}{|r-R|} + \int d^3r' \frac{\rho(r')}{|r-r'|} + \frac{\delta F_{xc}}{\delta \rho(r)}$$

$$\Delta_s = \Delta_{ext} + \Delta^H + \Delta_{xc}$$
$$= o + \frac{\chi(r,r')}{|r-r'|} + \frac{\delta F_{xc}}{\delta \chi^*(r,r')}$$

$$W_s = W_{ext} + W_{nn} + W_{en}^H + W_{xc}$$
$$= o + \frac{1}{2}\sum_{\alpha\beta}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|} - \sum_{\alpha}^{N_n} \int \frac{\rho(r)}{|r-R_\alpha|} d^3r + \frac{\delta F_{xc}}{\delta \Gamma(R)}$$

CONSTRUCTION OF APPROXIMATE F_{xc} :

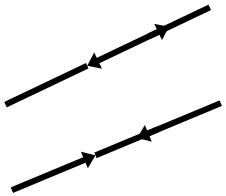
$$\hat{H} = \hat{H}_o + \hat{H}_1$$

$$\hat{H}_o = \sum_\sigma \int \hat{\psi}^+_\sigma(r) \left(-\frac{\nabla^2}{2} - \mu + v_S(r, \underline{\underline{R}}_{=o}) \right) \hat{\psi}_\sigma(r) d^3r$$

$$- \int d^3r \int d^3r' \left[\hat{\psi}_\uparrow(r) \hat{\psi}_\downarrow(r') \Delta^*_s(r, r') + \text{H.c.} \right] + \sum_q \Omega_q \hat{b}^+_q \hat{b}_q$$

develop diagrammatic many-body perturbation theory on the basis of the H_o-propagators:

G_s normal electron propagator (in superconducting state)



F_s

F_s^*

anomalous electron propagators

D_s phonon propagator

Immediate consequence:

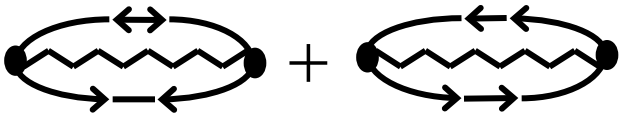
$$F_{xc} = F_{xc}^{ph} + F_{xc}^{el}$$

all diagrams containing D_s

all others diagrams

Phononic contributions

First order in phonon propagator:

$$F_{xc}^{ph}[n,\chi,\Gamma] =$$ 

$$= -\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\frac{\Delta_i \Delta_j^*}{E_i E_j}\left(I(E_i,-E_j,\Omega) - I(E_i,E_j,\Omega)\right)$$

$$-\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\left[\left(1+\frac{(\in_i -\mu)(\in_j -\mu)}{E_i E_j}\right) I(E_i,E_j,\Omega)\right.$$

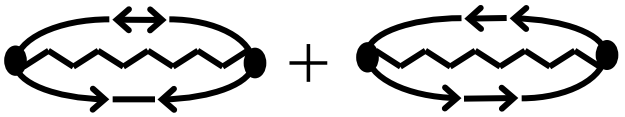
$$\left. +\left(1-\frac{(\in_i -\mu)(\in_j -\mu)}{E_i E_j}\right) I(E_i,-E_j,\Omega)\right]$$

Input to $\mathbf{F_{xc}^{ph}}$: Full k,k' resolved Eliashberg function

$$\alpha^2 F_{nk,n'k'}(\Omega) = \sum_{\lambda q}\left|g_{nk,n'k'}^{\lambda q}\right|^2 \delta(\Omega - \Omega_{\lambda q})$$

Phononic contributions

First order in phonon propagator:

$$F_{xc}^{ph}[n,\chi,\Gamma] =$$ 

$$= -\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\frac{\Delta_i \Delta_j^*}{E_i E_j}\left(I(E_i,-E_j,\Omega) - I(E_i,E_j,\Omega)\right)$$

$$-\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\left[\left(1+\frac{(\epsilon_i-\mu)(\epsilon_j-\mu)}{E_i E_j}\right) I(E_i,E_j,\Omega)\right.$$

$$\left. +\left(1-\frac{(\epsilon_i-\mu)(\epsilon_j-\mu)}{E_i E_j}\right) I(E_i,-E_j,\Omega)\right]$$

Input to $\mathbf{F_{xc}^{ph}}$: Full k,k' resolved Eliashberg function

$$\alpha^2 F_{nk,n'k'}(\Omega) = \sum_{\lambda q}\left|g_{nk,n'k'}^{\lambda q}\right|^2 \delta(\Omega-\Omega_{\lambda q})$$

Calculated ab-initio with ESPRESSO code

Construction of LDA-type functional for purely electronic correlations

S. Kurth, M. Marques, M. Lüders, E.K.U.G., PRL 83, 2628 (1999)

STRATEGY

- Calculate E_{xc} for homogeneous superconductor
- Then use the result as LDA for inhomogeneous system

Normal state LDA:

Given an approximation of $e_{xc}^{hom}(\rho)$ (xc energy per volume)

$$E_{xc}^{LDA}[\rho] := \int d^3r\, e_{xc}^{hom}(\rho)\Big|_{\rho=\rho(r)}$$

LDA for superconductors: Given an approximation of $e_{xc}^{hom}[\rho, \chi(k)]$

<u>Note:</u> $e_{xc}^{hom}[\rho, \chi(k)]$ is already a FUNCTIONAL

$$E_{xc}^{LDA}[\rho, \chi] := \int d^3R\, e_{xc}^{hom}[\rho(R), \chi_w(R,k)]$$

where χ_w is the Wigner transform of the nonlocal order parameter

$$\chi(r, r') = \chi(R, r - r') = \int \frac{d^3k}{(2\pi)^3} \chi_w(R, k) e^{ik(r-r')}$$

$$R = \frac{r + r'}{2}$$

Calculation of $e_{xc}^{hom}[\rho,\chi(k)]$ by diagrammatics

unperturbed system: uniform non-interacting superconductor

$$\hat{H}_o = \hat{T} - \mu \hat{N} + \int d^3k \left(\hat{\chi}(k)\, \Delta^*(k) + \hat{\chi}^+(k)\, \Delta(k) \right)$$

perturbation = W_{Clb} (bare Coulomb interaction)

many-body perturbation theory yields

$e_{xc}^{hom} = e_{xc}^{hom}[\mu,\Delta(k)]$

$\rho = \rho\,[\mu,\Delta(k)]$

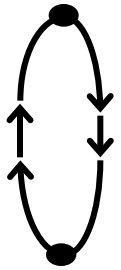
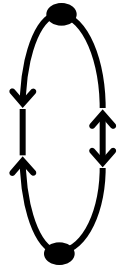
$\chi(q) = \chi[\mu,\Delta(k)](q)$

invert: $\mu = \mu[\rho, \chi]$, $\Delta = \Delta[\rho,\chi]$ (invertibility guaranteed by HK theorem)

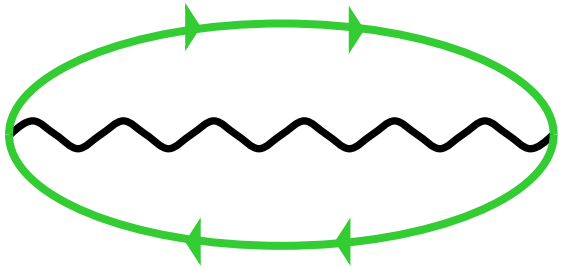
$e_{xc}^{hom} = e_{xc}^{hom}[\rho, \chi(k)]$

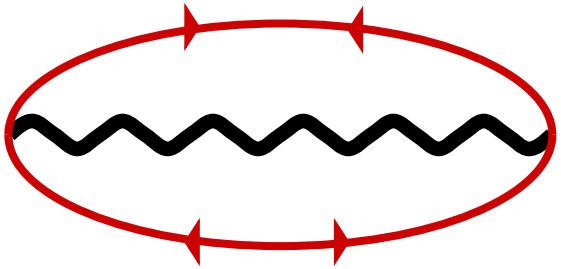
Complete RPA resummation of all normal and anomalous bubble diagrams

$$F_C^{RPA} = \frac{1}{\beta}\sum_{q,\nu_n} \log\{1 - w(q)\cdot[\Pi_G(q,\nu_n) + \Pi_F(q,\nu_n)]\} + w(q)\cdot[\Pi_G(q,\nu_n) + \Pi_F(q,\nu_n)]$$

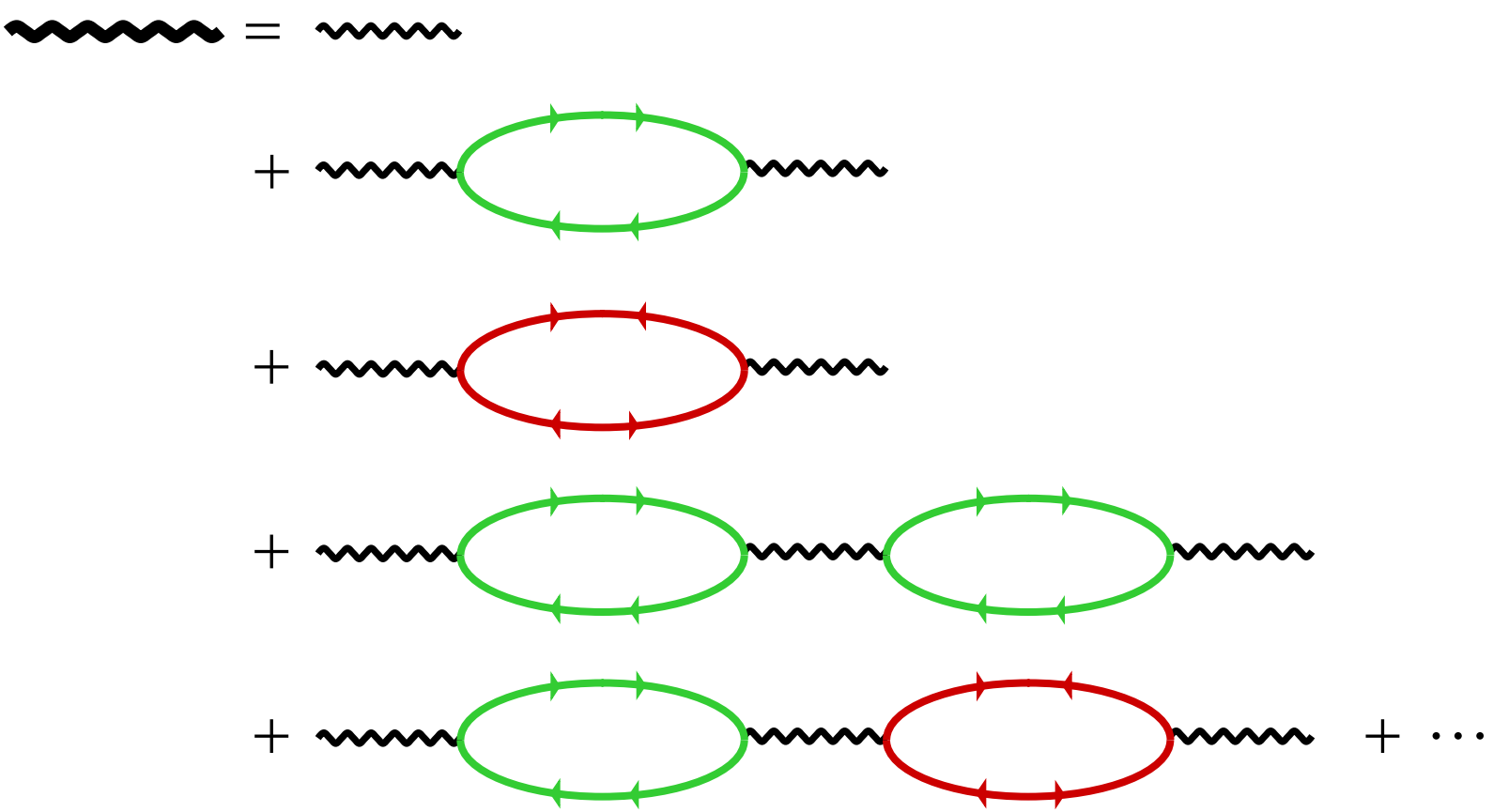
where $w(q) = \frac{4\pi}{q^2}$ and $\Pi_G(q,\nu_n) \equiv$  $\Pi_F(q,\nu_n) \equiv$ 

$$\Pi_G = \frac{1}{2}\sum_k \frac{1}{E_k E_{k+q}}\cdot\left\{\frac{(E_k + \in_k)(E_{k+q} + \in_{k+q})}{i\nu_n + E_k - E_{k+q}}\cdot\left(f_\beta(E_k) - f_\beta(E_{k+q})\right)\right.$$
$$+ \frac{(E_k + \in_k)(E_{k+q} - \in_{k+q})}{i\nu_n + E_k + E_{k+q}}\cdot\left(f_\beta(E_k) - f_\beta(-E_{k+q})\right)$$
$$+ \frac{(E_k - \in_k)(E_{k+q} + \in_{k+q})}{i\nu_n - E_k - E_{k+q}}\cdot\left(f_\beta(-E_k) - f_\beta(E_{k+q})\right)$$
$$\left. + \frac{(E_k - \in_k)(E_{k+q} - \in_{k+q})}{i\nu_n - E_k + E_{k+q}}\cdot\left(f_\beta(-E_k) - f_\beta(-E_{k+q})\right)\right\}$$

$E_x(S) =$ 

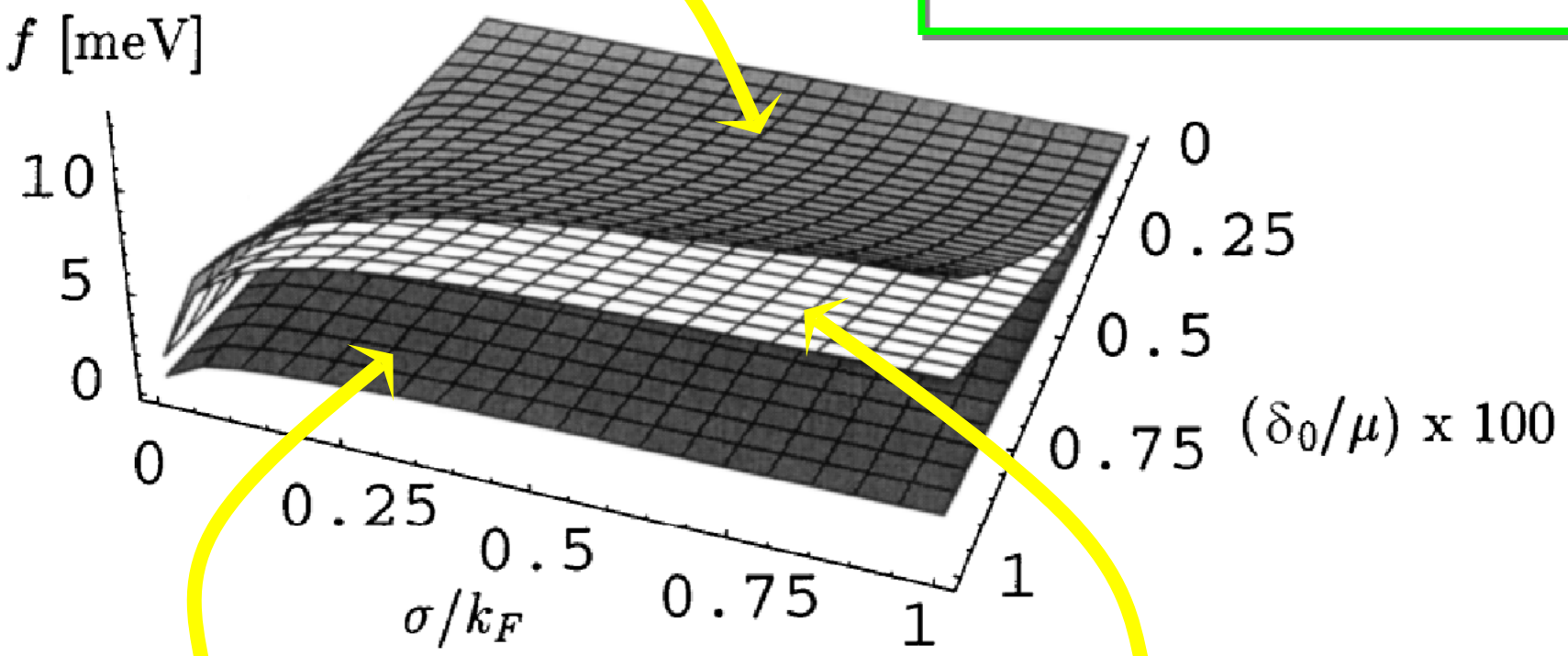
$E_{Hc}(S) =$ 

with



Contributions to condensation energy at $r_s = 1$

$$\Delta(k) = \delta_0 \exp\left(-\frac{(k-k_F)^2}{\sigma^2}\right)$$

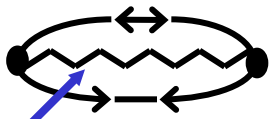


$E^{(1)}_x(S) - E^{(1)}_x(N)$

$-\left[E^{RPA}_c(S) - E^{RPA}_c(N)\right]$

Improved approximation for the purely electronic contributions

$$F_{xc}^{ee}[\rho,\chi] = \quad + F_{xc}^{GGA}[\rho]$$



RPA-screened electron-electron interaction of the **inhomogeneous system**

Crucial point: NO ADJUSTABLE PARAMETERS

To separate the normal (band-structure) energy scale from the superconducting energy scale, the Bogoliubov-KS equations are decomposed into:

$$\left(-\frac{\nabla^2}{2}+v_s(r)\right)\varphi_{nk}(r)=\epsilon_{nk}\ \varphi_{nk}(r)$$

$$\Delta_{nk}=-\frac{1}{2}\sum_{n'k'} w_{eff}(nk,n'k')\frac{\tanh\left(\frac{\beta}{2}\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}\right)}{\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}}\Delta_{n'k'}$$

$$w_{eff}(nk,n'k')=\int d^3r\int d^3r'\int d^3x\int d^3x'\,\varphi^*_{nk}(r)\varphi^*_{n(-k)}(r')\,w_{eff}(r,r',x,x')\,\varphi_{n'k'}(x)\varphi_{n'(-k')}(x')$$

$$w_{eff}(r,r',x,x')=w^{el}_{xc}(r,r',x,x')+w^{ph}_{xc}(r,r',x,x')$$

with $$w^{ph/el}_{xc}=\frac{\delta^2 F^{ph/el}_{Hxc}[\rho,\chi]}{\delta\chi^*(r,r')\delta\chi^*(x,x')}\bigg|_{\chi=0}$$

Transition temperatures from DFT calculation

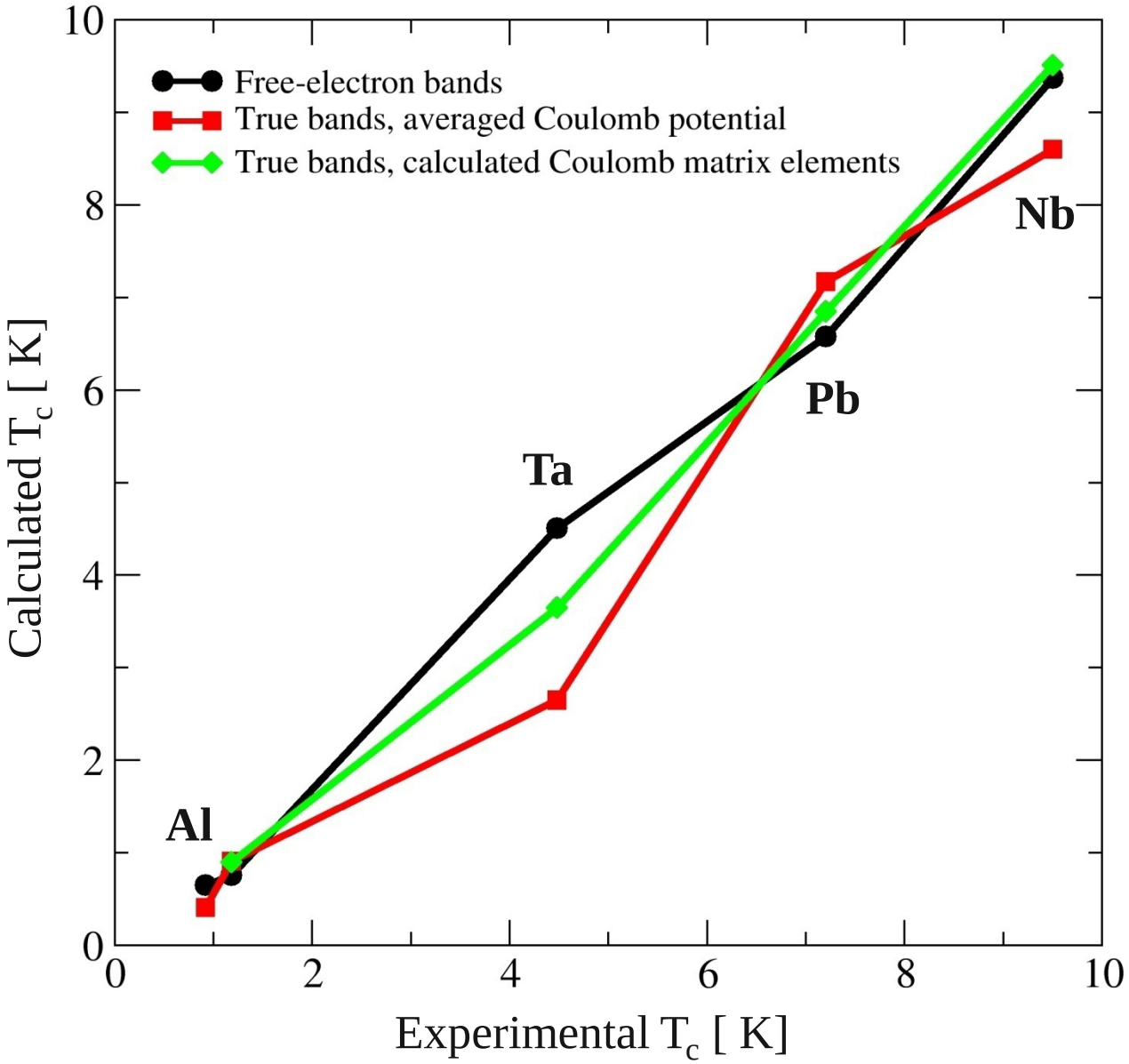
	Al	Nb	Ta	Pb	Cu
DFT	0.9	9.5	3.7	6.9	<0.01
Experimental	1.18	9.3	4.5	7.2	-

Gap at zero temperature

	Al	Nb	Ta	Pb	Cu
DFT	0.14	1.74	0.63	1.34	-
Experimental	0.179	1.55	0.69	1.33	-

M. Lüders et al, PRB 72, 024545 (2005), M. Marques et al, PRB 72, 024546 (2005)

T_c: Theory vs Experiment



Phonon-only transition temperatures

	Al	Nb	V	Ta	Pb	Cu
DFT	7.10	23.0	34.2	11.7	12.8	0.055
Eliashberg	9.75	24.7	36.4	14.0	12.2	0.065

DFT with $w_{xc}^{el}(r, r', x, x') = 0$

Eliashberg with $\mu^* = 0$

Confirmation that retardation effects are fully included in the DFT framework

Isotope effect:

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

	Calculations			Experiment		
Pb		0.47			0.47	
Mo		0.37			0.33	

The deviations from BCS value α=0.5 are correctly described

Jump of specific heat at T_c

	Theory	Experiment
Pb	2.93	3.57-3.71
Nb	2.87	2.8-3.07
Ta	2.64	2.63
Al	2.46	2.43

Gap $\Delta_n(k)$ is a function of 3D k-vector for each band n.

