# Electron-phonon calculations for metals, insulators, and superconductors

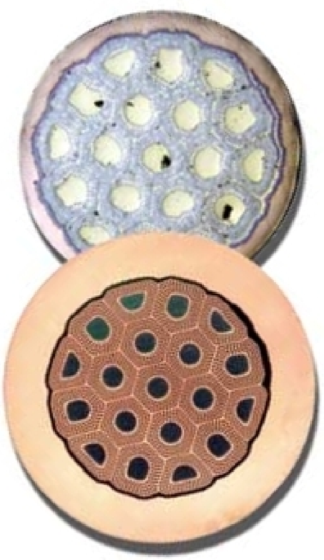
Feliciano Giustino

Department of Materials, University of Oxford

## Metals

## Insulators

## Superconductors

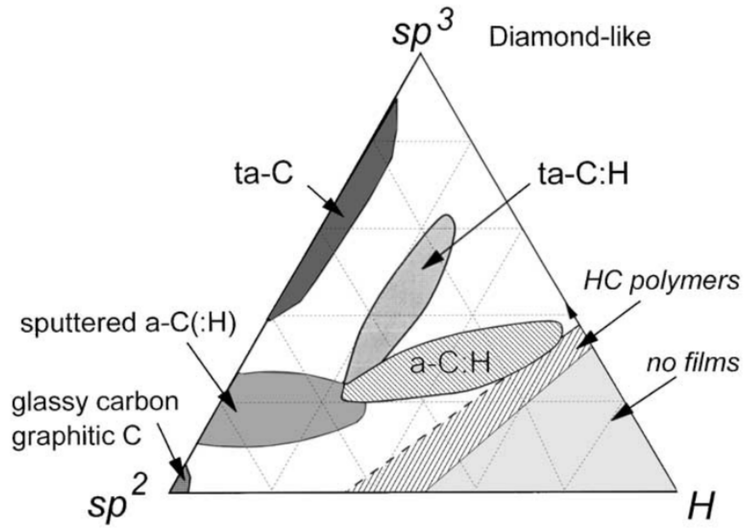


6

**C**

Carbon

12.01




J Robertson, Mat Sci Eng 2002

TABLE II. Radii (in atomic units) for maxima in radial wave functions of atomic C, Si, and Ge. The values $r_s$ and $r_p$ are for valence $s,p$ orbitals of the $s^1p^3$ atomic configuration. The value $r_d$ is for the $d$ orbital of the $s^1p^2d^1$ atomic configuration.

| | $r_s$ | $r_p$ | $r_d$ |
|---|---|---|---|
| C | 1.21 | 1.21 | 8.51 |
| Si | 1.75 | 2.13 | 4.89 |
| Ge | 1.76 | 2.14 | 6.25 |