How can one visualize the gap?

a) Define surface $S_n(E) = \{k : \varepsilon_n(k) = E\}$.
In particular: $S_n(E_F)$ = Fermi surface
$\rightarrow$Plot the values of $\Delta_n(k)$ on $S_n(E)$ by color coding.

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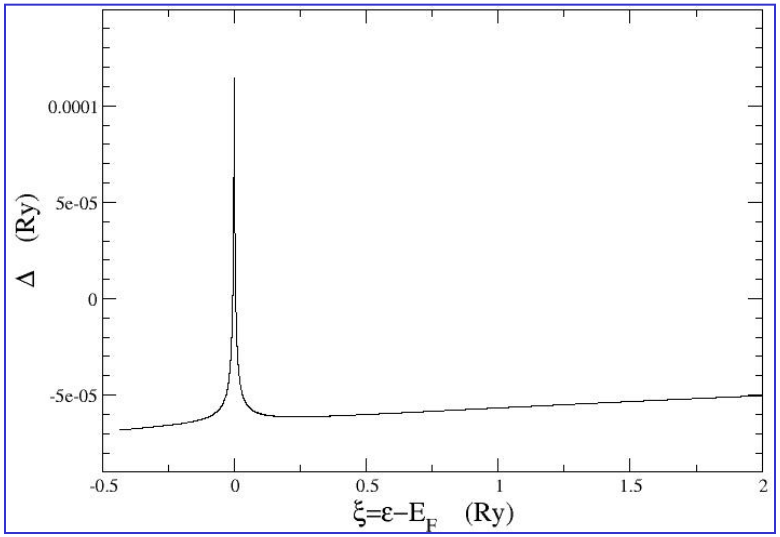
In particular: $S_n(E_F)$ = Fermi surface
$\rightarrow$Plot the values of $\Delta_n(k)$ on $S_n(E)$ by color coding.

b) **Plot $\Delta_n(E)$ as function of E, where for each E the gap values $\Delta_n(k)$ are plotted for a large random set of $k \in S_n(E)$**

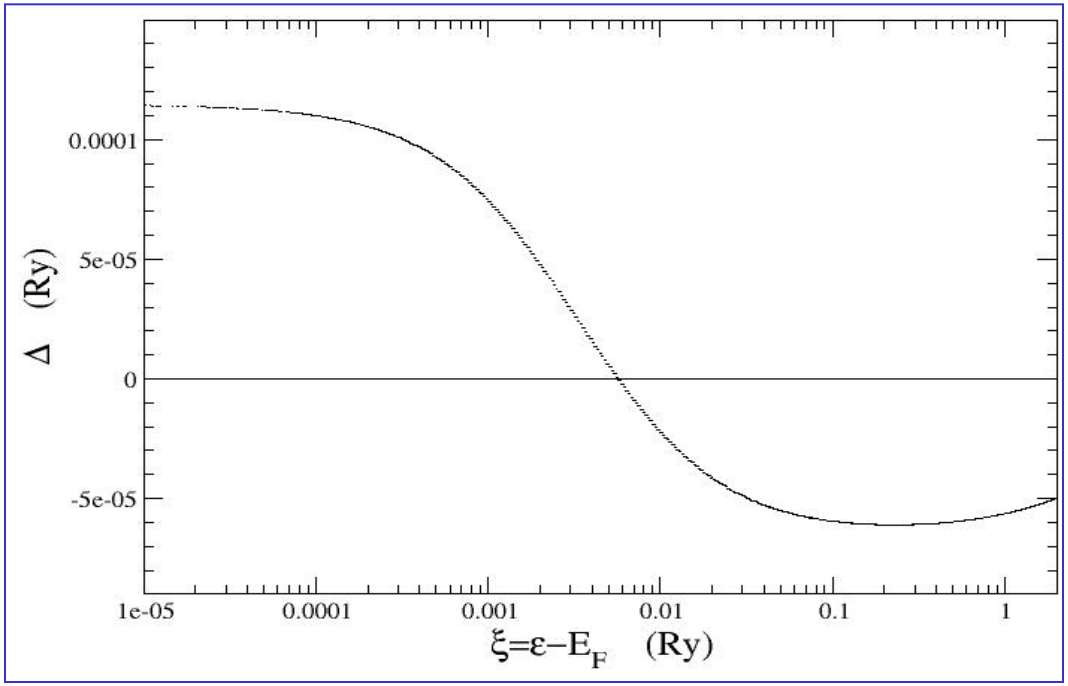
Gap as a function of energy, Nb



Linear scale

$\xi = \varepsilon - E_F$

Log scale



$$\left(-\frac{\nabla^2}{2}+v_s(r)\right)\varphi_{nk}(r)=\epsilon_{nk}\ \varphi_{nk}(r)$$

$$\Delta_{nk}=-\frac{1}{2}\sum_{n'k'} w_{eff}(nk,n'k')\frac{\tanh\left(\frac{\beta}{2}\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}\right)}{\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}}\Delta_{n'k'}$$

$$w_{eff}(nk,n'k')=\int d^3r\int d^3r'\int d^3x\int d^3x'\,\varphi^*_{nk}(r)\varphi^*_{n(-k)}(r')\,w_{eff}(r,r',x,x')\,\varphi_{n'k'}(x)\varphi_{n'(-k')}(x')$$

$$w_{eff}(r,r',x,x')=w^{el}_{xc}(r,r',x,x')+w^{ph}_{xc}(r,r',x,x')$$

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$$w_{eff}(r,r',x,x')=w^{el}_{xc}(r,r',x,x')+w^{ph}_{xc}(r,r',x,x')$$

$w^{ph}_{eff}(nk,n'k')$ **strongly attractive, short-ranged**

$$\left(-\frac{\nabla^2}{2}+v_s(r)\right)\varphi_{nk}(r)=\epsilon_{nk}\ \varphi_{nk}(r)$$

$$\Delta_{nk}=-\frac{1}{2}\sum_{n'k'} w_{eff}(nk,n'k')\frac{\tanh\left(\frac{\beta}{2}\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}\right)}{\sqrt{(\epsilon_{n'k'}-\mu)^2+|\Delta_{n'k'}|^2}}\Delta_{n'k'}$$

$$w_{eff}(nk,n'k')=\int d^3r\int d^3r'\int d^3x\int d^3x'\,\varphi^*_{nk}(r)\varphi^*_{n(-k)}(r')\,w_{eff}(r,r',x,x')\,\varphi_{n'k'}(x)\varphi_{n'(-k')}(x')$$

$$w_{eff}(r,r',x,x')=w^{el}_{xc}(r,r',x,x')+w^{ph}_{xc}(r,r',x,x')$$

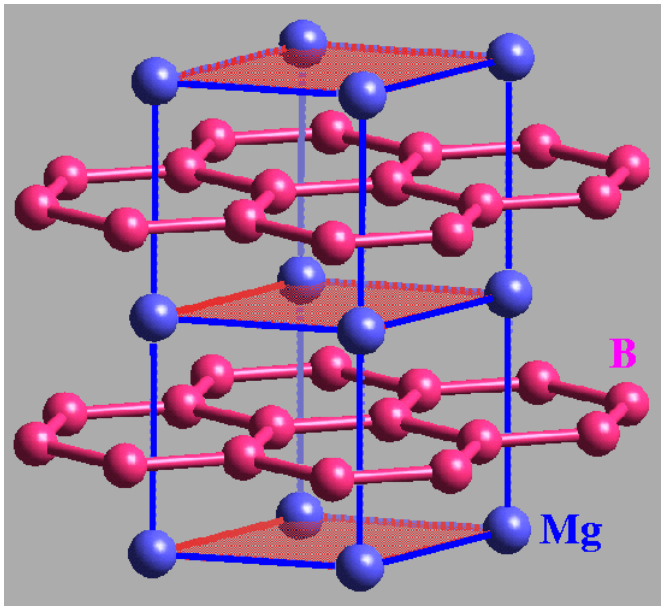
$w^{ph}_{eff}(nk,n'k')$ **strongly attractive, short-ranged**

$w^{el}_{eff}(nk,n'k')$ **repulsive, very long-ranged**

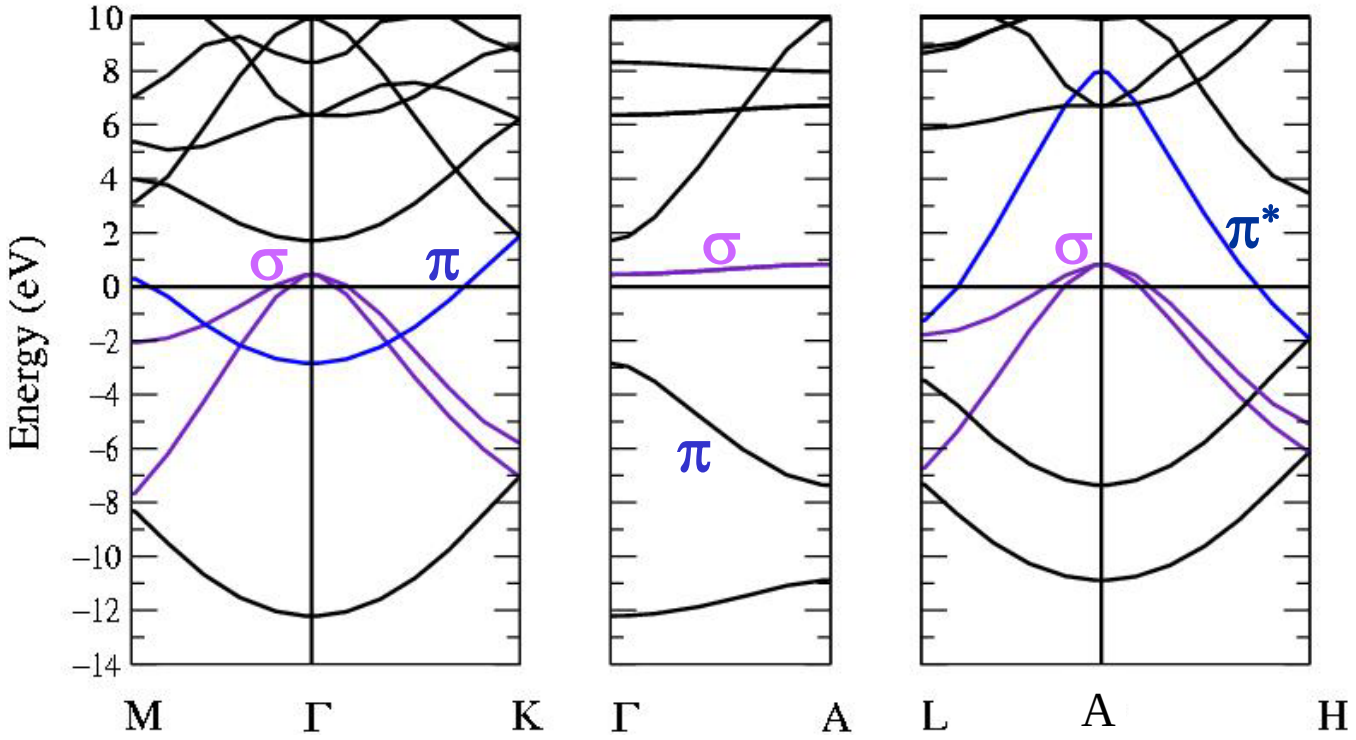
MgB_2

MgB_2

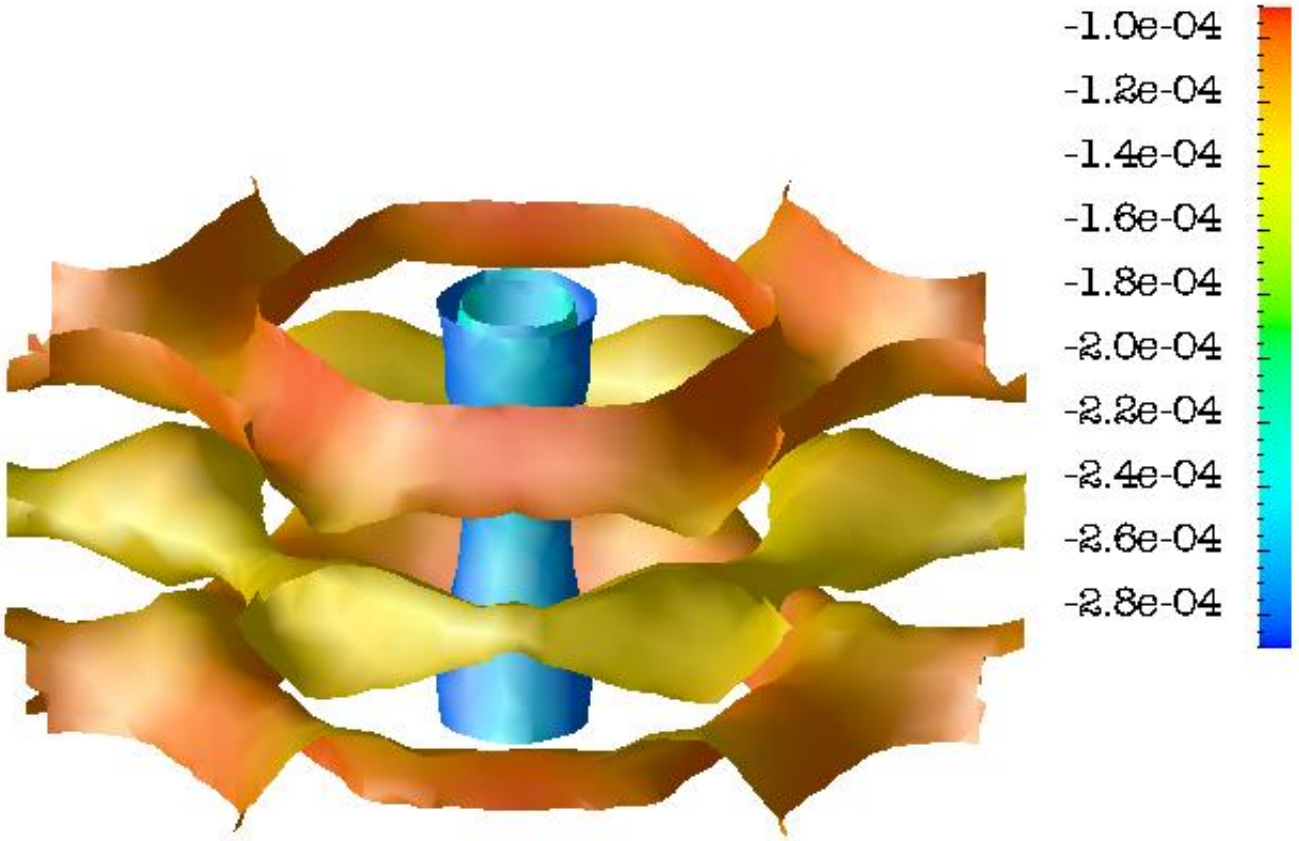
T_c= 39.5 K



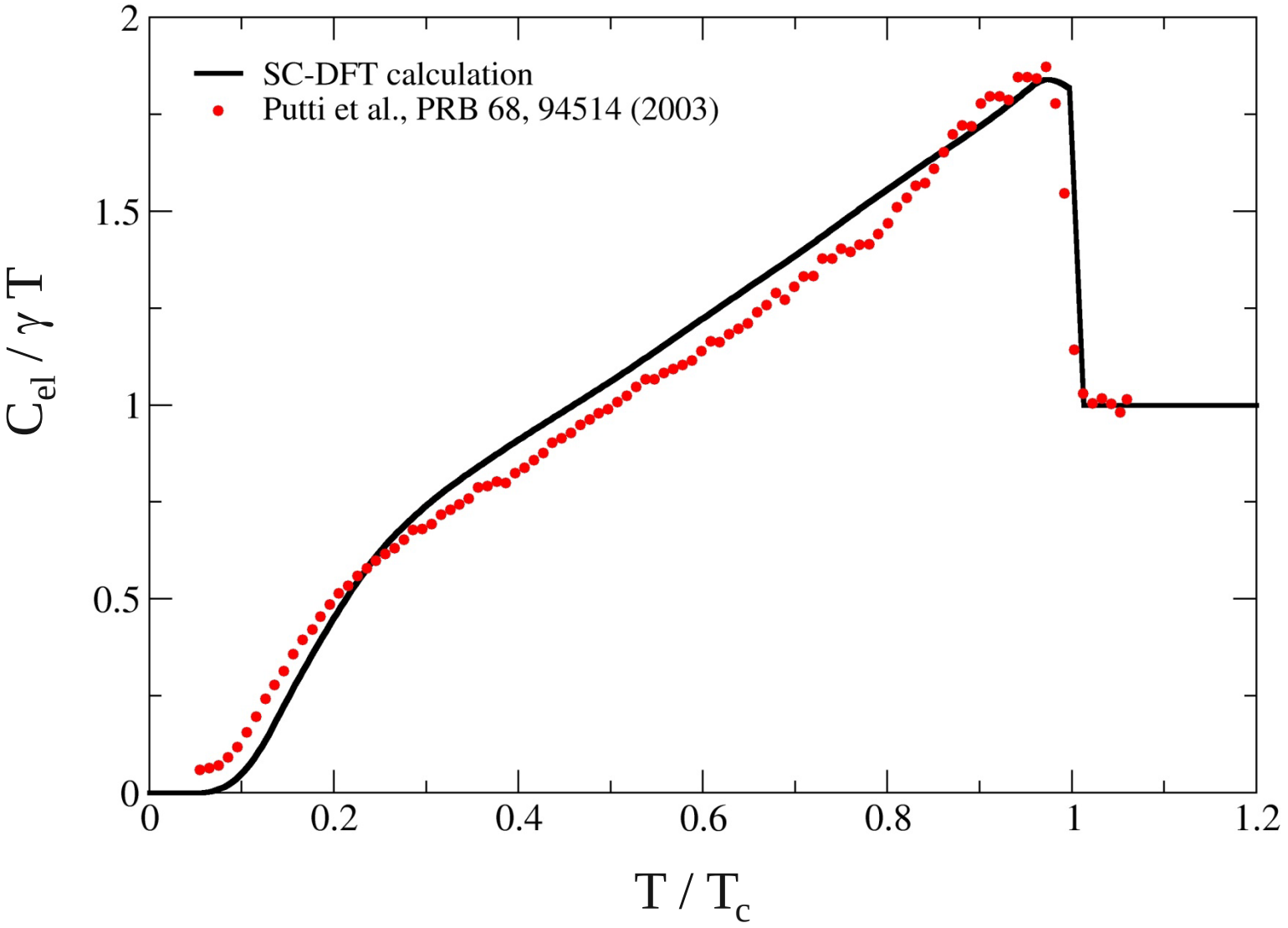
2-D σ-bonding hole pockets
3-D π and π* Fermi surfaces



Fermi Surface of MgB_2

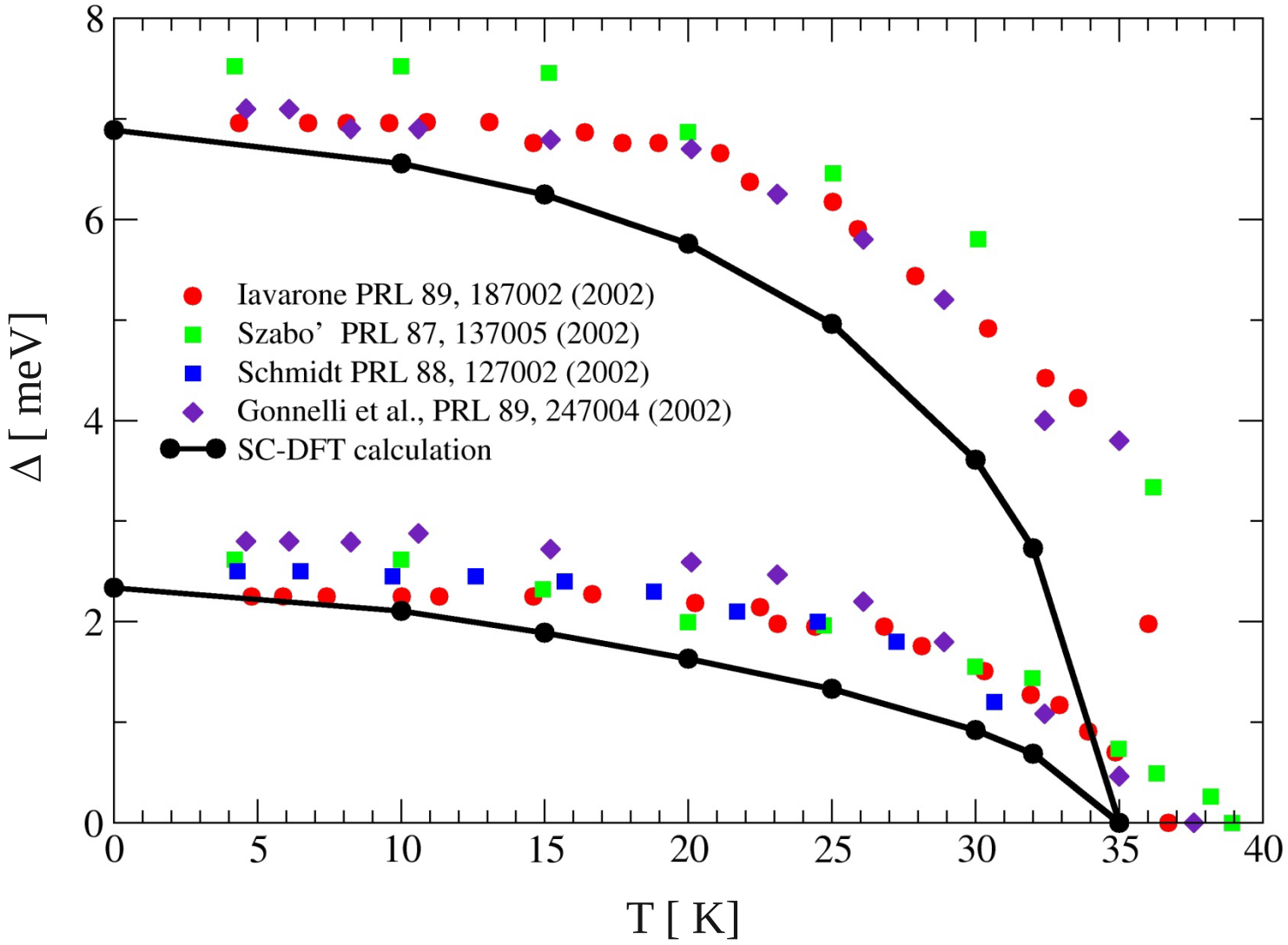


Specific heat of MgB_2

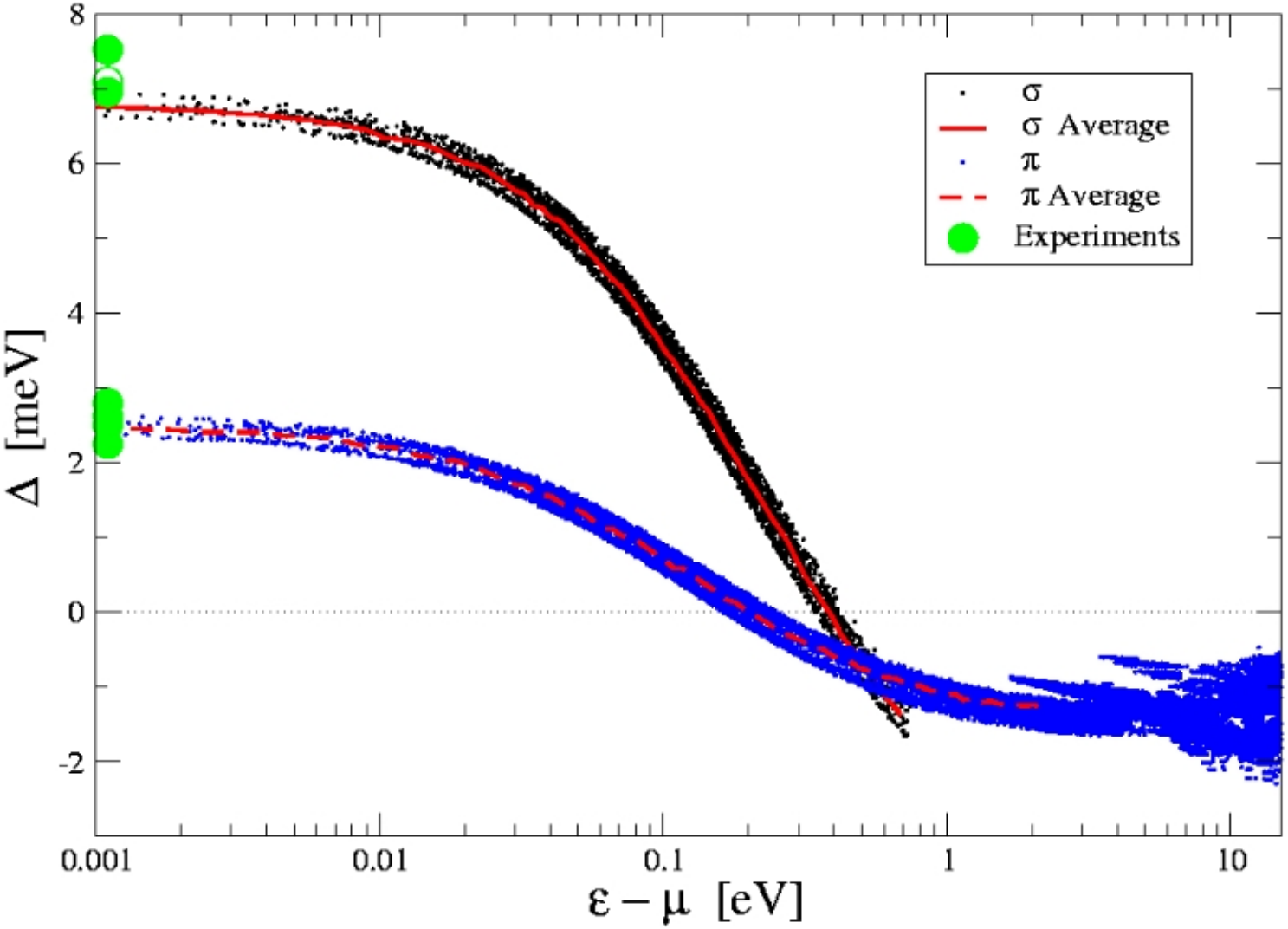


A. Floris et al, Phys. Rev. Lett. 94, 037004 (2005)

MgB_2



A. Floris et al, Phys. Rev. Lett. 94, 037004 (2005)


σ
σ Average
π
π Average
Experiments
Δ [meV]
ε − μ [eV]
8
6
4
2
0
-2
0.001
0.01
0.1
1
10