MT Yin & ML Cohen, PRL 1983

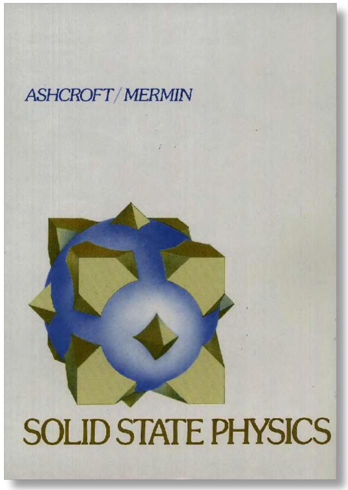
Metals

Insulators

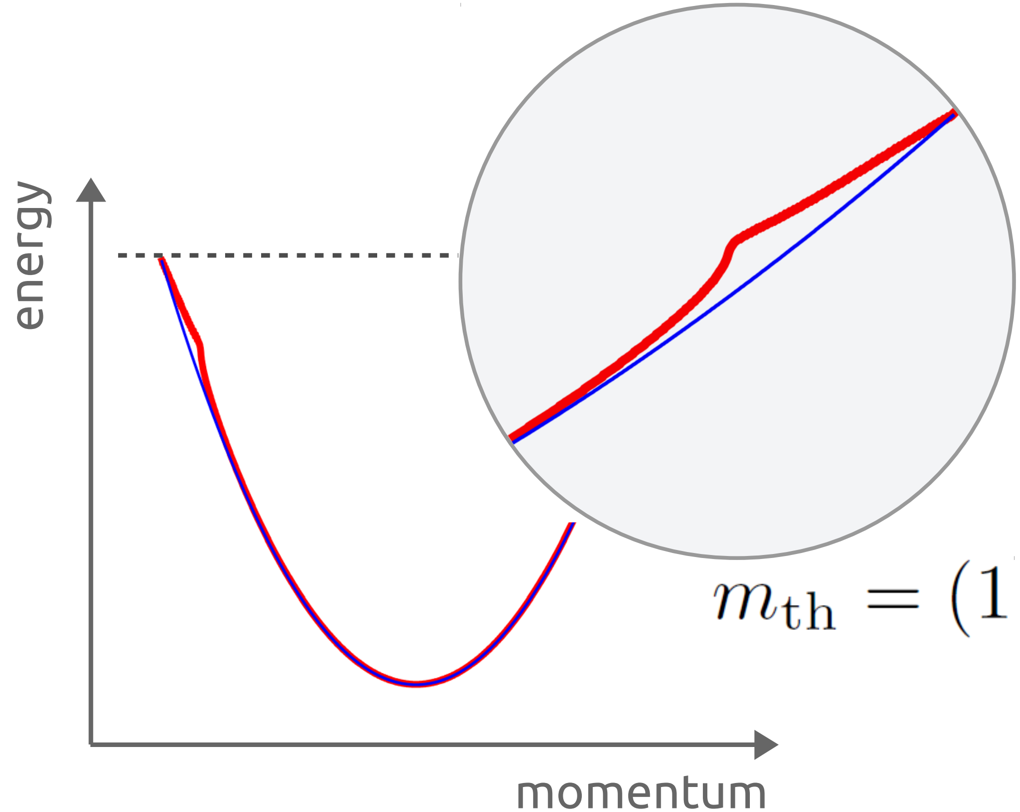
Superconductors

# Mass enhancement in **metals**

low-T heat capacity

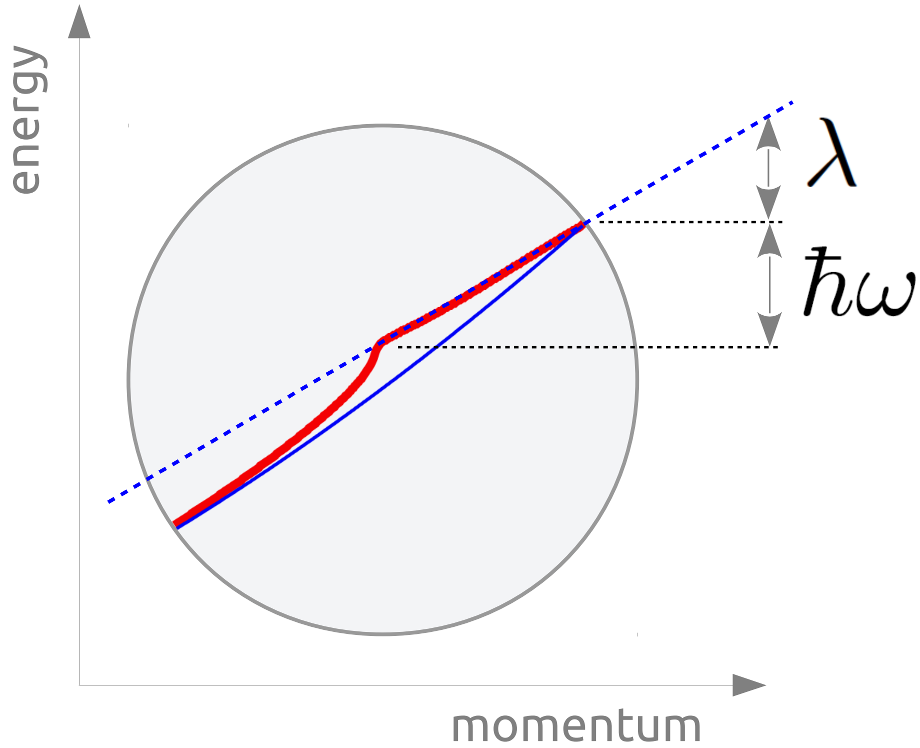


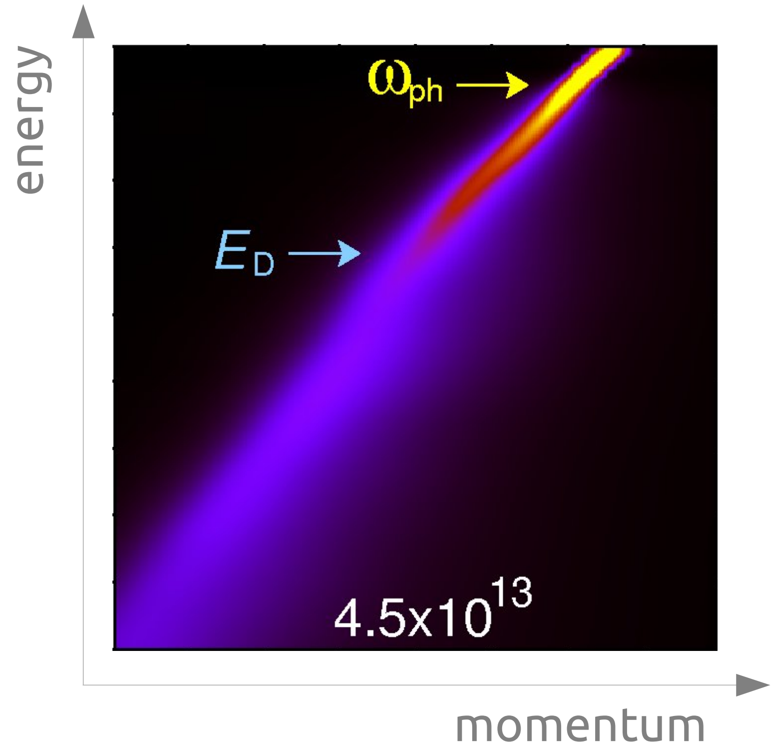

p. 521




$$m_{\rm th} = (1+\lambda) m_{\rm b}$$

# **ARPES** kinks in 2D materials




CH Park, FG et al, Nano Lett 2009