Anisotropy in MgB2: effects on T_c and Δ

MgB2	Tc (K) (DFT)	Tc (K) (exp)	Δ (meV), (DFT)	Δ (meV), (exp)
Coulomb RPA-ME	36.5	38.2	σ = 7.3 π = 2.6	σ = 7.1 π = 2.9
El-ph Averaged	20.8		3.8	
Coulomb averaged	50.2		σ = 9.4 π = 1.5	

- El-ph interaction anisotropy: increases Tc
- Coulomb interaction anisotropy: decreases Tc

A. Floris, A. Sanna, M. Lüders, G. Profeta, N.N. Lathiotakis, M.A.L. Marques, C. Franchini, E.K.U. Gross, A. Continenza, S. Massidda, Physica C 456, 45 (2007)

Li and Al under high pressure

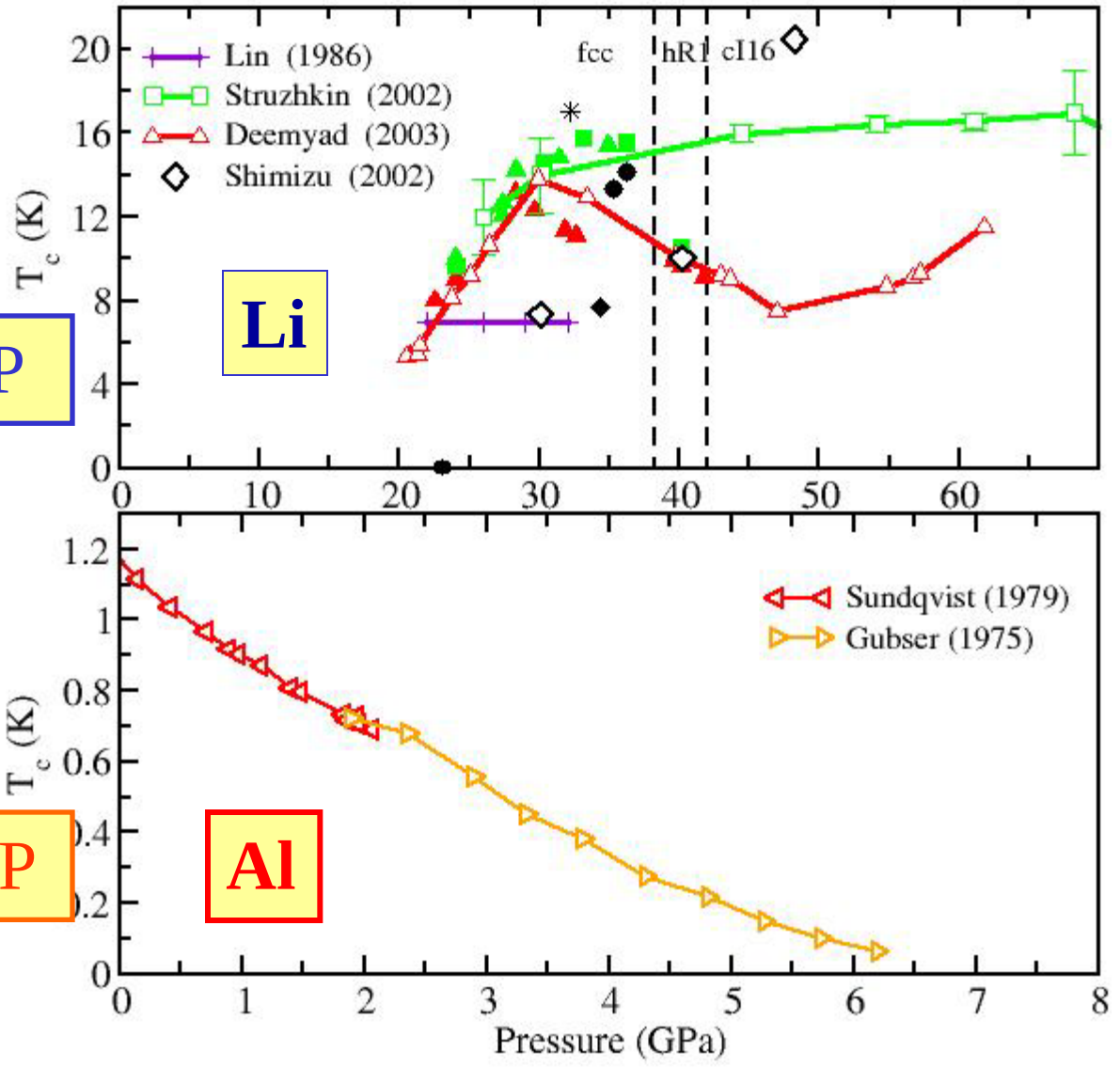
***Simple* metals?**

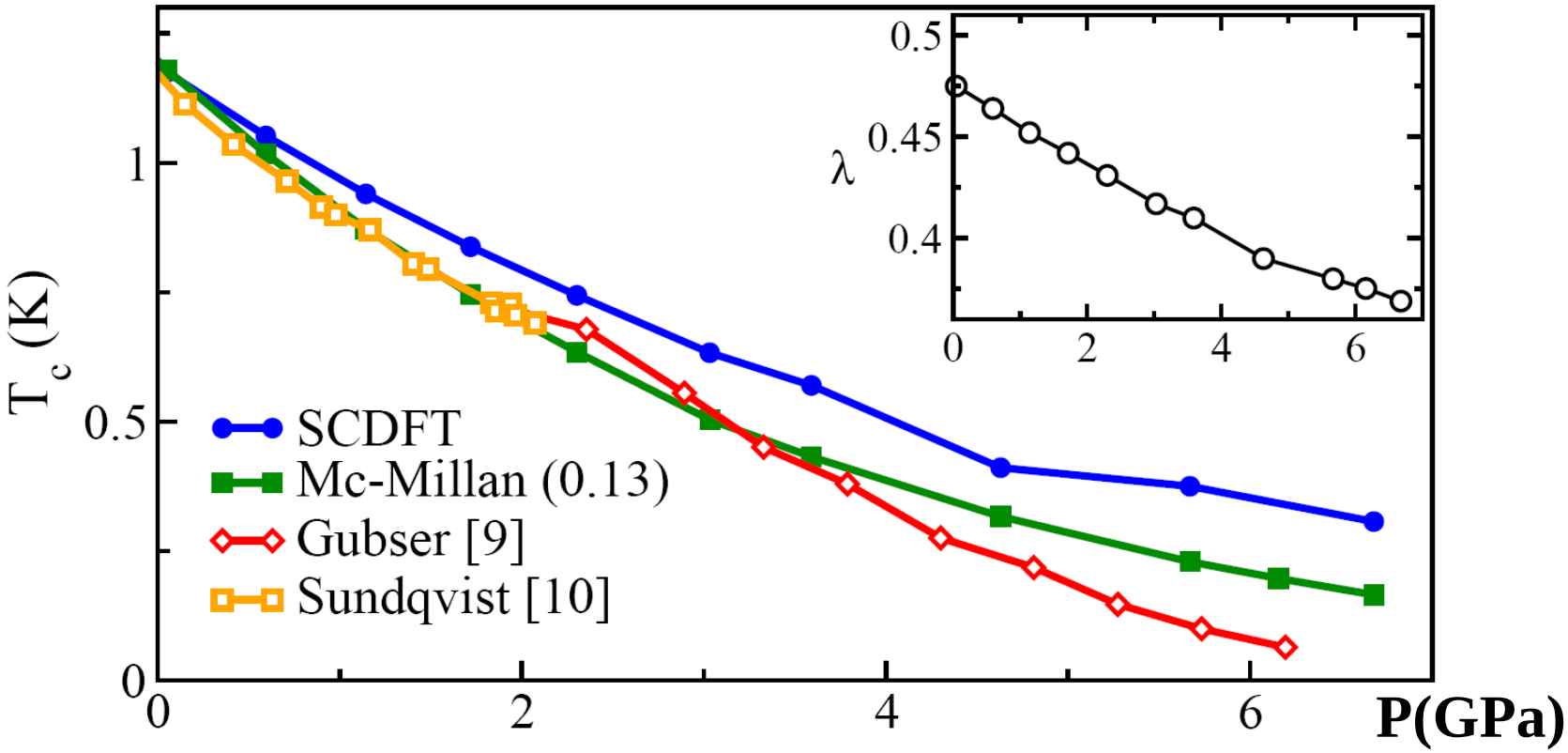
Li

T_c increases under P

Al

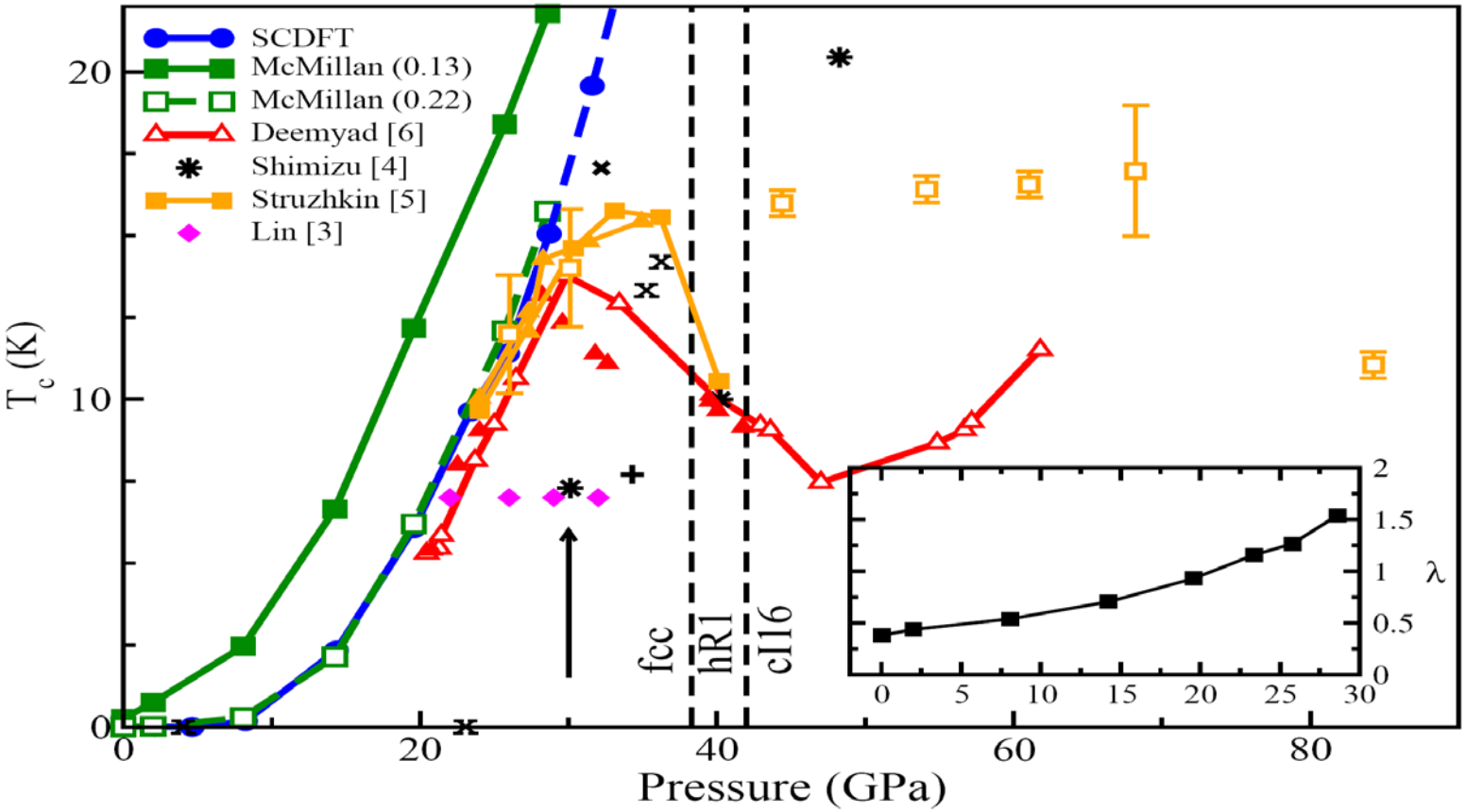
T_c decreases under P





Calculated and experimental critical temperatures for fcc-Al as a function of pressure.

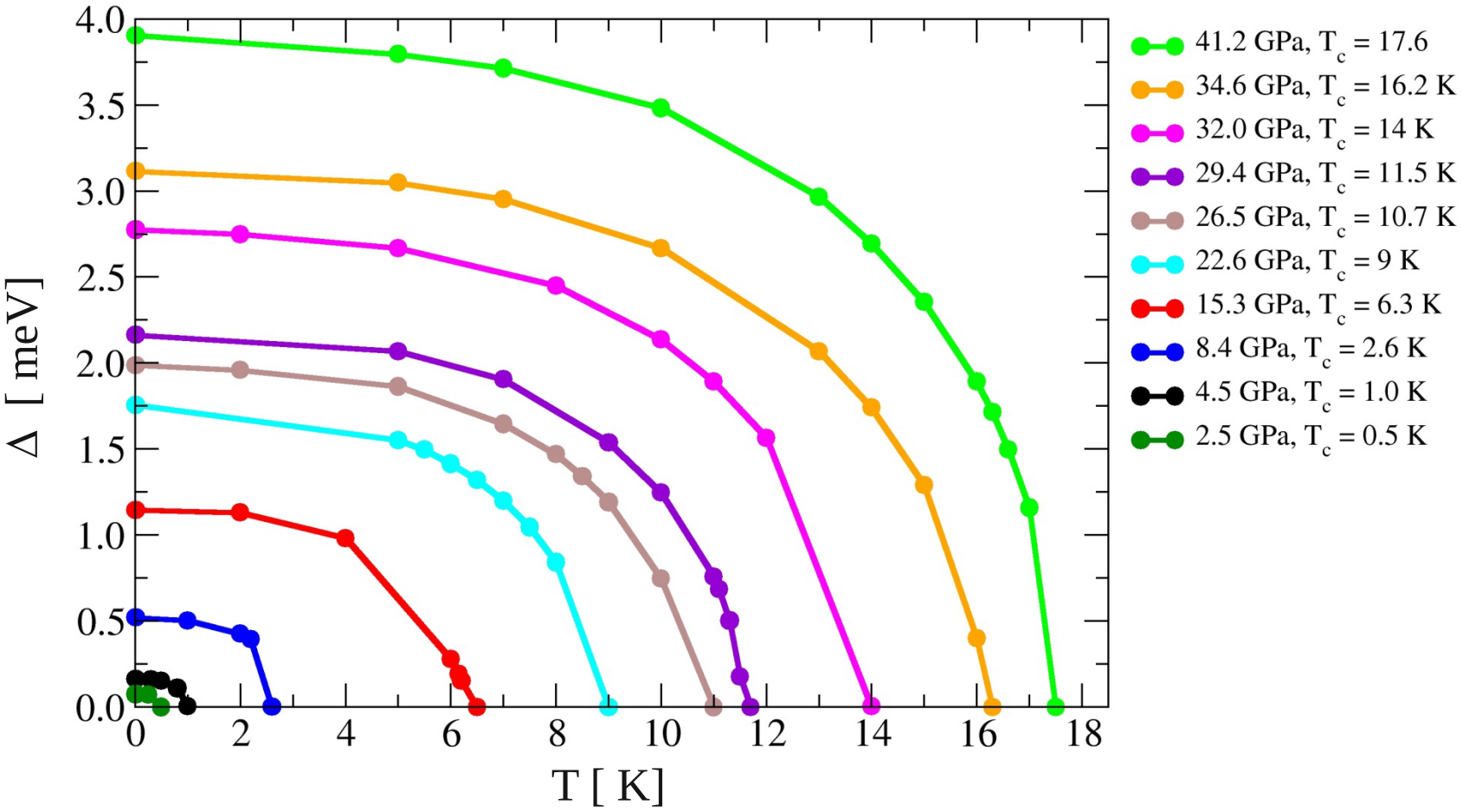
Blue circles represent the ab initio SCDFT values, green squares are the semi-empirical McMillan results (with $\mu^* = 0.13$).



Calculated and experimental critical temperatures for fcc-Li as a function of pressure. Blue circles: SCDFT results (dashed part: fcc structure unstable); Green full squares: McMillan's formula with μ* = 0.13; Green empty squares: McMillan's formula with μ* = 0.22. Vertical dashed lines indicate the structural transition pressures for Li (experimental). Inset: e-ph coupling constant λ vs pressure in GPa.

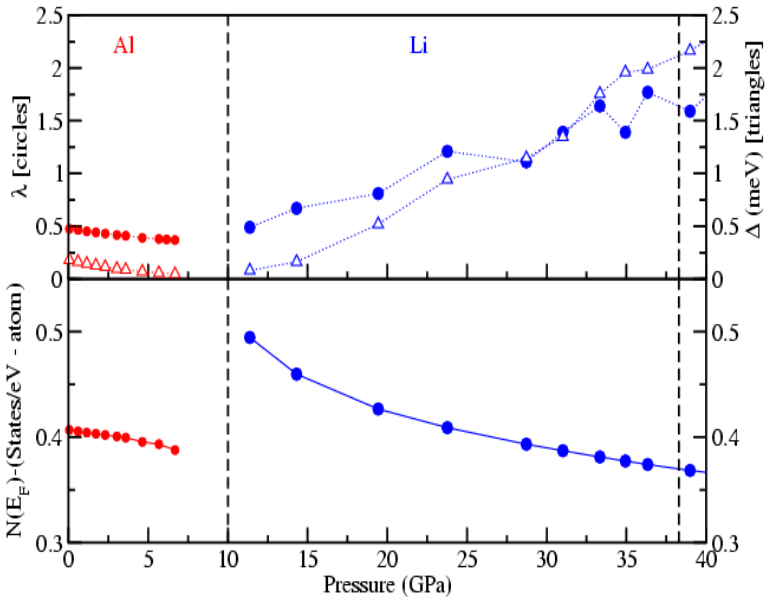
G. Profeta et al, Phys. Rev. Lett. 96, 047003 (2006)

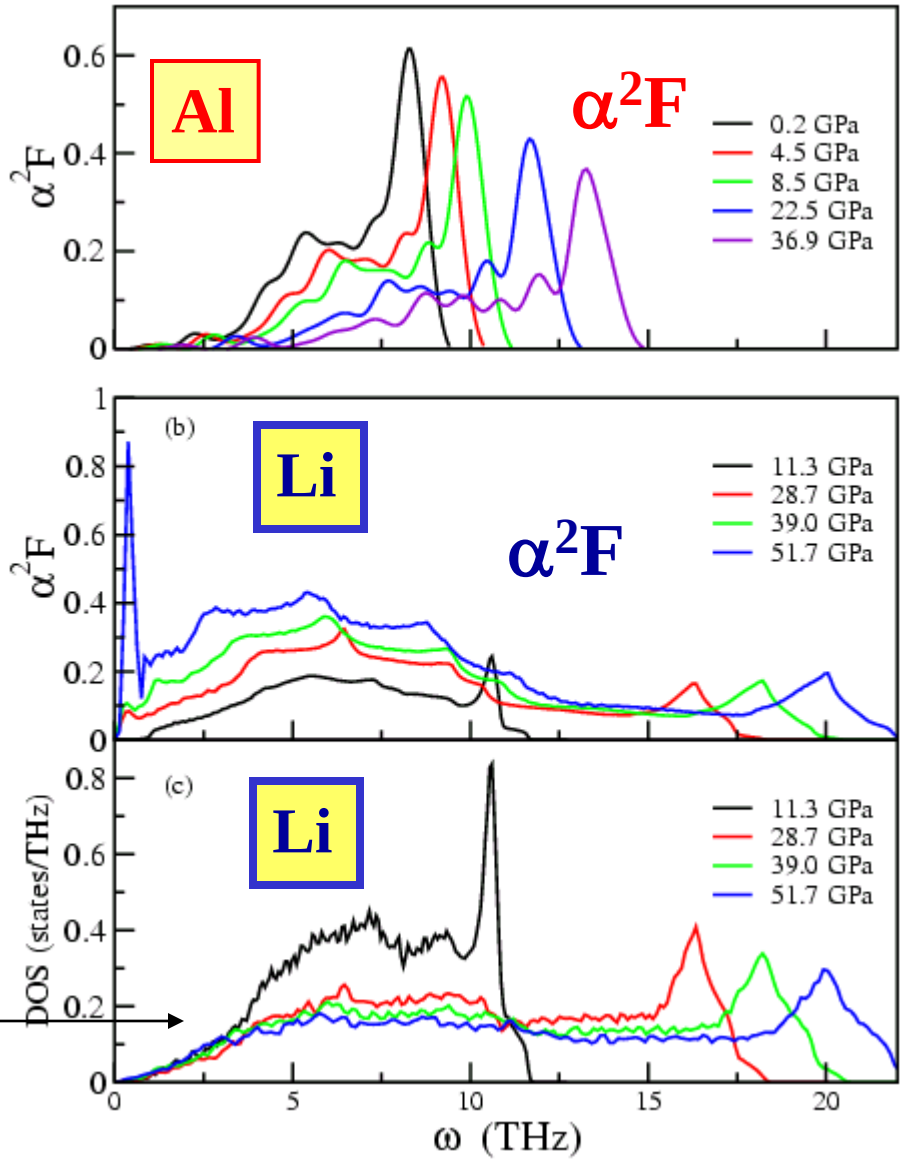
Superconducting gap Δ as function of temperature for compressed fcc Li