# **Quasiparticle** theory of e-ph interaction in metals

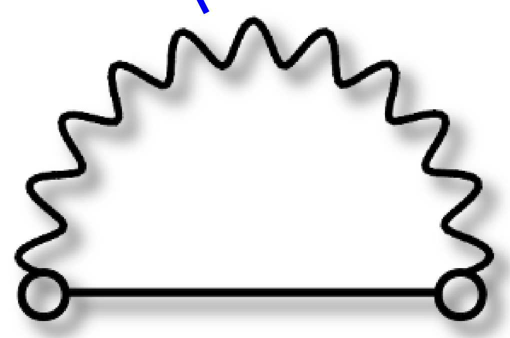
S Engelsberg, JR Schrieffer, Phys Rev 1963

$$G(\mathbf{k},\omega) = \frac{1}{\omega - \epsilon_{\mathrm{k}} - \Sigma(\mathbf{k},\omega)}$$

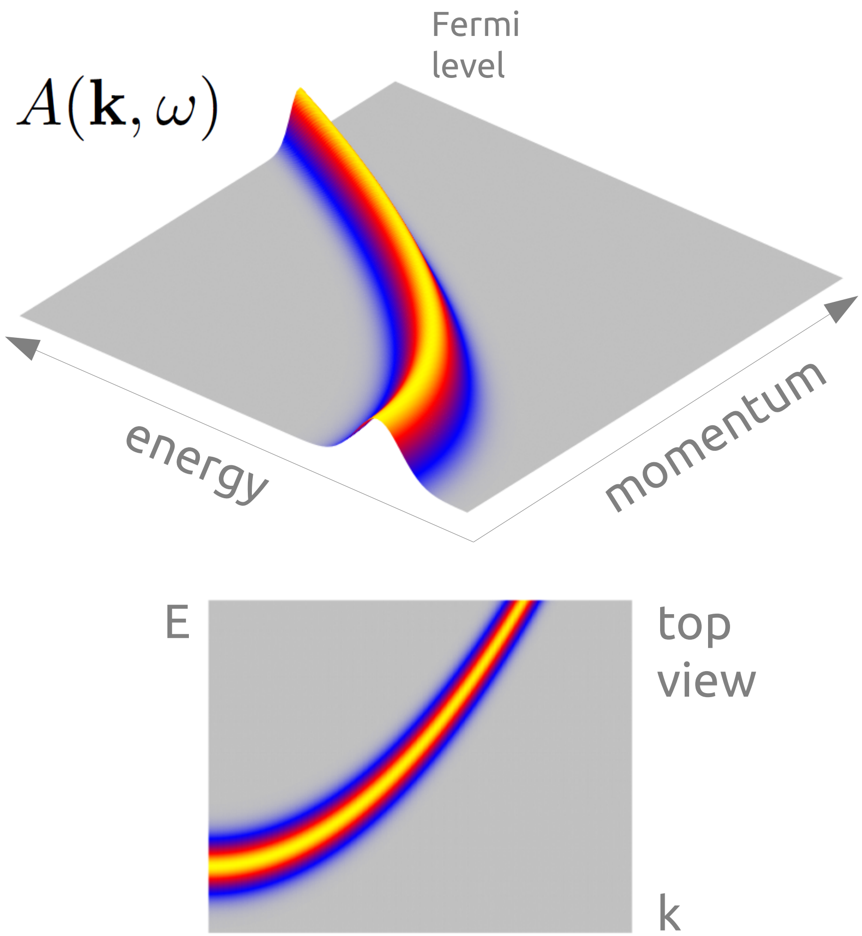
$$A(\mathbf{k},\omega) = \frac{1}{\pi}|\mathrm{Im}G(\mathbf{k},\omega)|$$