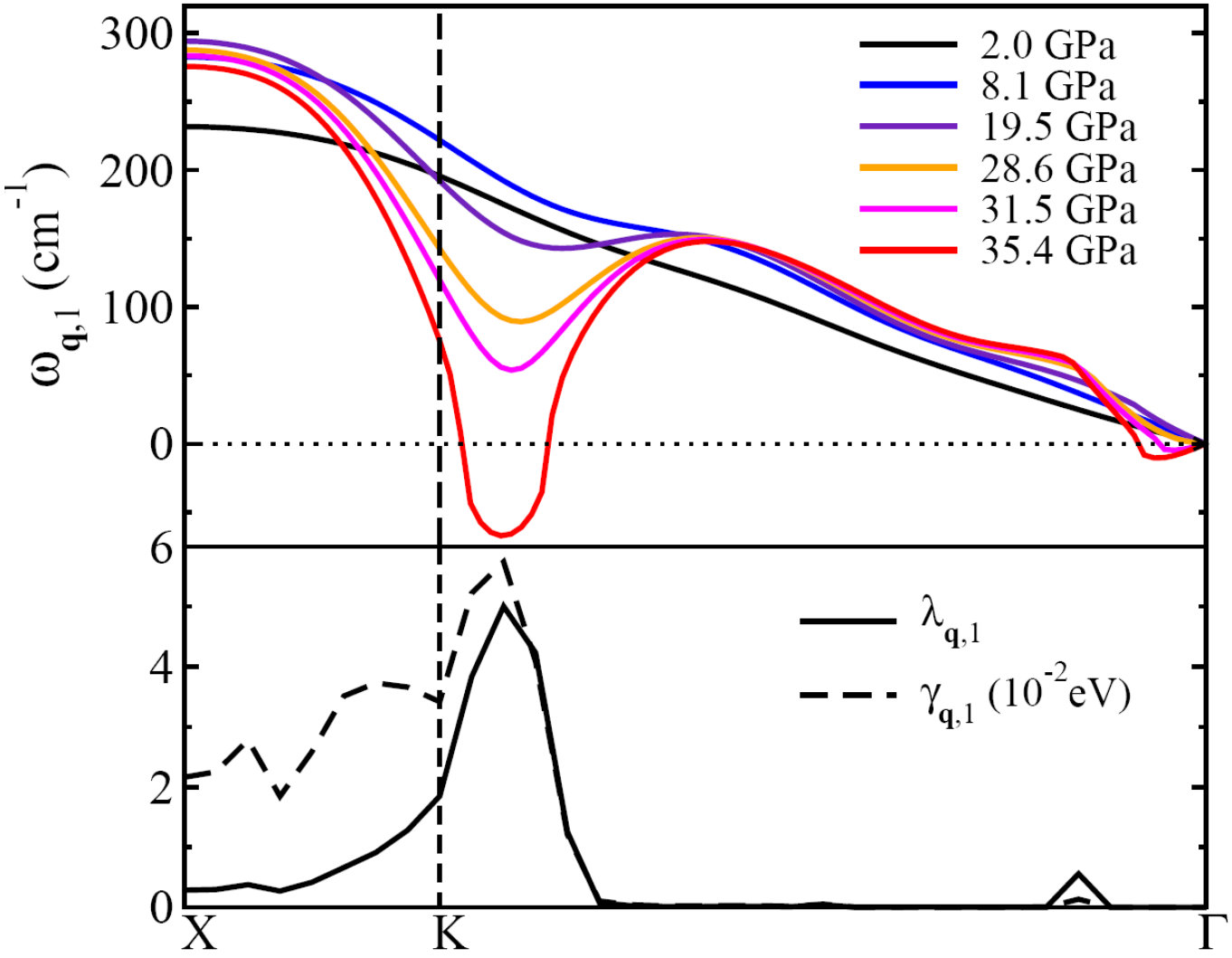
WHY ARE THE TWO MATERIALS DIFFERENT?

Al **Li**



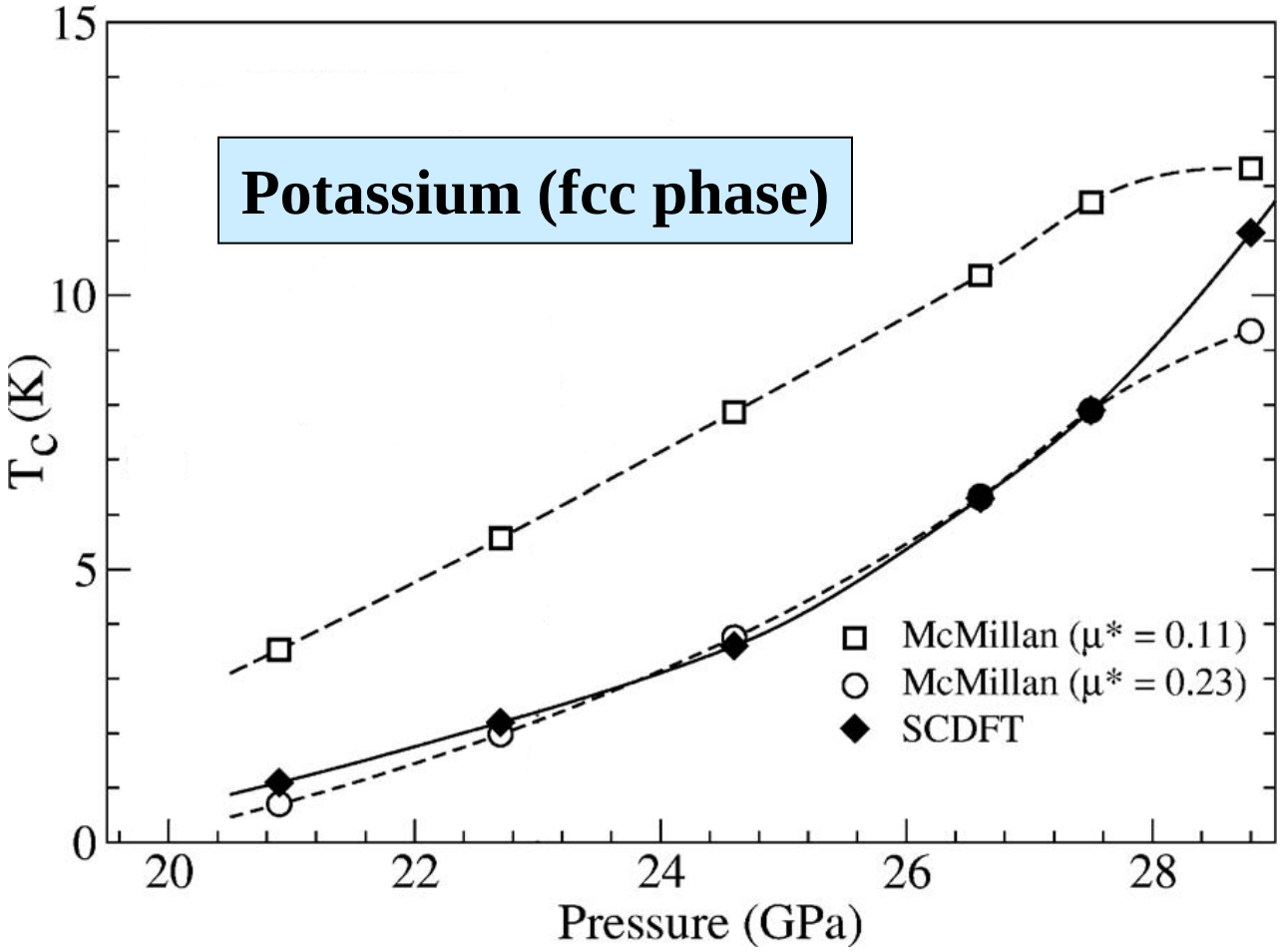


Phonon DOS



Upper panel: phonon dispersion of Li along the X-K-Γ line, at several different pressures, for the lower frequency mode. (Frequencies below the zero axis denote imaginary values.) Lower panel: electron-phonon coupling $\lambda_{q;1}$ and phonon line-width $\gamma_{q;1}$.

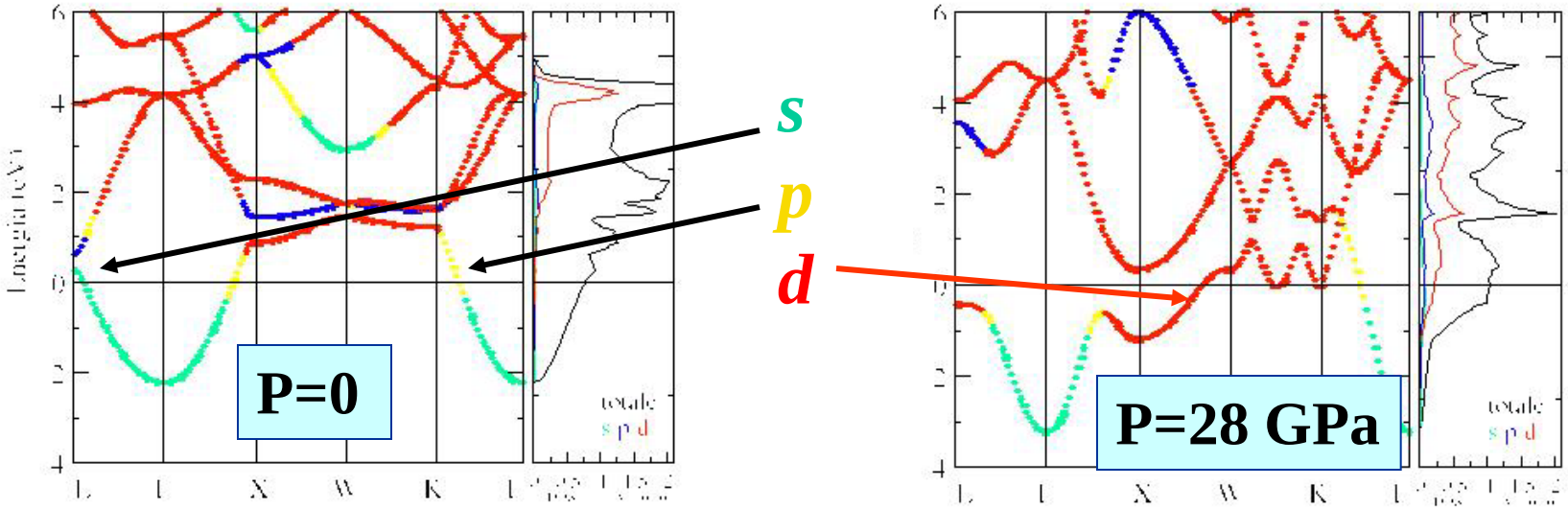
Prediction: T_c rises with pressure



A. Sanna, C. Franchini, A. Floris, G. Profeta, N.N. Lathiotakis, M. Lüders, M.A.L. Marques, E.K.U. Gross, A. Continenza and S. Massidda, Phys. Rev. B 73, 144512 (2006).

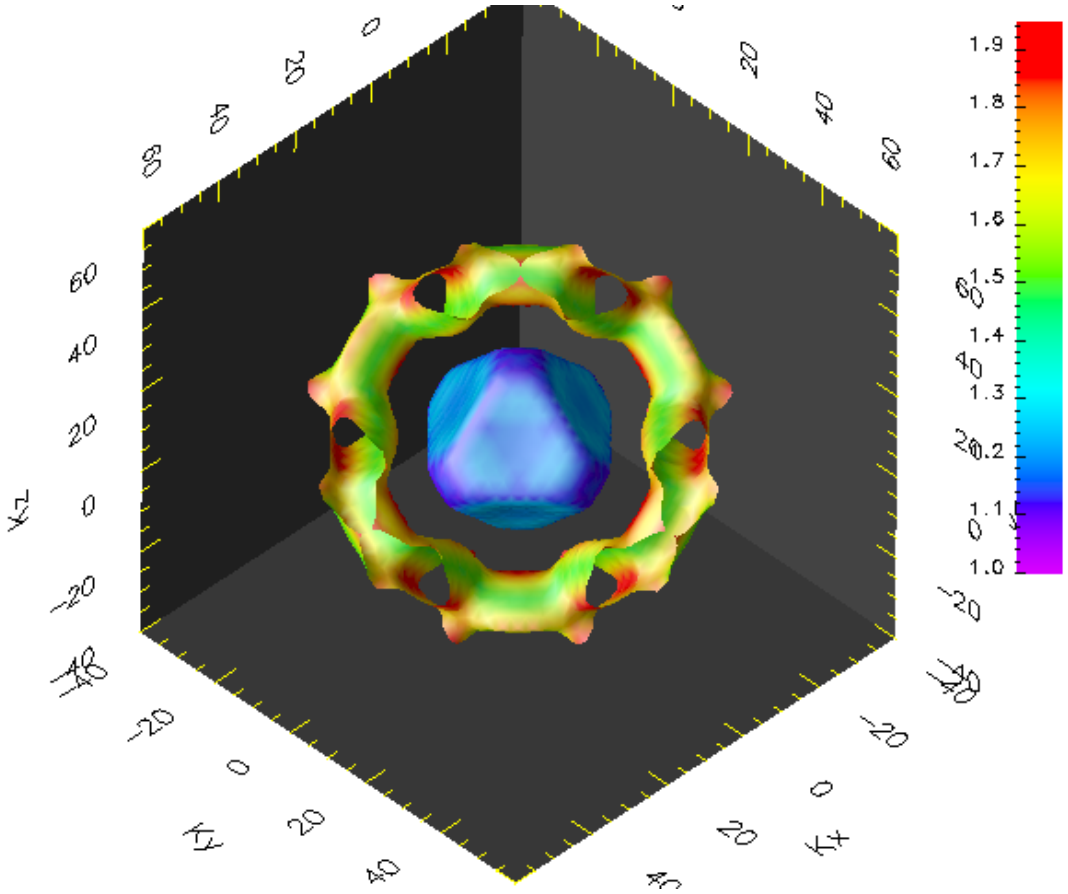
Analysis of K under pressure

***sp* to *d* transfer at E_F under pressure**

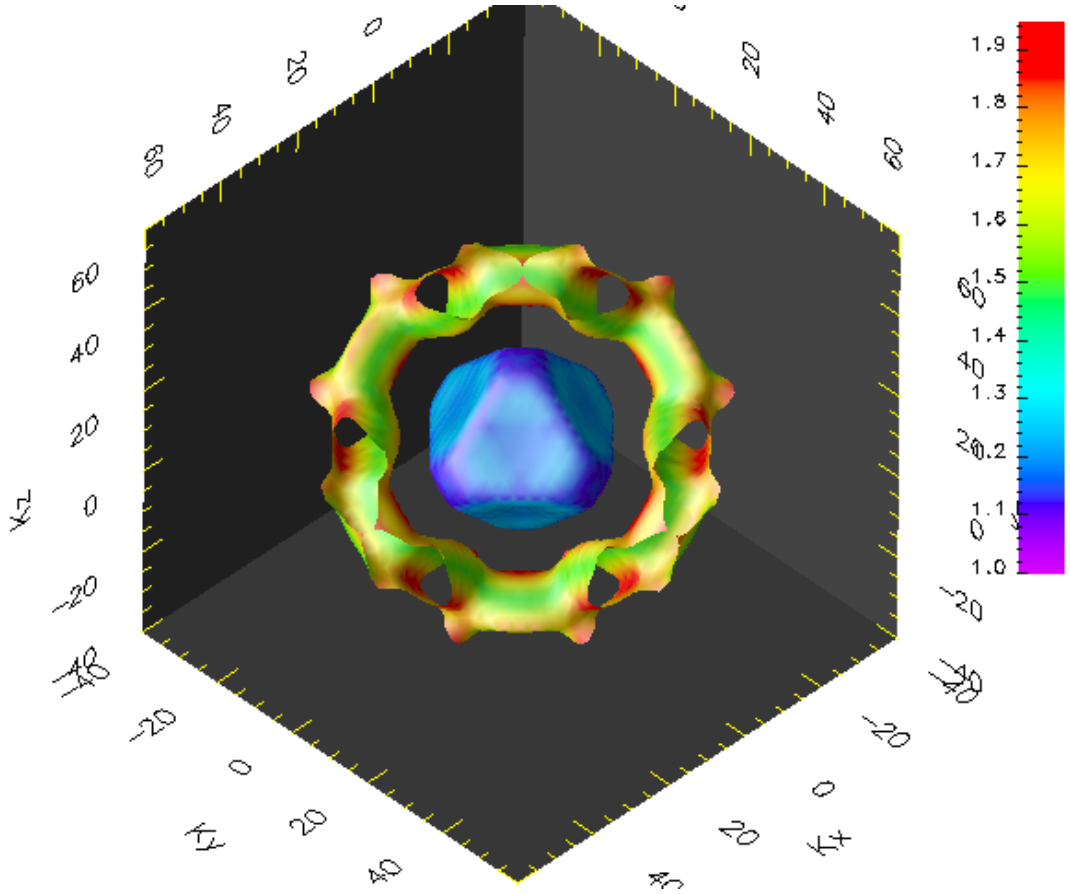


Pb revisited

Fermi surface

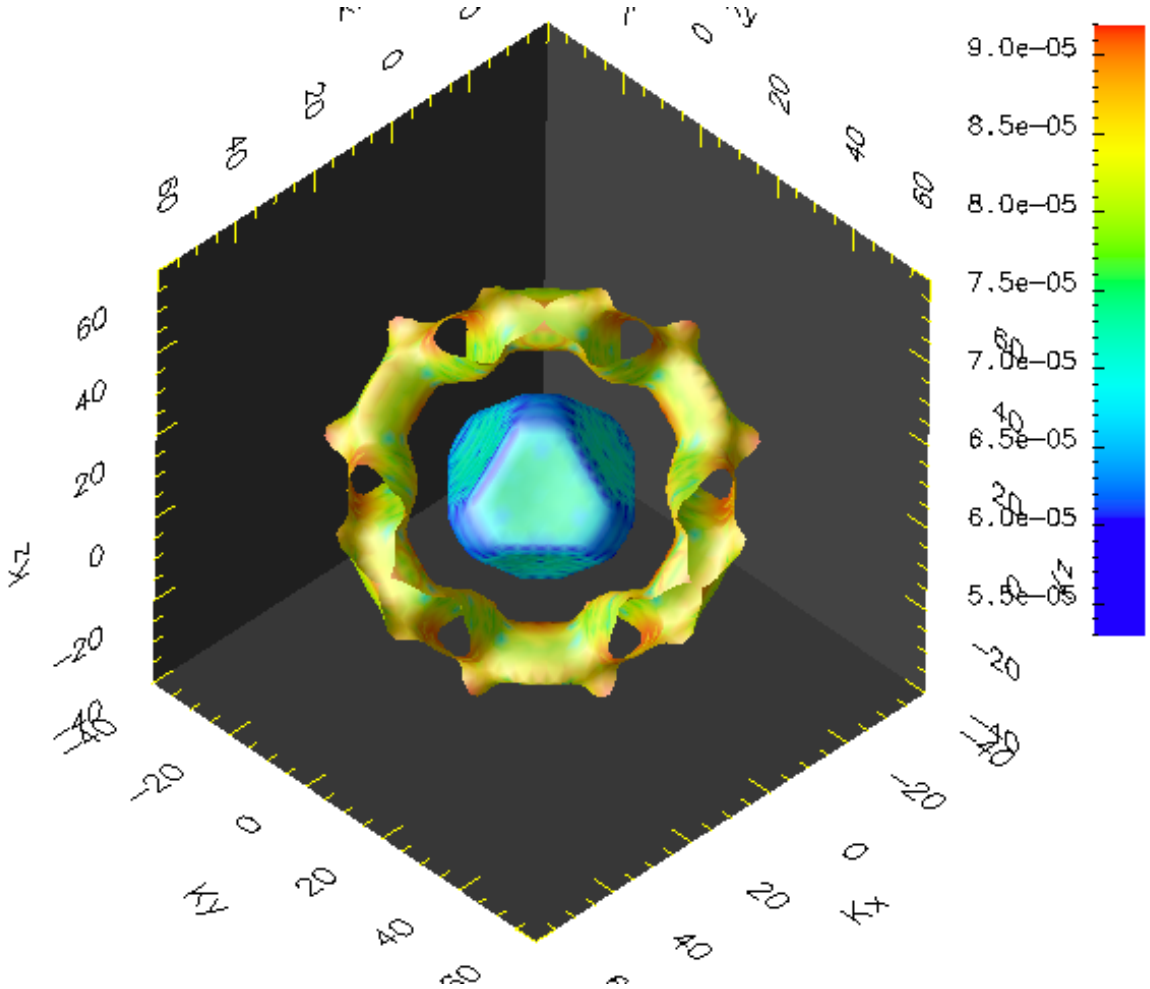


Fermi surface

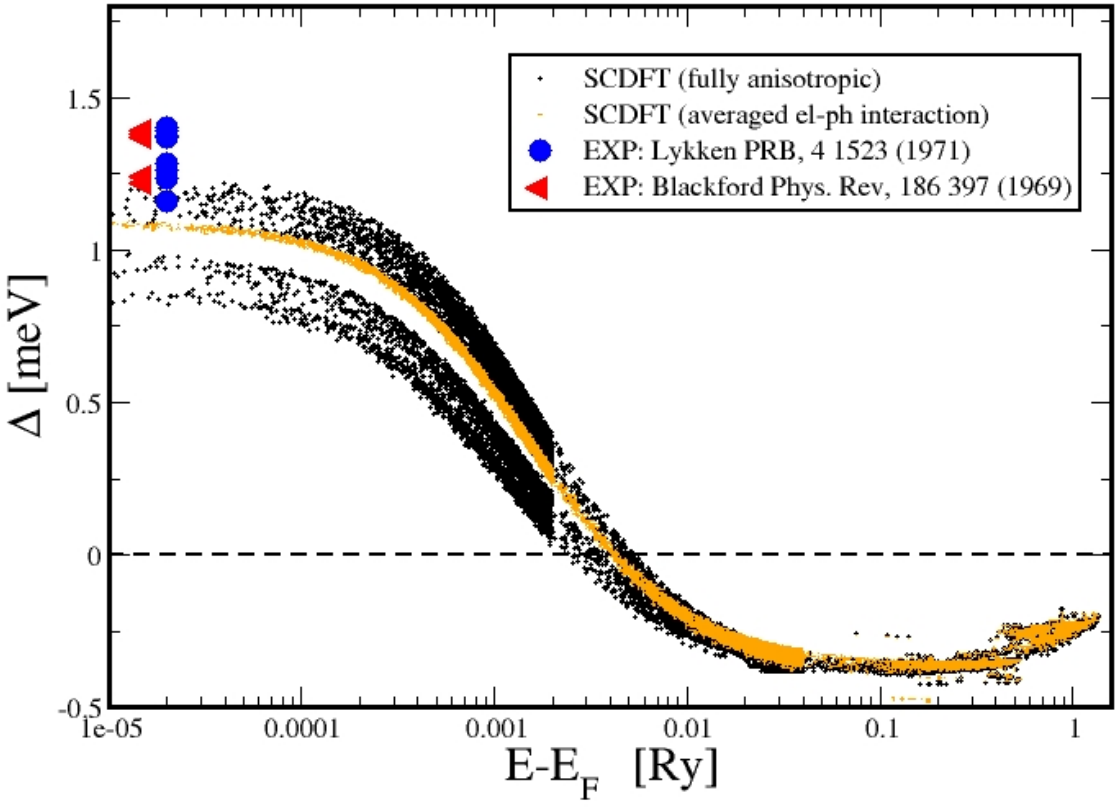


$$\lambda_{nk} = \sum_{n'k',\nu} \left| g^{\nu}_{nk,n'k'} \right|^2 \delta(\varepsilon_{nk} - E_F)\delta(\varepsilon_{n'k'} - E_F)/\Omega^{\nu}_{k'-k}$$

Gap on Fermi surface



Pb (Gap at T = 0.01 K)



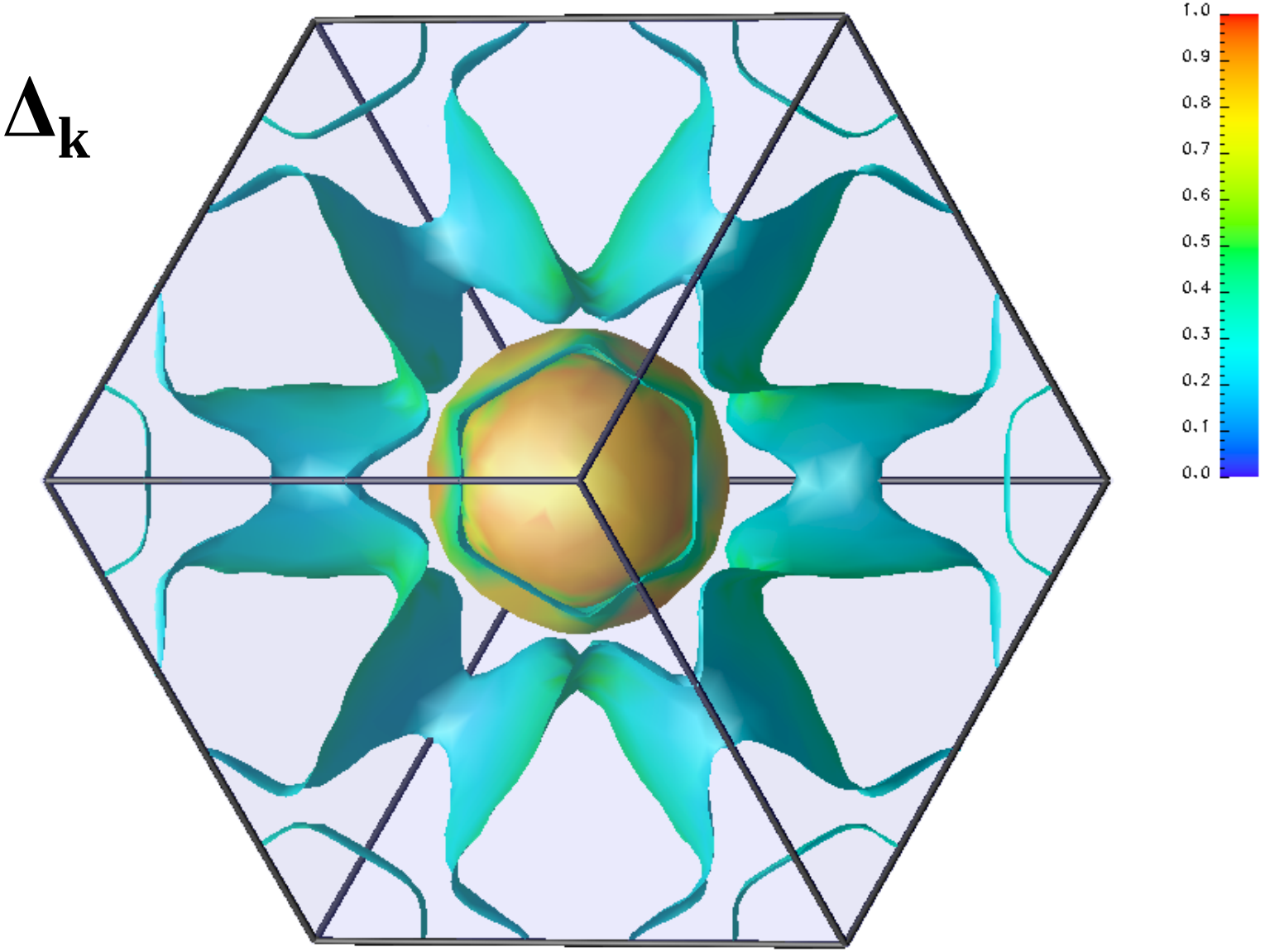
CaC_6

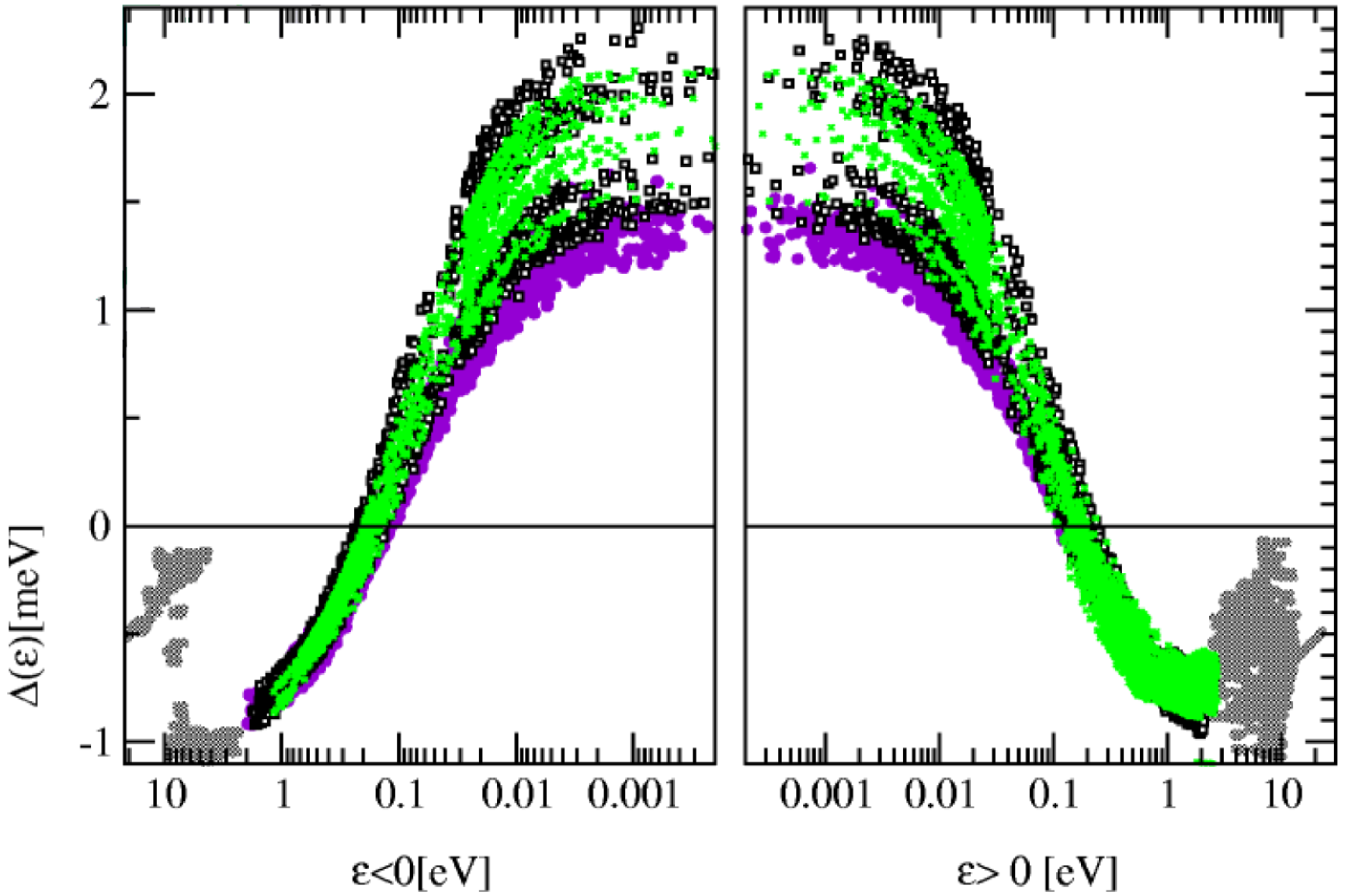
History:

Graphite doped with K (1965), Na (1986), Li (1989): $T_c \approx 1K$

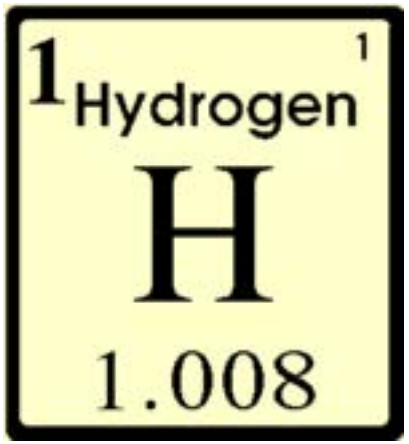
Graphite doped with Ca, Yb (2005):

CaC_6: $T_c = 11.5K$, YbC_6: $T_c = 6.5K$


Δ_k
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0



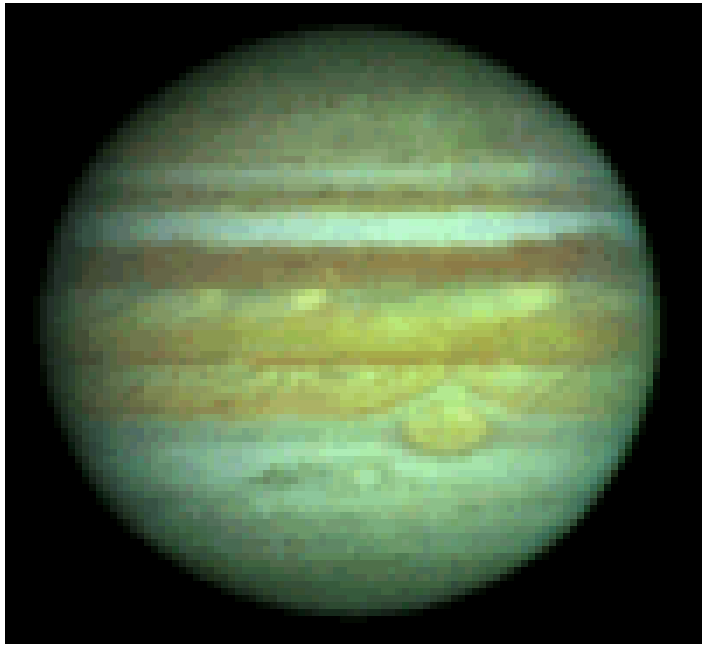
Calculated T_c: 9.5 K



How does hydrogen behave under extreme pressure?

- **Metallic phase?**
- **High-T_c superconductor?**

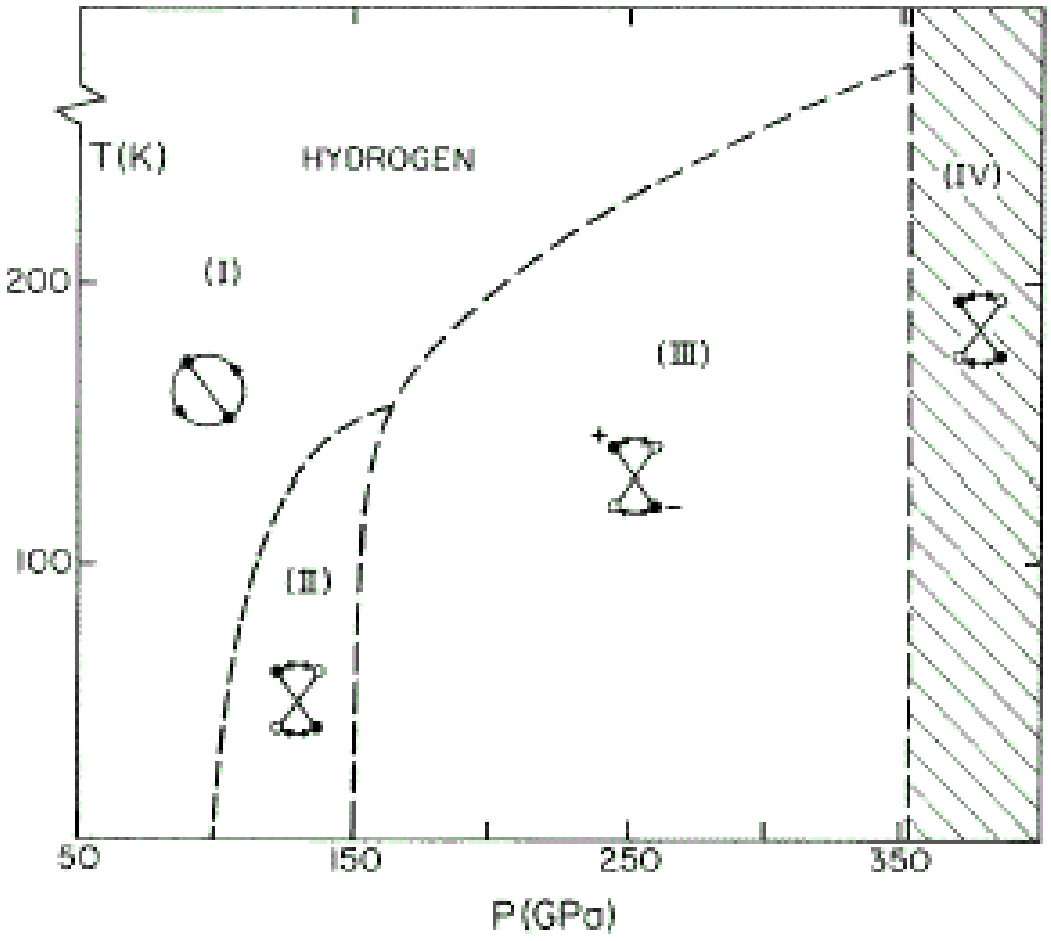
N.W. Ashcroft (1968); C.F. Richardson and N.W. Ashcroft, PRB (1996), K.A. Johnson and N.W. Aschcroft, Nature (2000); N.W. Ashcroft, J. Phys. C (2004)



The idea comes from Jupiter:

- 90% of Jupiter's mass is hydrogen
- extremely high magnetic field
  (suggesting large circulating currents)

In search for the metallic phase, experiments (on earth) showed so far only insulating phases



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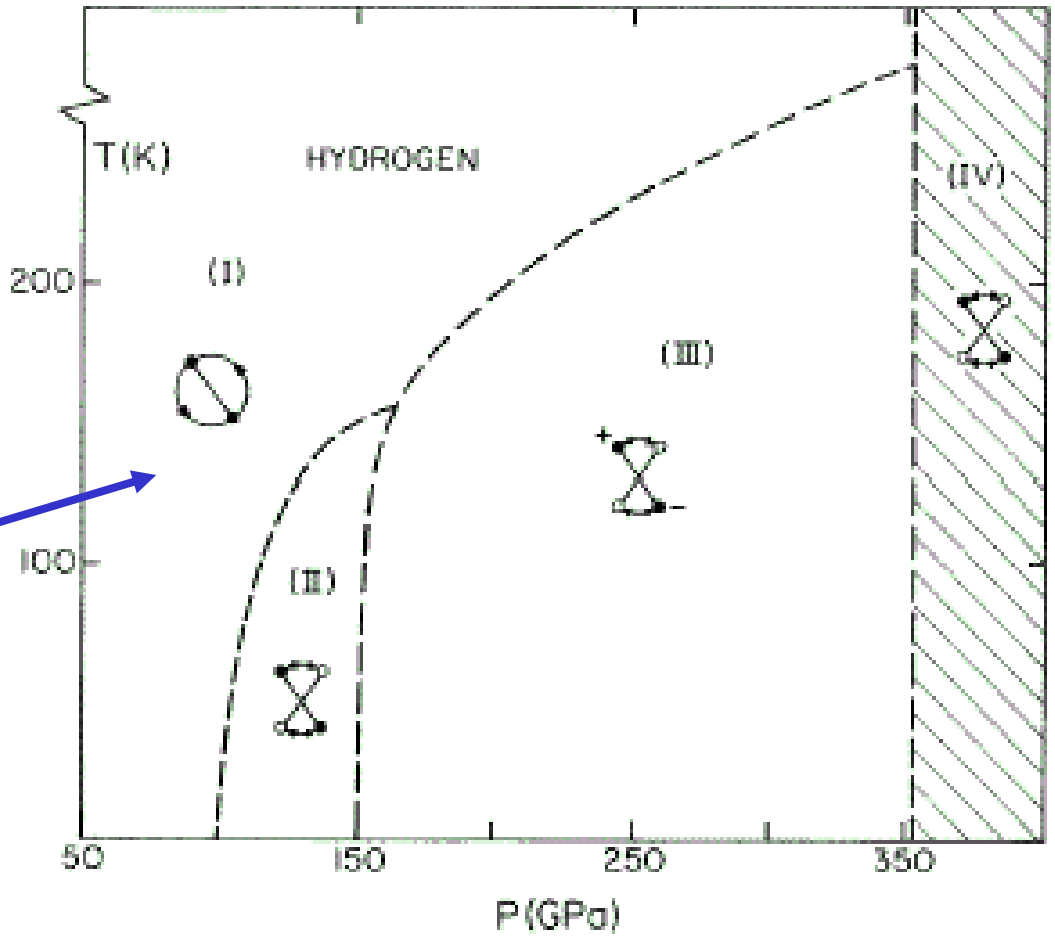

hcp: rotational disorder

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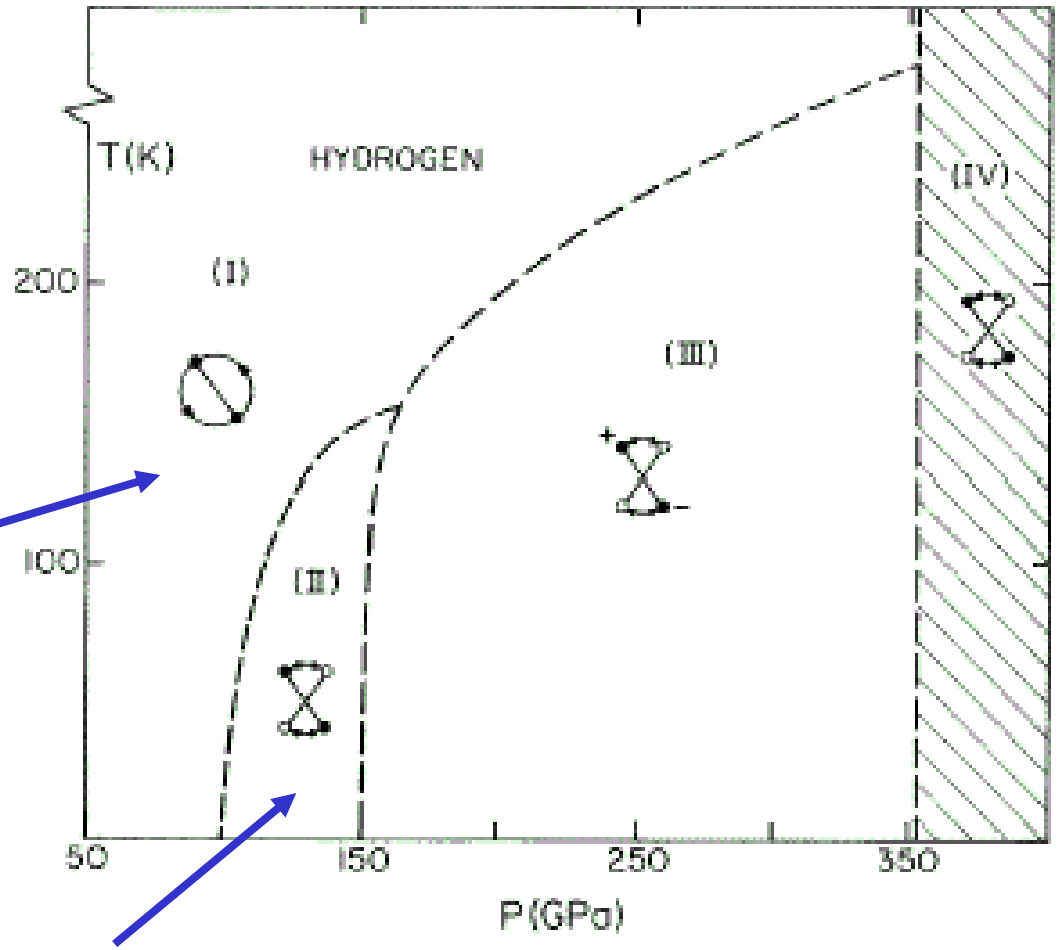

hcp: rotational disorder

rotational degrees of freedom frozen

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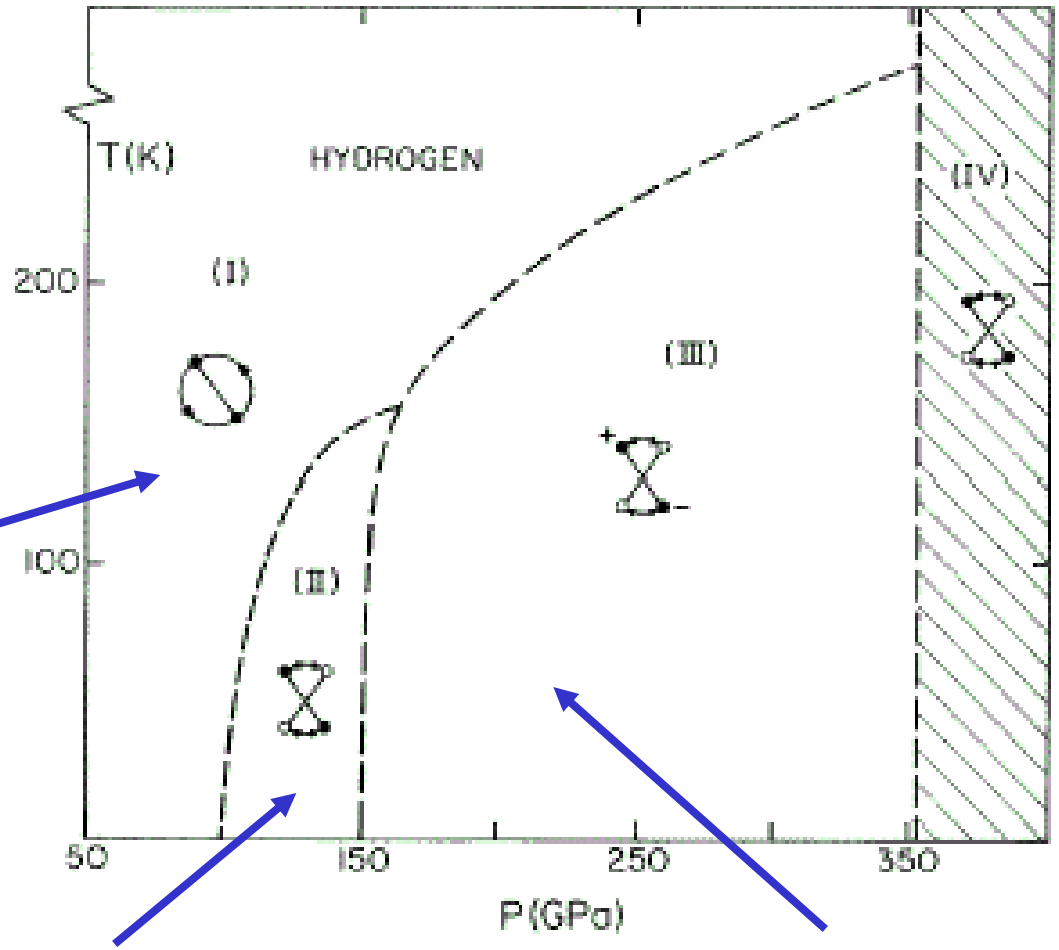