Holstein model + Migdal theorem

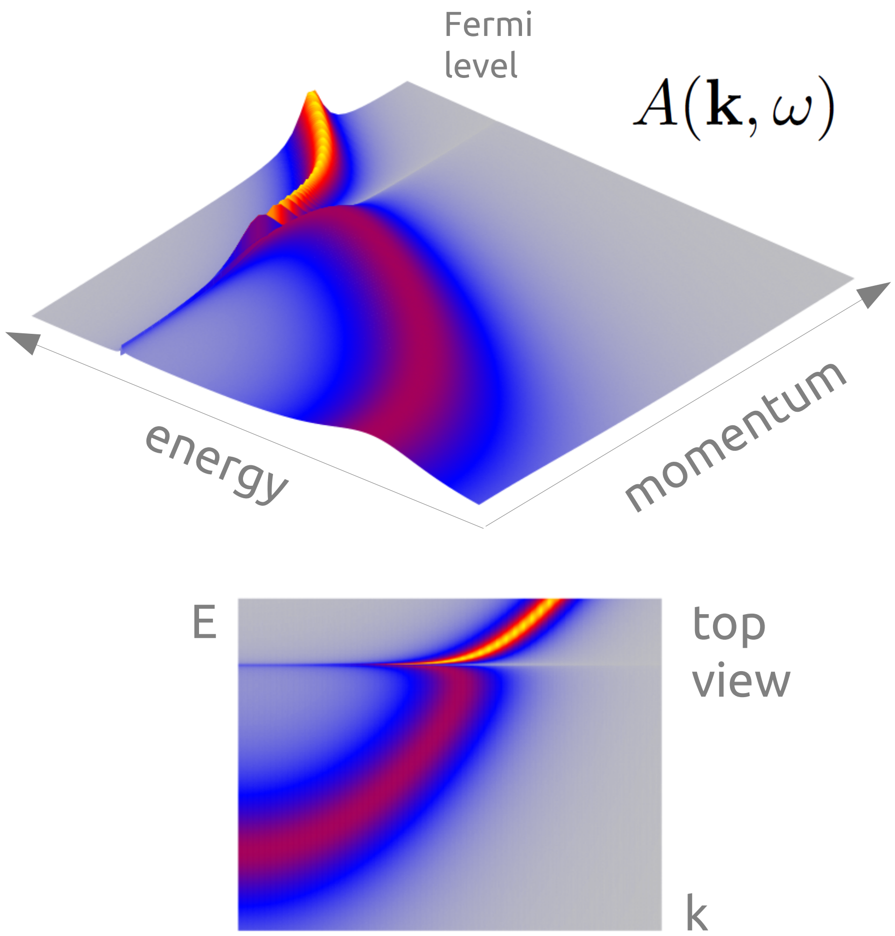
$$\hat{H}_{\mathrm{ep}} = g \sum_{\mathbf{k},\mathbf{q}} a^{\dagger}_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}} (b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}})$$