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still molecular crystal, increased IR activity

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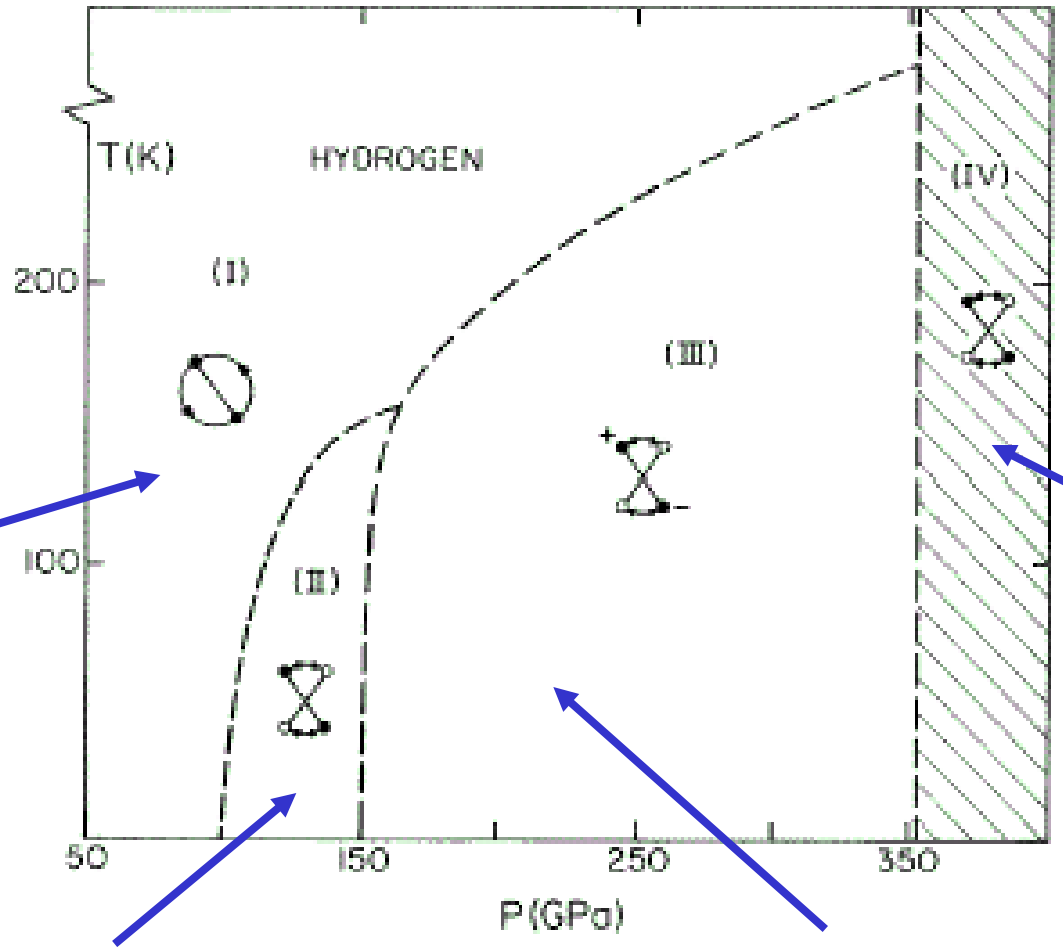

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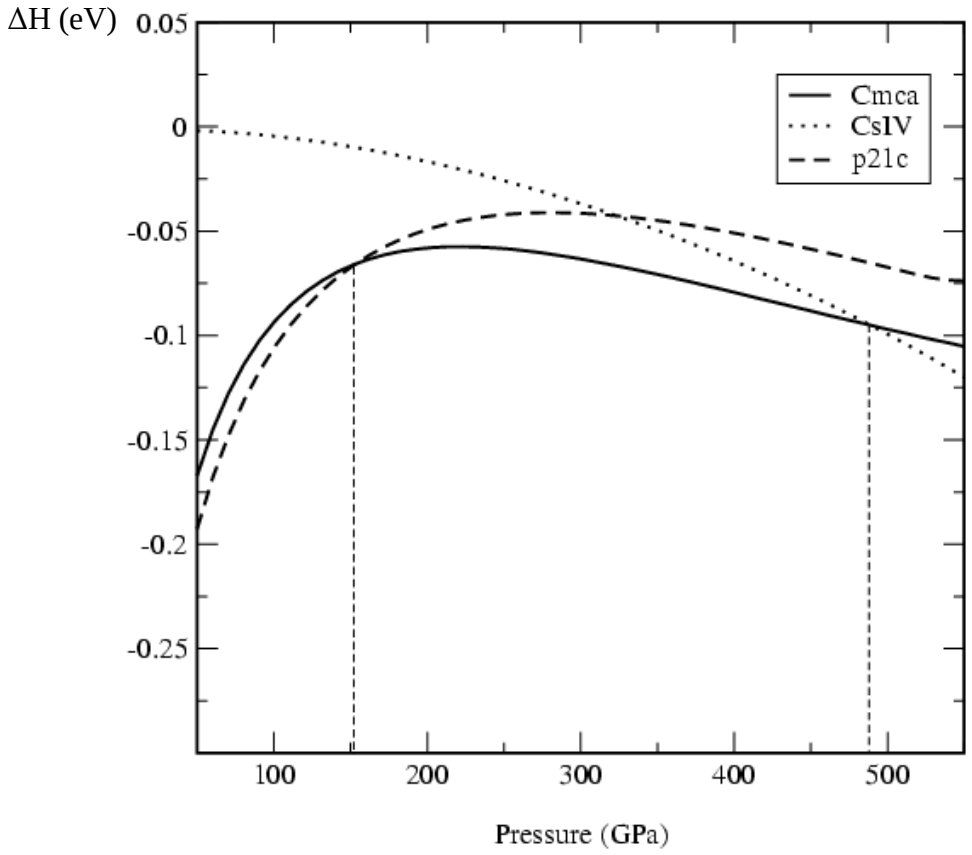
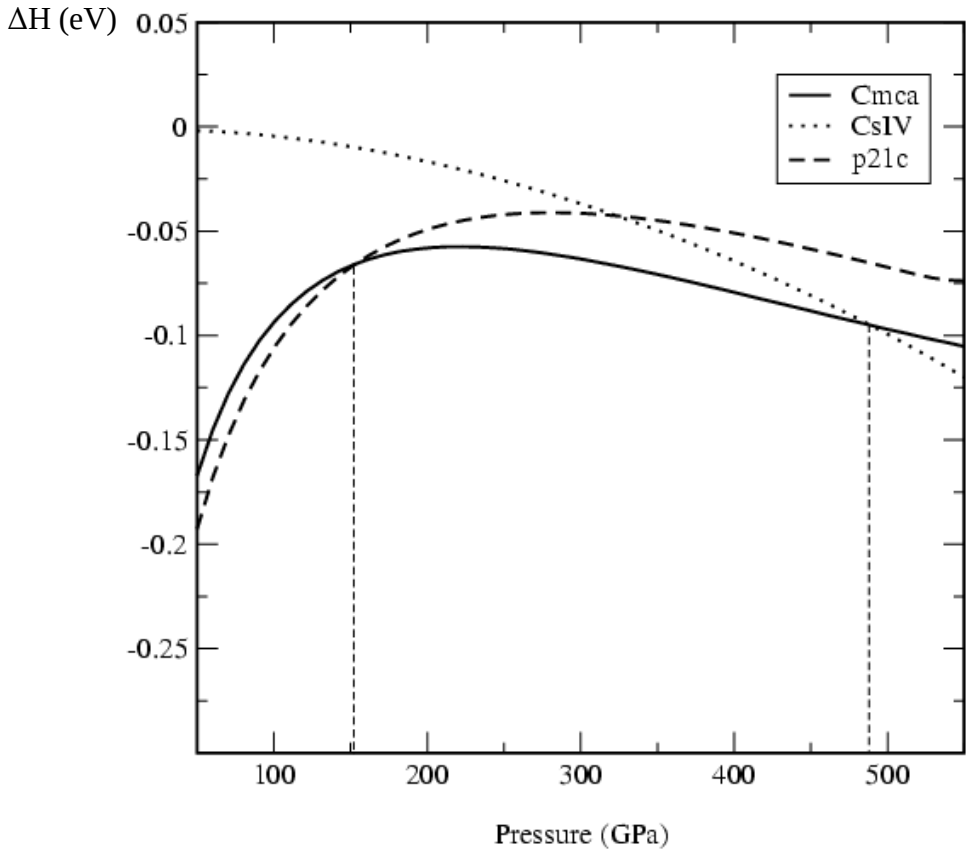
still molecular crystal, increased IR activity

Metallic phase??

Calculated phase diagram of hydrogen



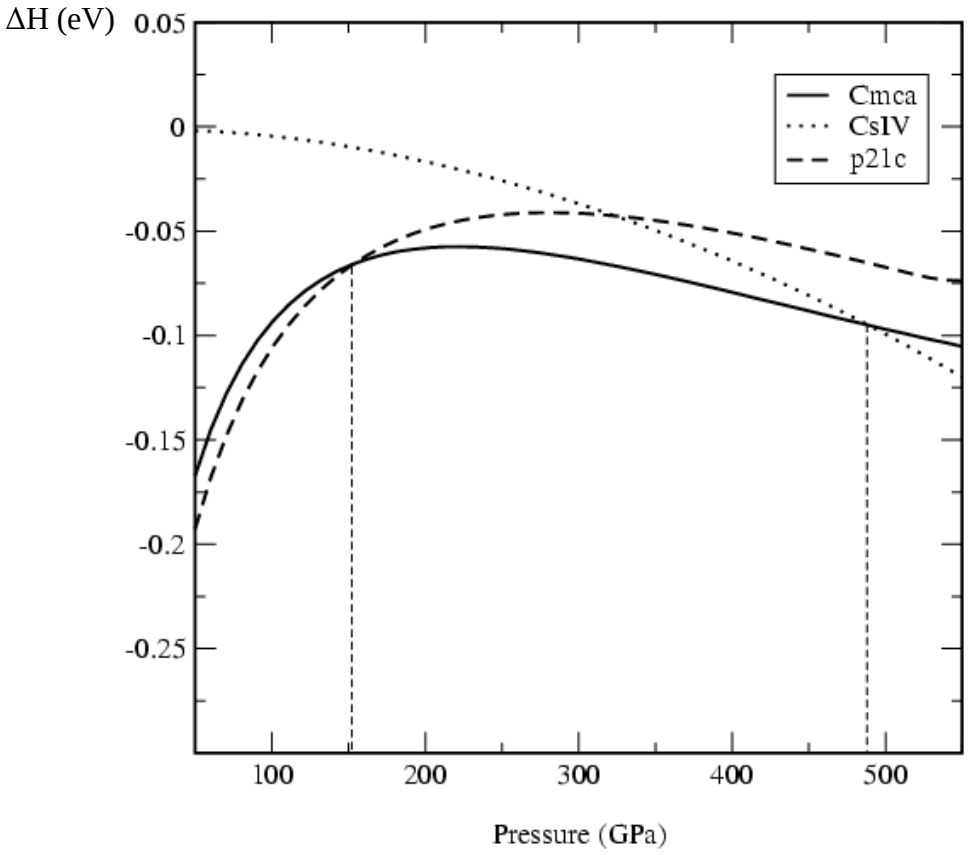
Calculated phase diagram of hydrogen



Molecular phase (Cmca) stable until ~ 500 GPa

C.J. Pickard R.J. Needs, Nature Physics **3**, 473 (2007)

Calculated phase diagram of hydrogen



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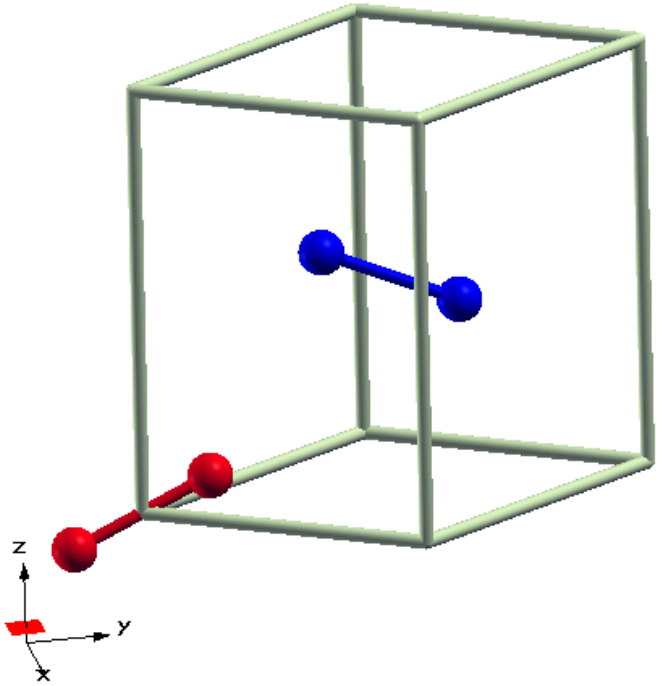
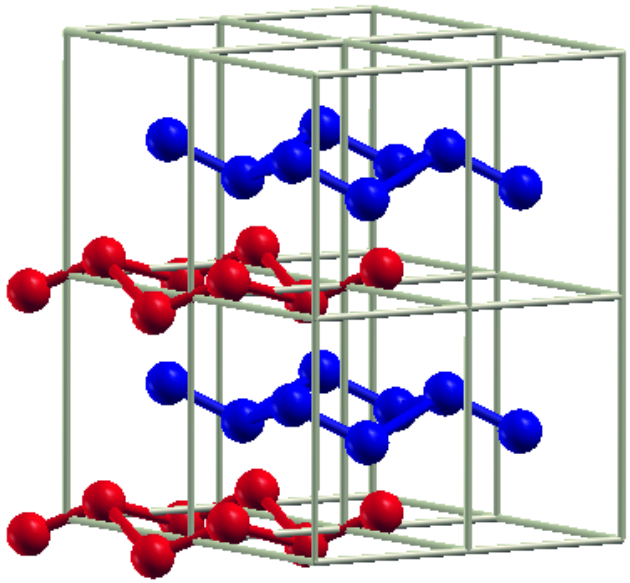
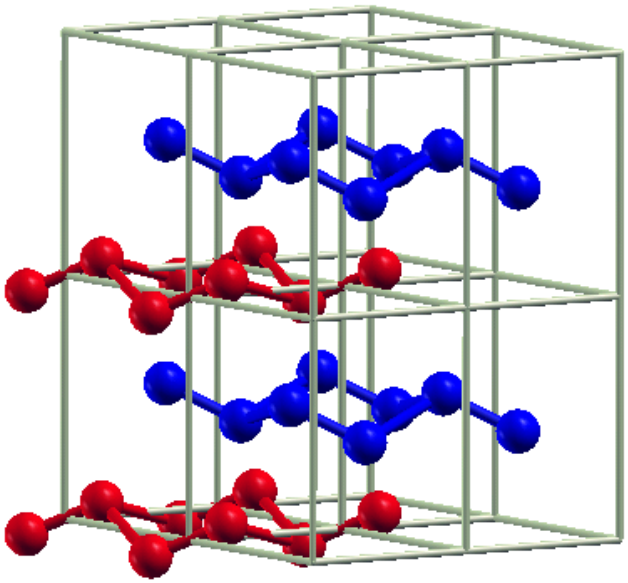
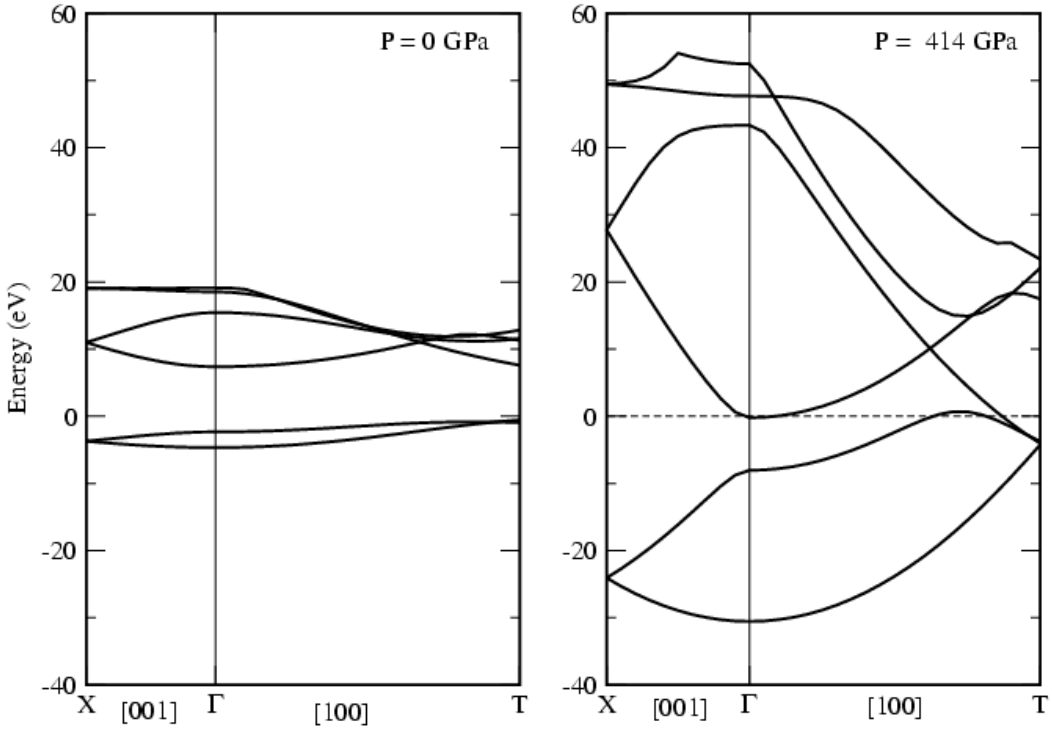