## Non-interacting




## Including e-ph interaction




See also: A Eiguren, C Ambrosch-Draxl, PM Echenique, PRB 2009

# **First-principles** theory of e-ph interaction

L Hedin and S Lundqvist, Solid State Physics 1969

GW framework

$$\Sigma_{\rm ph}(\mathbf{x},\mathbf{x}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' G(\mathbf{x},\mathbf{x}',\omega+\omega') W_{\rm ph}(\mathbf{r},\mathbf{r}',\omega') e^{i\omega'\delta}$$

**Ionic contribution** to screened Coulomb interaction

$$W_{\rm ph}(\mathbf{r},\mathbf{r}';\omega) = \sum_\nu \int \frac{d\mathbf{q}}{\Omega_{\rm BZ}} \frac{2\omega_{\mathbf{q}\nu}}{\omega^2-\omega_{\mathbf{q}\nu}^2} \Delta V_{\mathbf{q}\nu}(\mathbf{r}) \Delta V_{\mathbf{q}\nu}^*(\mathbf{r}')$$

UNIVERSITY OF OXFORD

$$\Sigma_{n\mathbf{k}}(\omega) = \sum_{m\nu} \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} |g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2 \times$$

$$\times \left[ \frac{1 - f_{m\mathbf{k}+\mathbf{q}} + n_{\mathbf{q}\nu}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}\nu} - i\delta} + \frac{f_{m\mathbf{k}+\mathbf{q}} + n_{\mathbf{q}\nu}}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}\nu} - i\delta} \right]$$