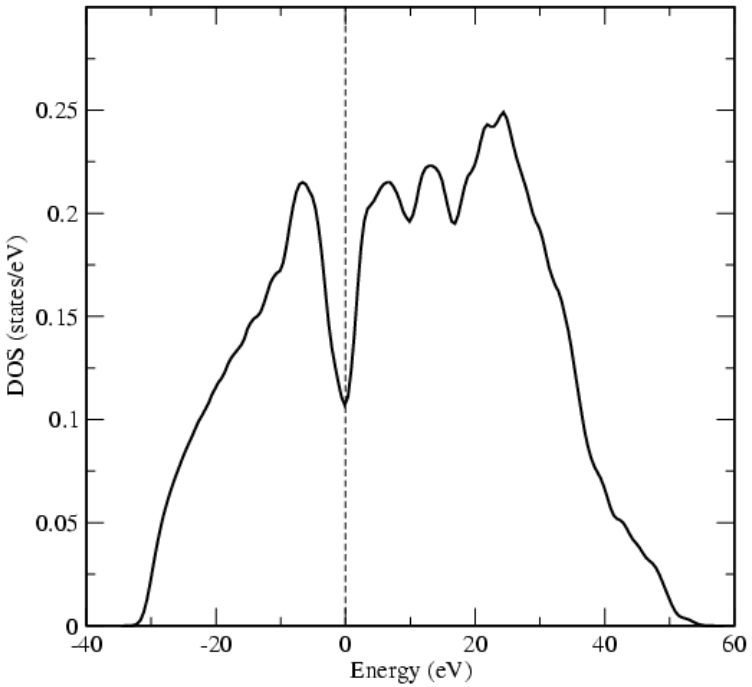
Band structure



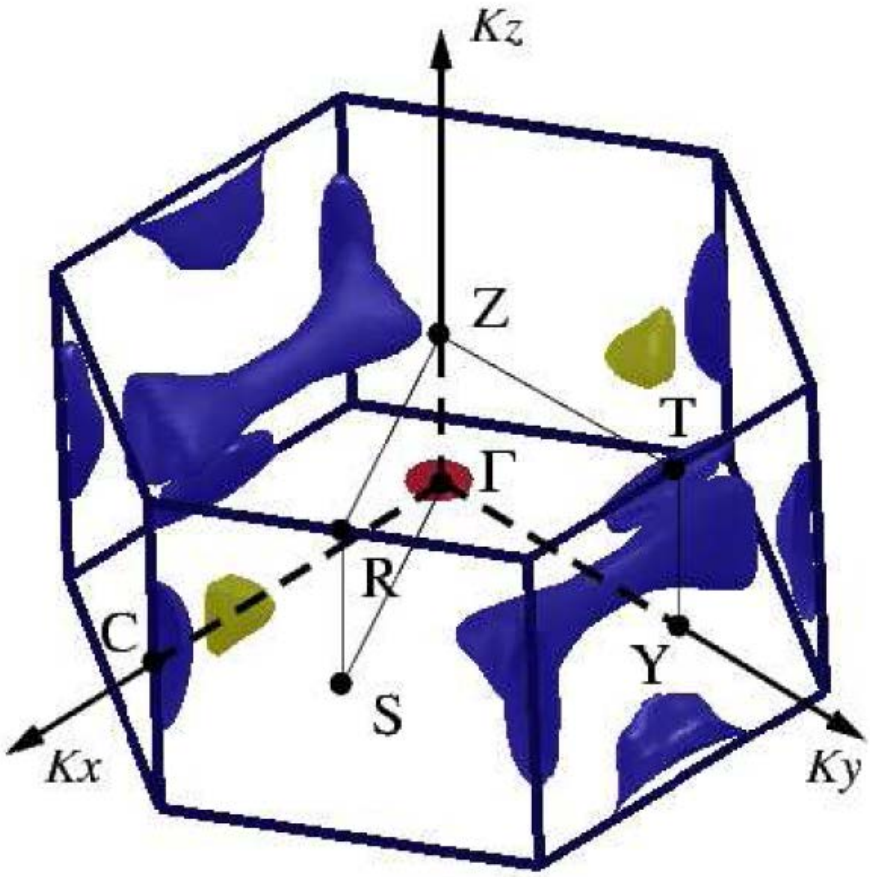


Band-overlap metallization found at P=400 GPa

M. Städele, R.M. Martin, PRL 84, 6070 (2000)

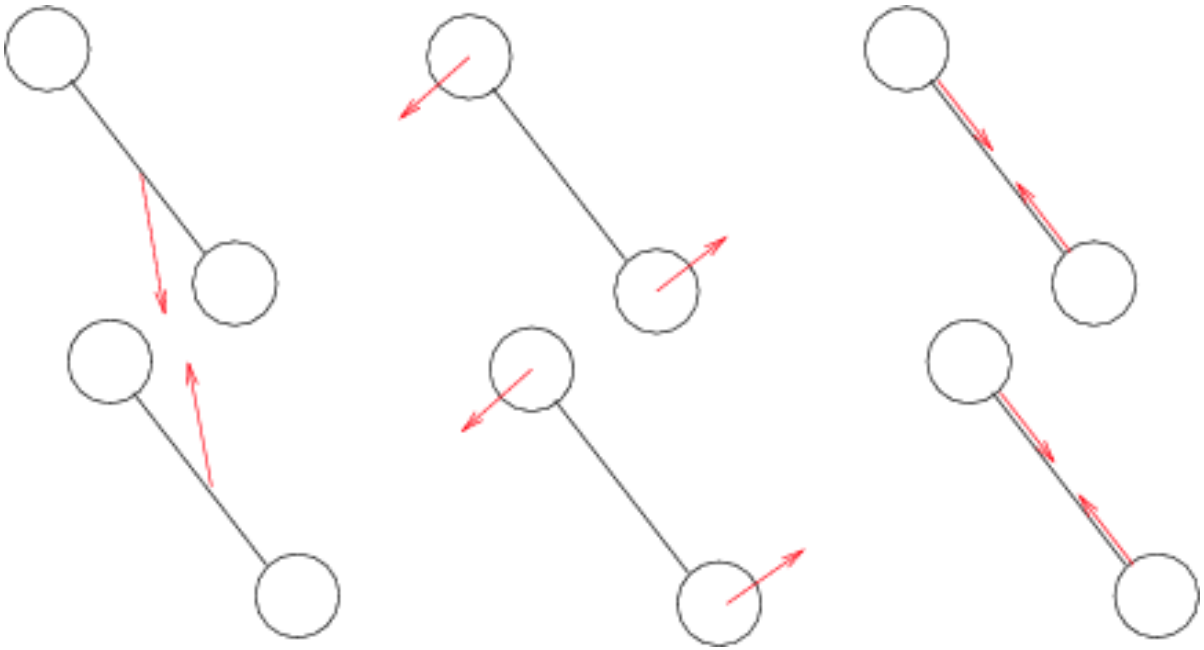


DOS at 414 GPa



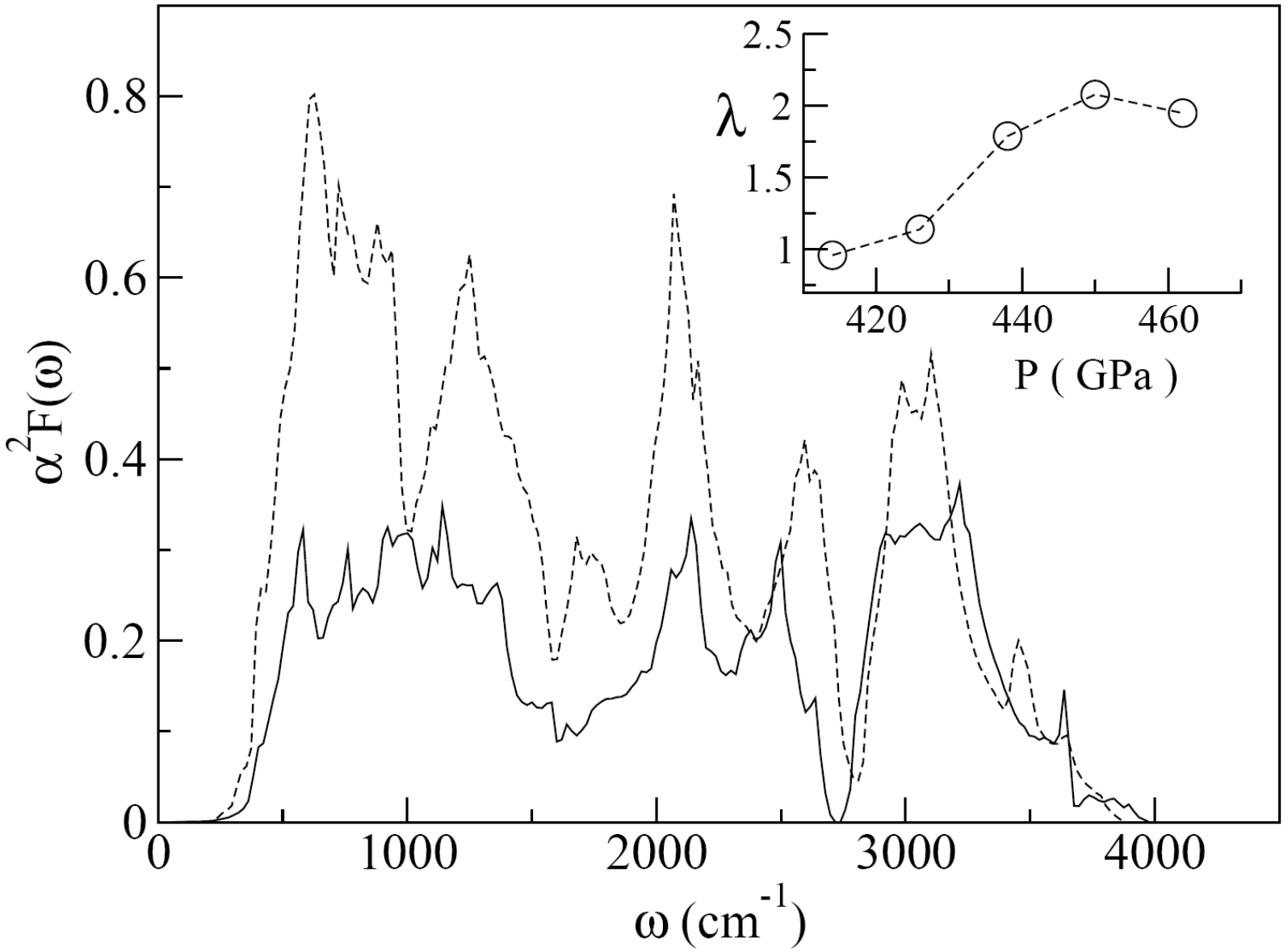
FS at 414 GPa

Three types of vibrational modes:



phononic libronic vibronic

$\alpha^2F(\Omega)$ at 414 (solid line) and 462 (dashed line) GPa.



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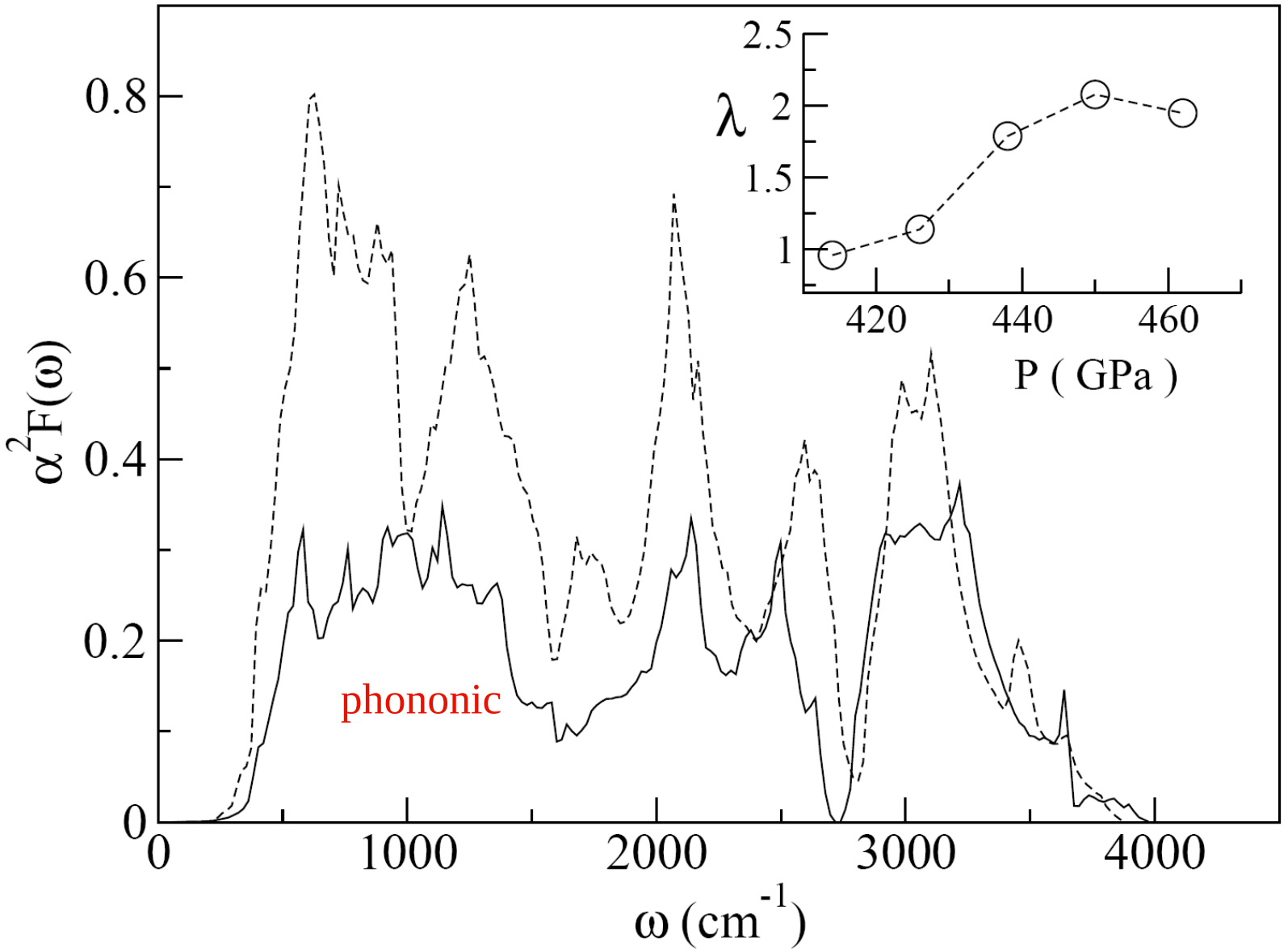

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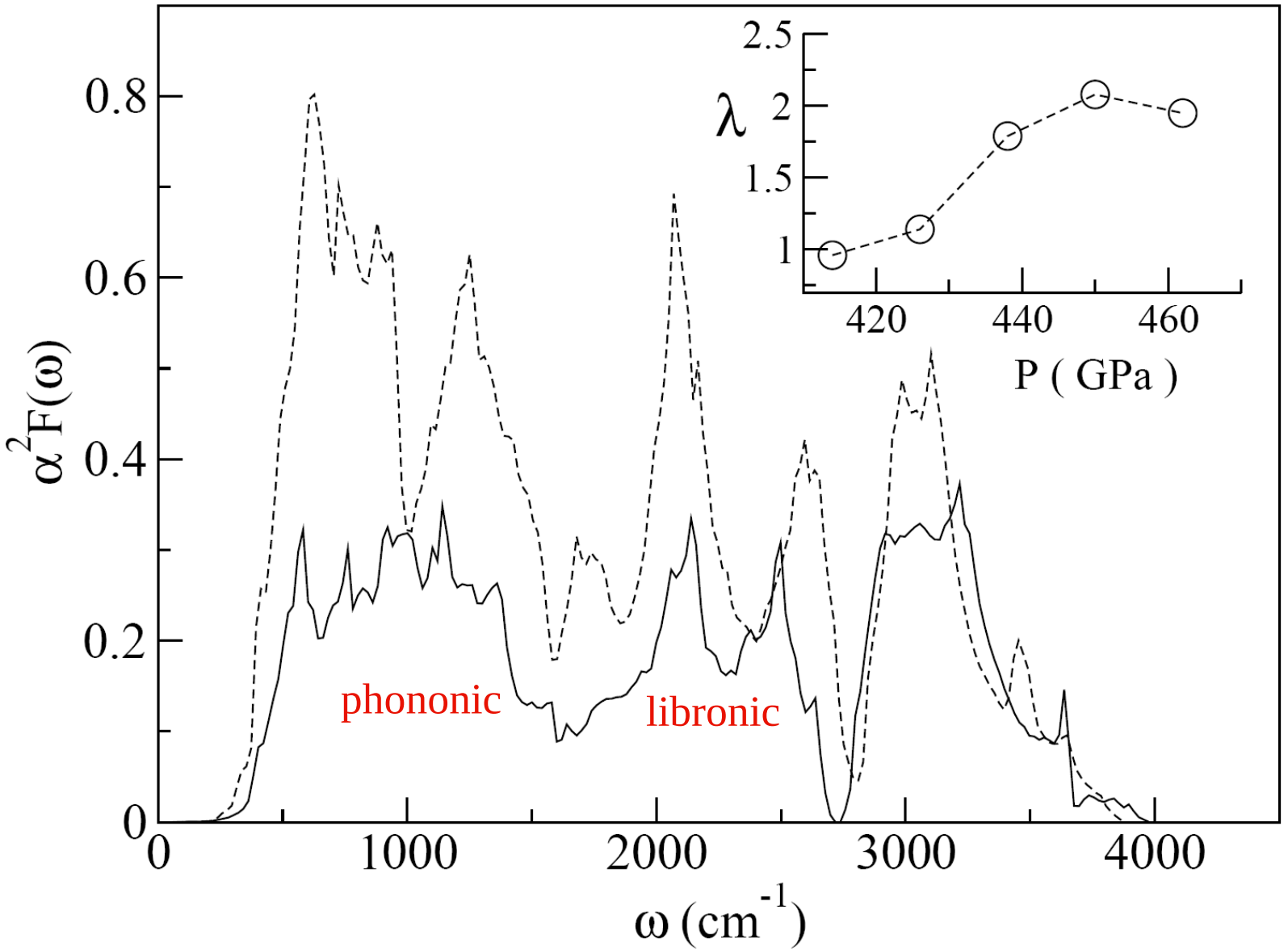

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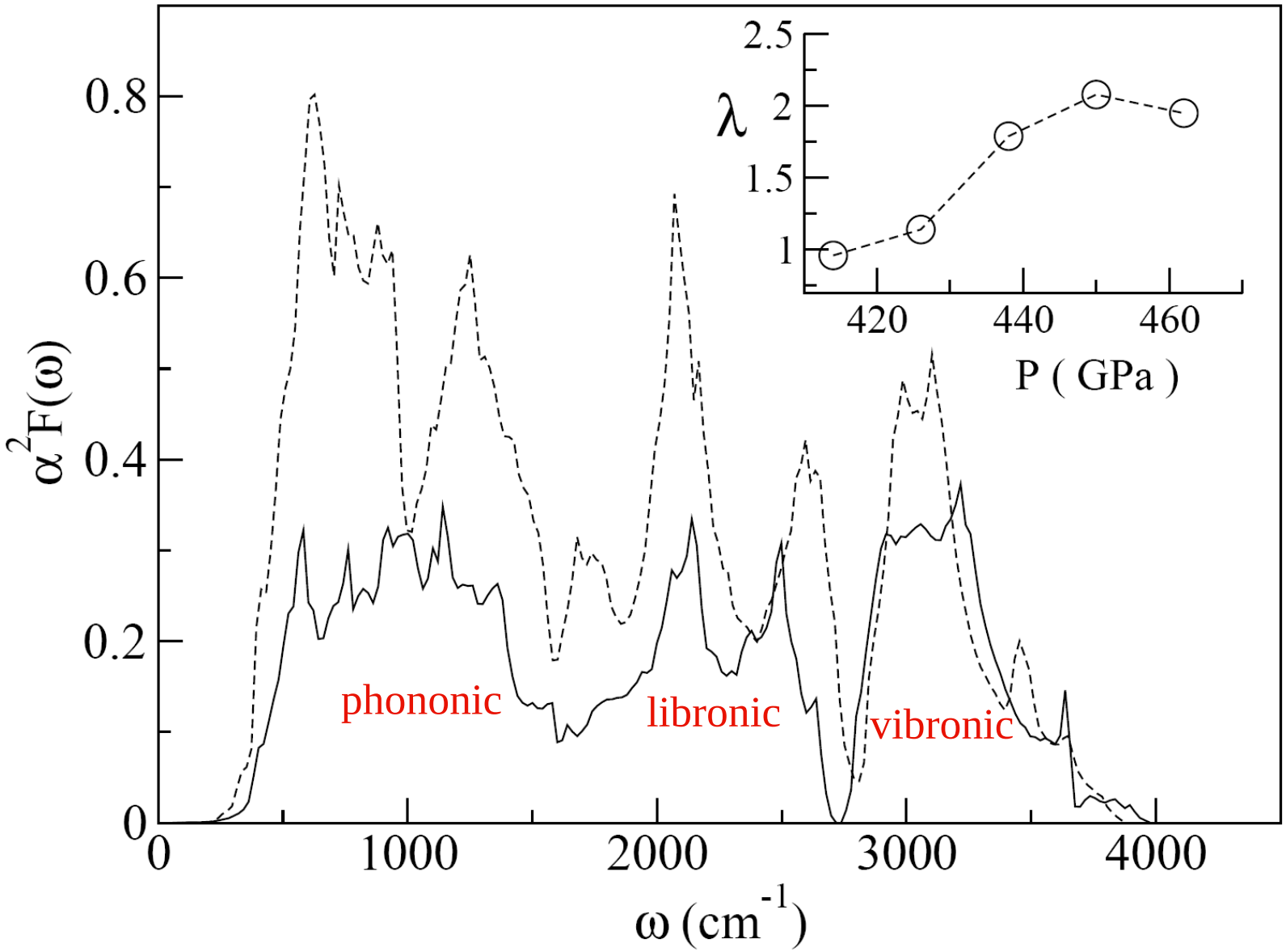
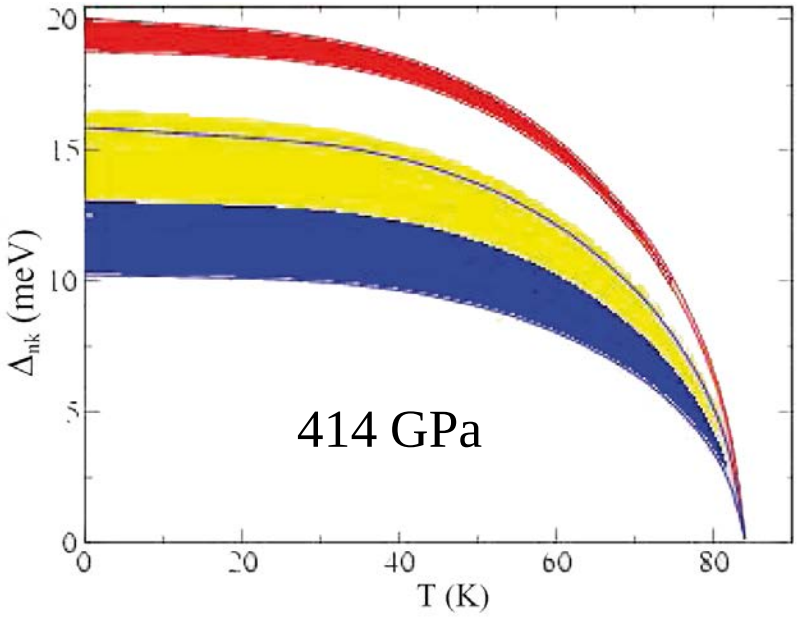
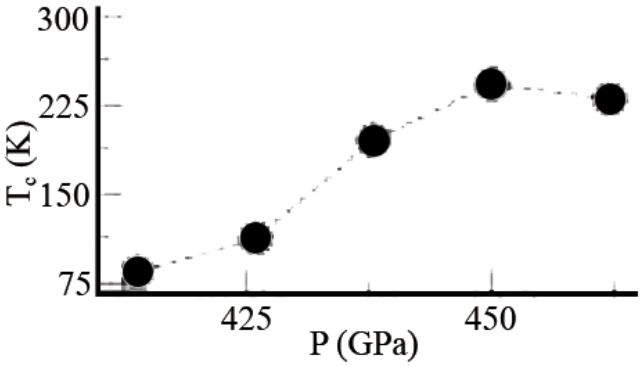


Hydrogen under extreme pressure





Predictions:

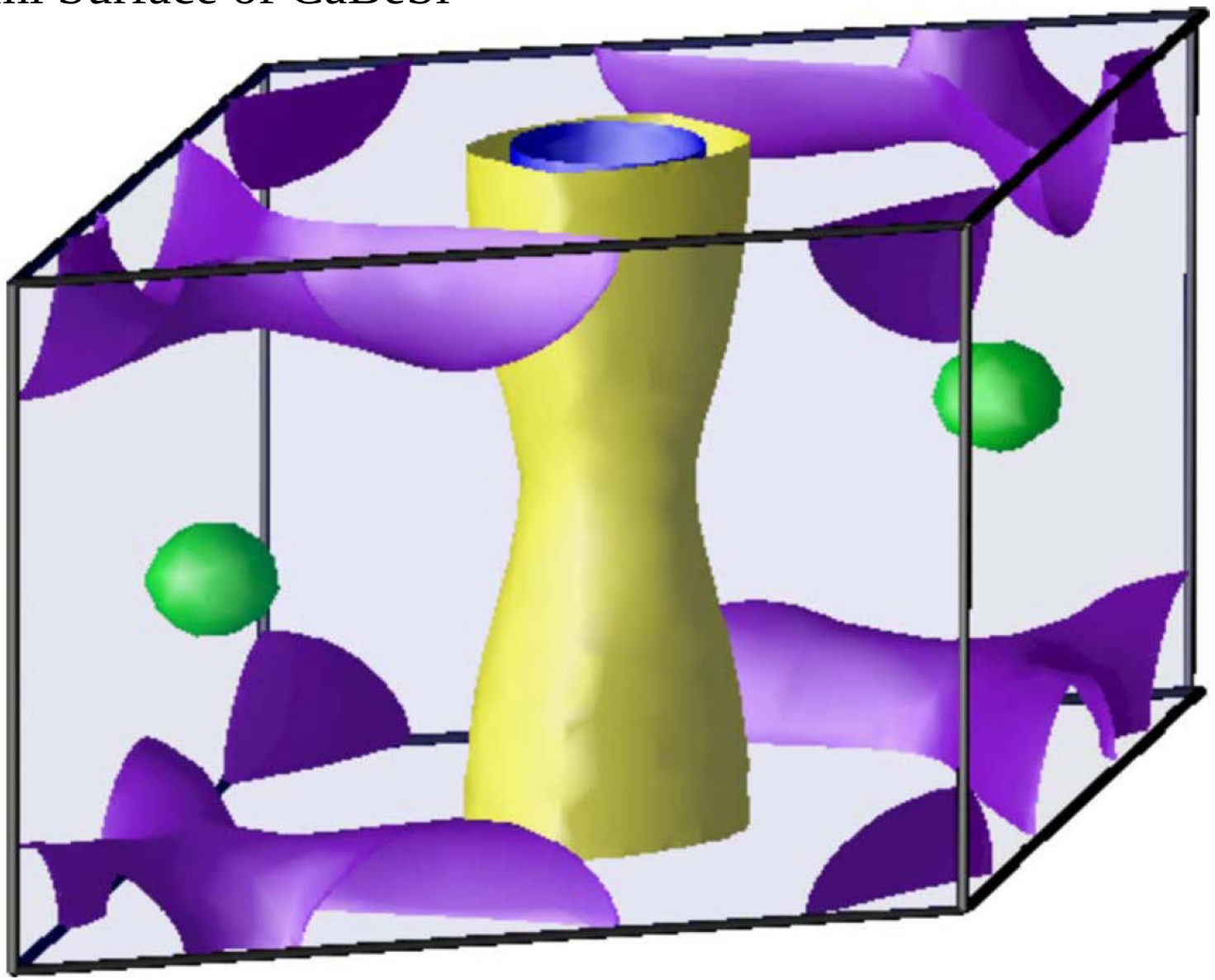
- Three-gap superconductivity
- Increase of T_c with increasing P until T_c ~ 242K at 450 GPa

P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, E.K.U.G., PRL 100, 257001 (2008)

Correlation of T_c with bonding properties (localization of σ charges)

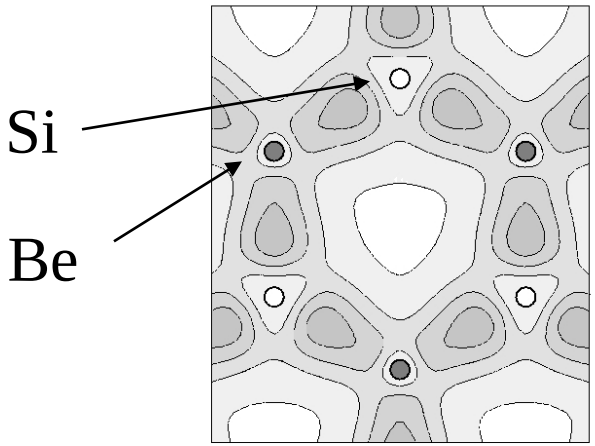
CaBeSi: T_c= 0.4 K (experiment and calculation)
CaBeB: T_c= 3.1 K (calculation)
MgB_2: T_c= 39.5 K (experiment and calculation)
LiBC: T_c= 75 K (calculation: Picket et al)

Fermi Surface of CaBeSi

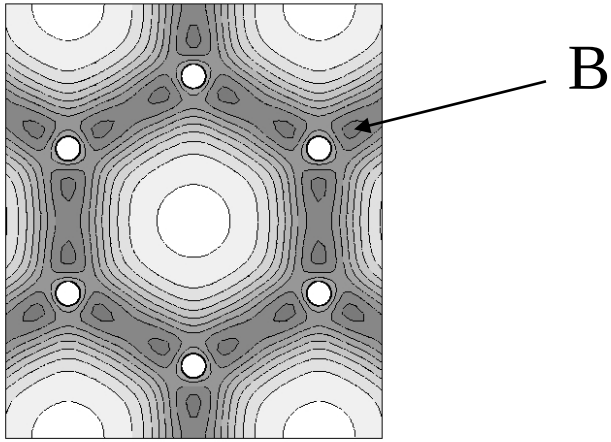


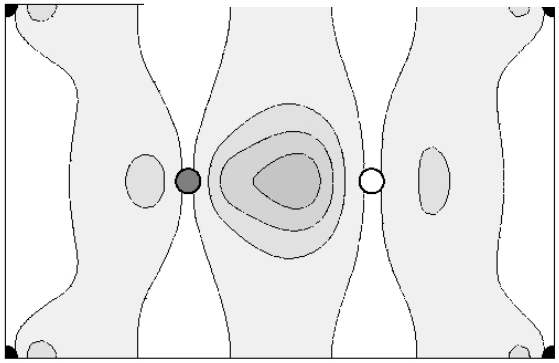
σ charge in CaBeSi vs MgB_2

C. Bersier, A. Floris, A. Sanna, G. Profeta, A. Continenza, EKUG, S. Massidda, Phys. Rev. B 79, 104503 (2009)

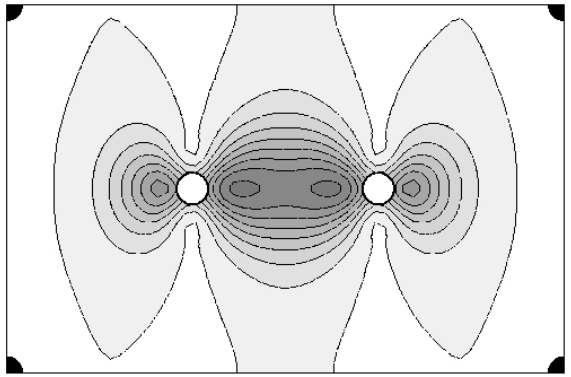


in plane





out of plane



CaBeSi

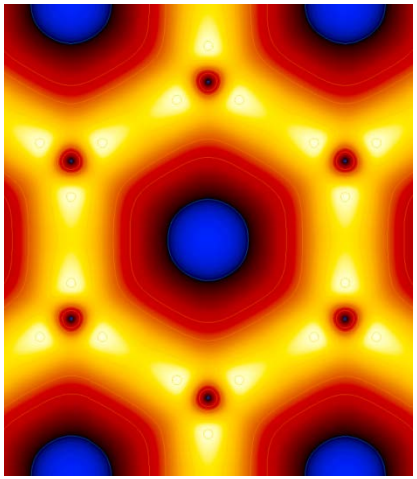
MgB2

In MgB_2 much stronger σ charge localization than in CaBeSi

Ab-initio calculation of SC order parameter χ(r,r') for MgB2

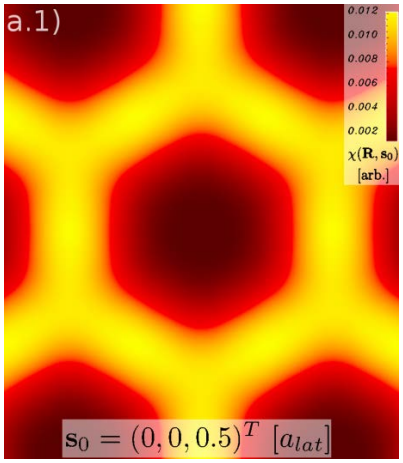
$\chi(r,r') \equiv \chi(R,s)$

$R = (r+r')/2,\ \ s = r-r'$

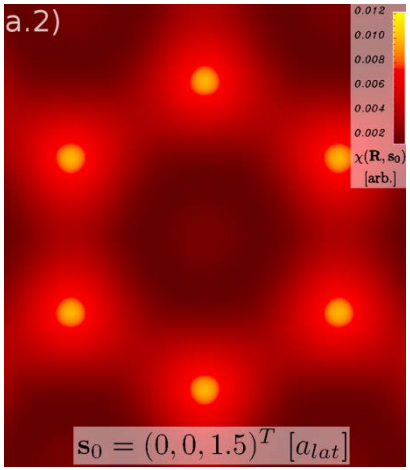


s = 0

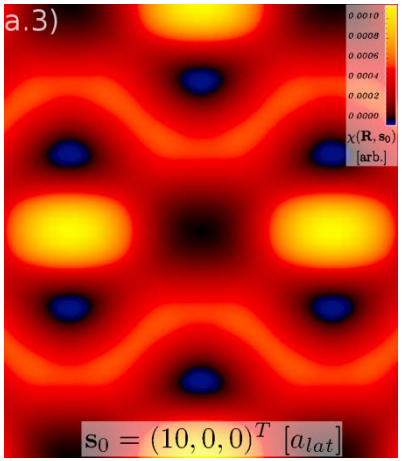
χ(R,s) as function of R for fixed s.



s = (0,0, 0.5)

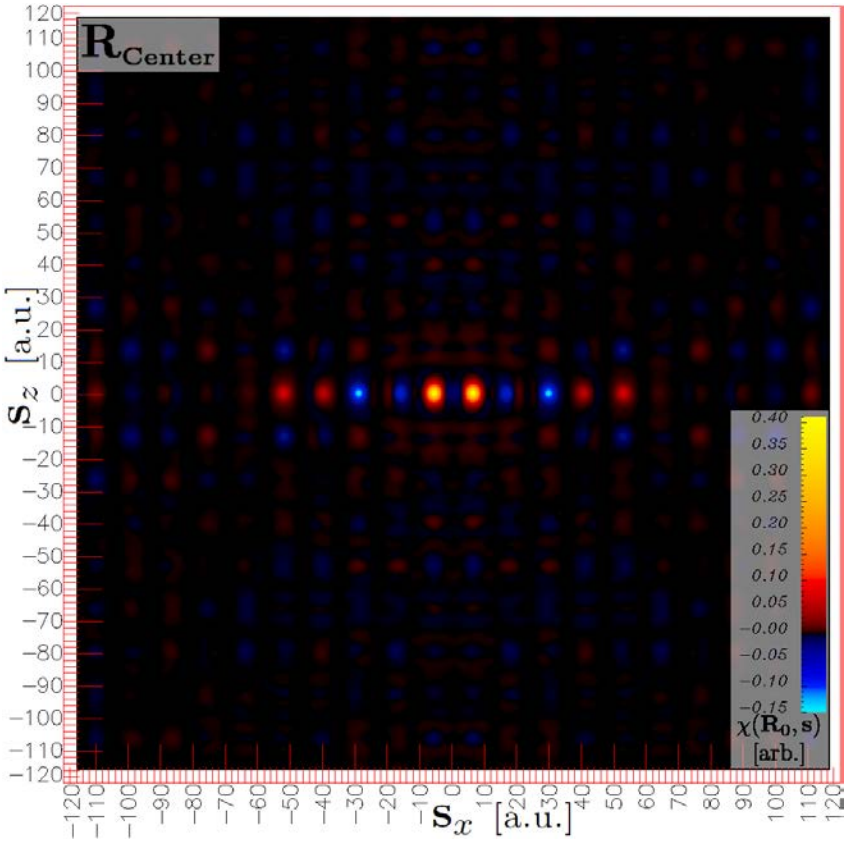


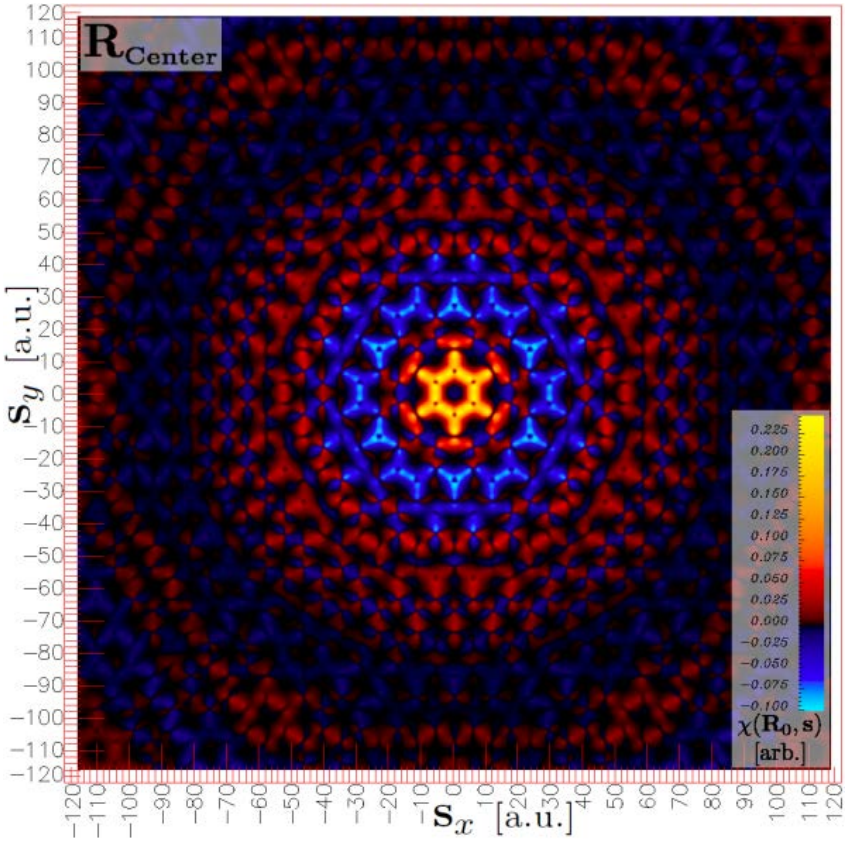
s = (0,0, 1.5)



s = (10,0,0)

χ(R,s) as function of s for fixed R (at center of B hexagon)

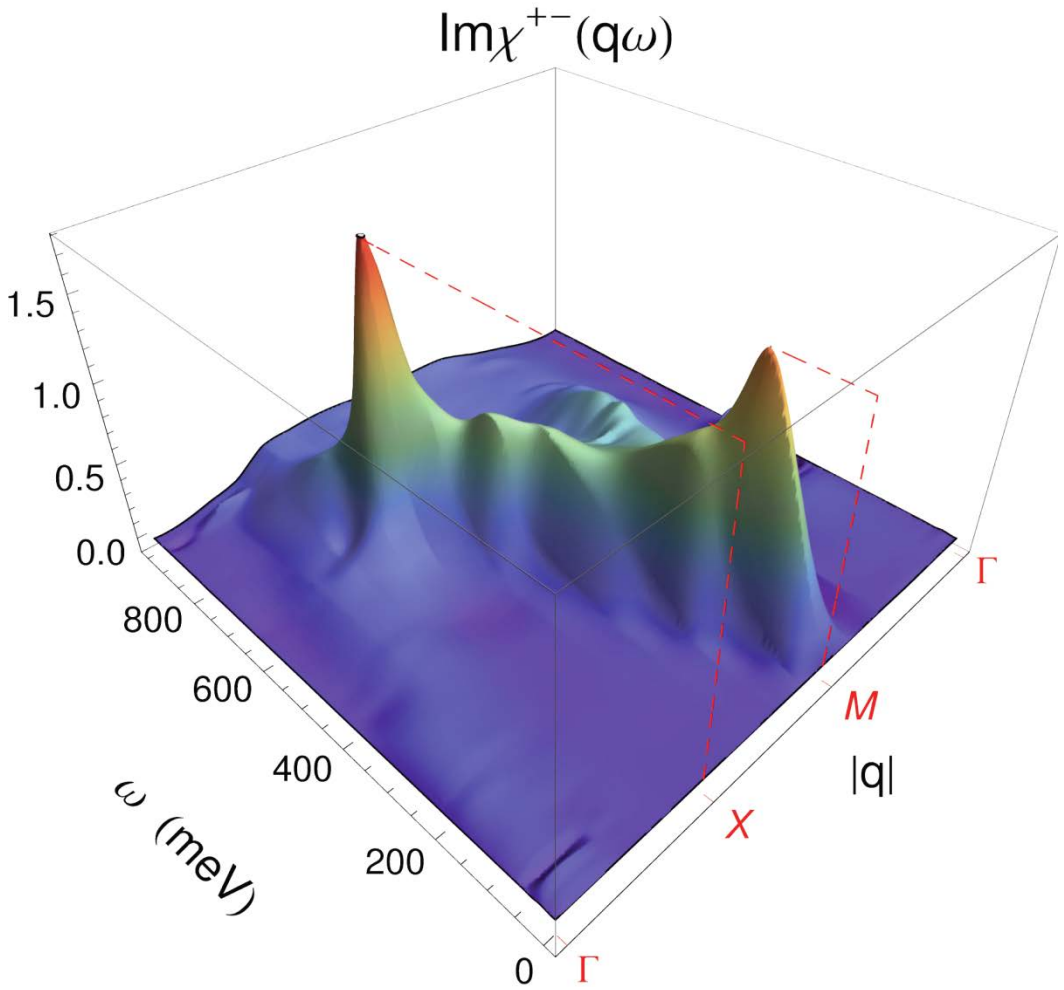




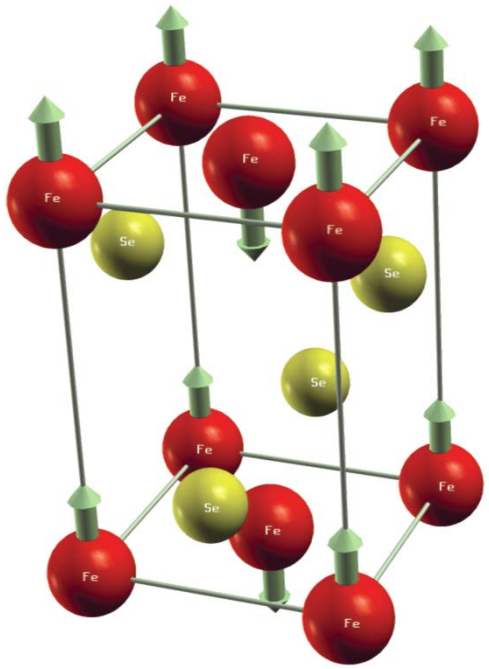
Description of pnictide superconductors

- **λ too small to allow for phononic mechanism**

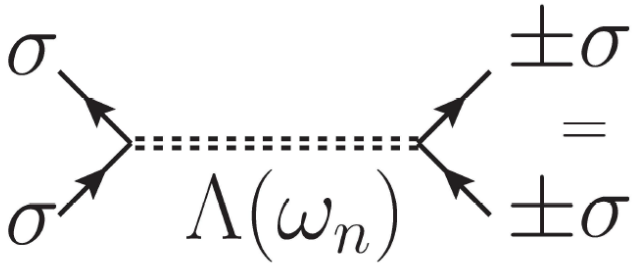
- **paramagnon suspected to be responsible for mechanism of superconductivity**



FeSe

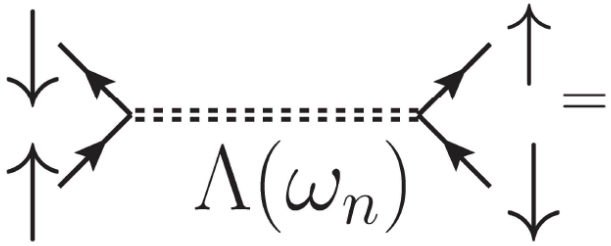


Spin-dependet effective interaction

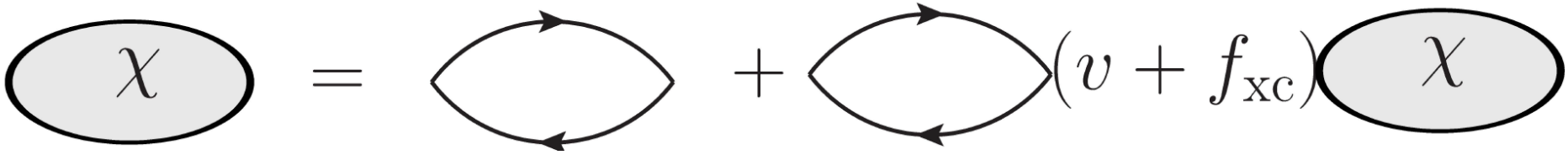


$$= \quad v \quad + \quad (v + f_{\rm xc}^{00})\chi_{00}(v + f_{\rm xc}^{00})$$

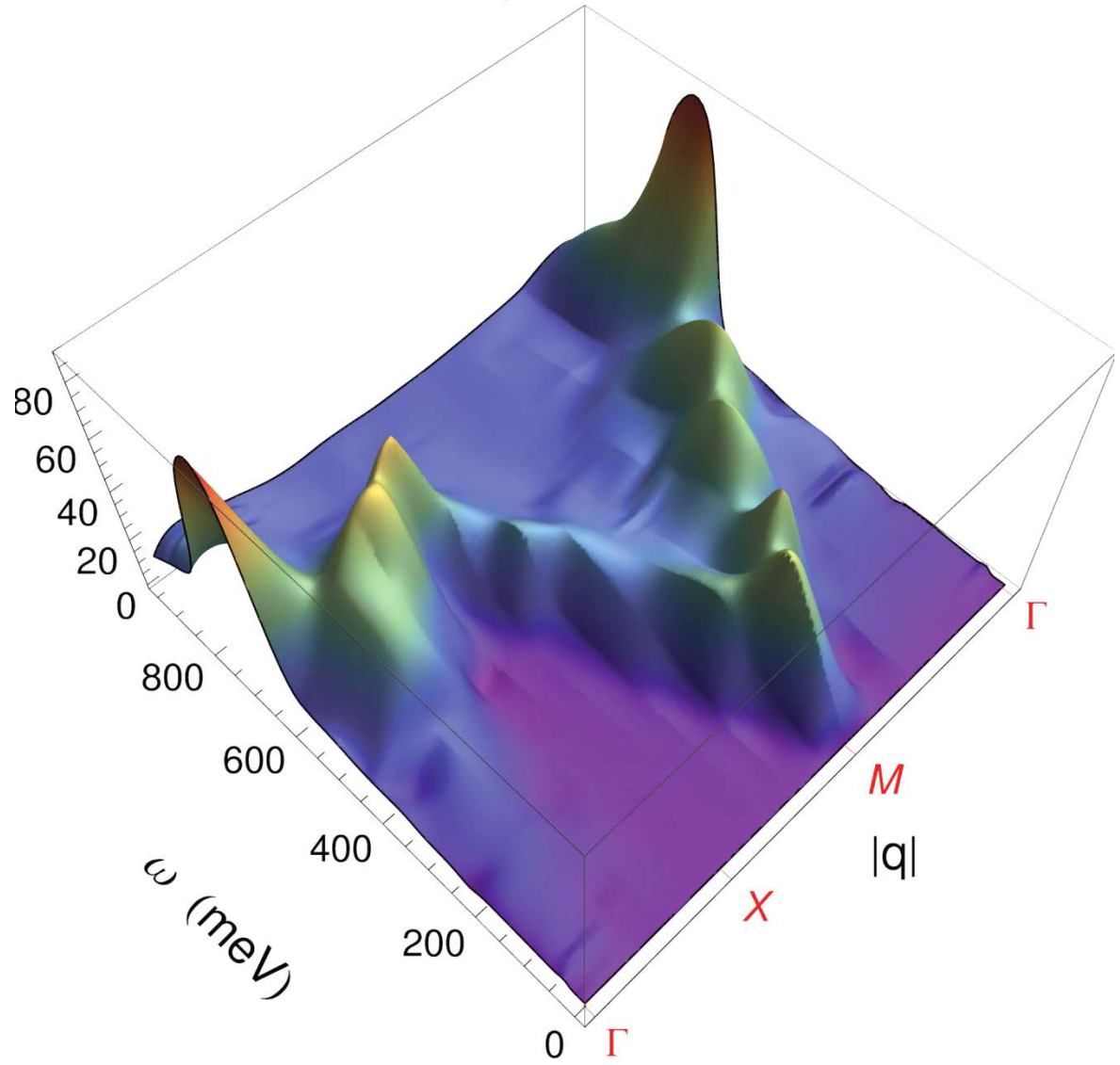
$$\pm \quad f_{\rm xc}^{zz}\chi_{zz}f_{\rm xc}^{zz}$$



$$= \quad f_{\rm xc}^{+-}\chi_{+-}f_{\rm xc}^{+-}$$



Use Λ as effective interaction in the gap equation


λ(qω) of χ+−
80
60
40
20
0
800
600
400
200
0
ω (meV)
Γ
X
M
Γ
|q|

SUMMARY of DFT for Superconductors

Coulomb and el-ph interactions enter the theory on the same footing

↓

no adjustable parameters, such as μ^*, are used

↓

TRUE AB-INITIO PREDICTION OF T_c AND Δ

Thanks !

Nanoquanta
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