matrix elements

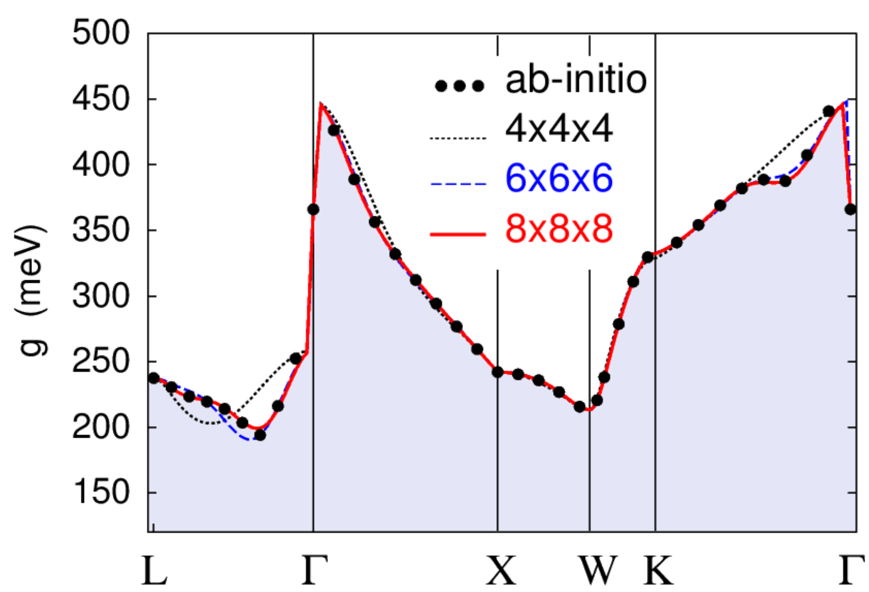
electrons

phonons

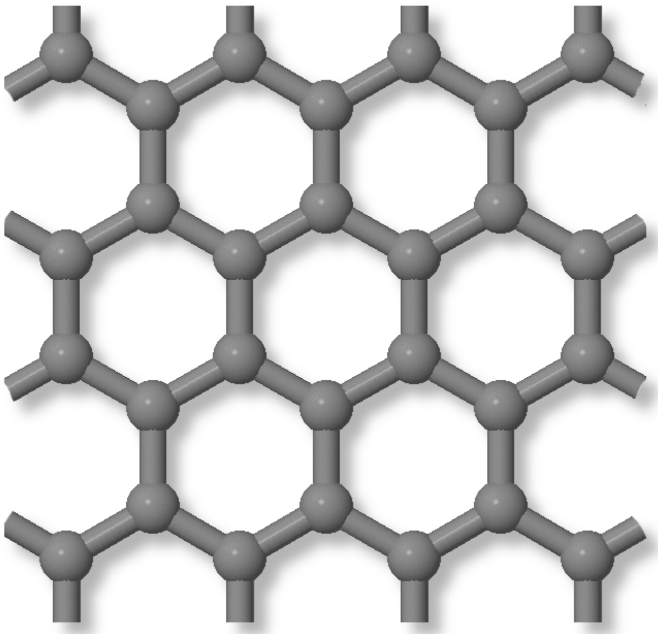
Wannier e-ph interpolation

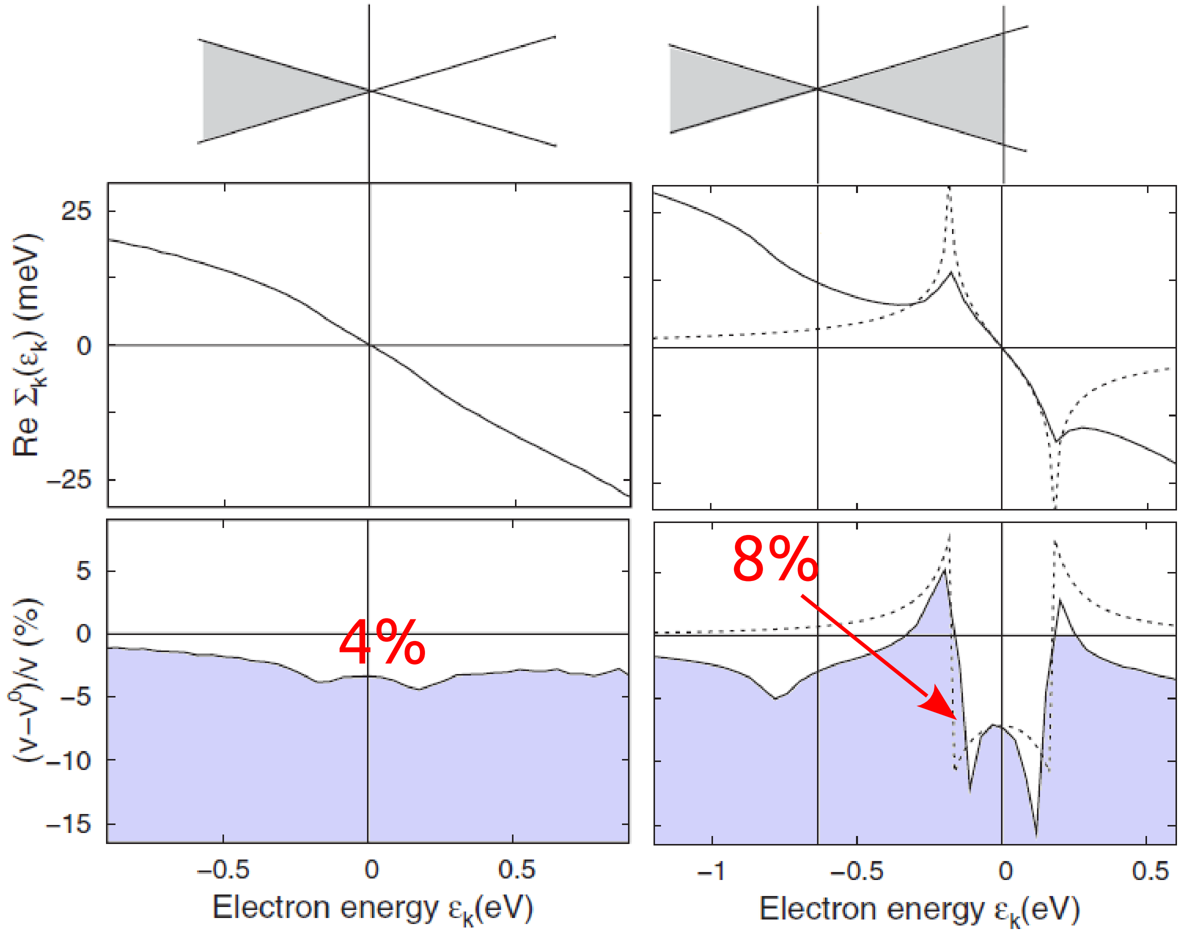
EPW.org.uk

FG, ML Cohen, SG Louie, PRB 2007



# Example: graphene





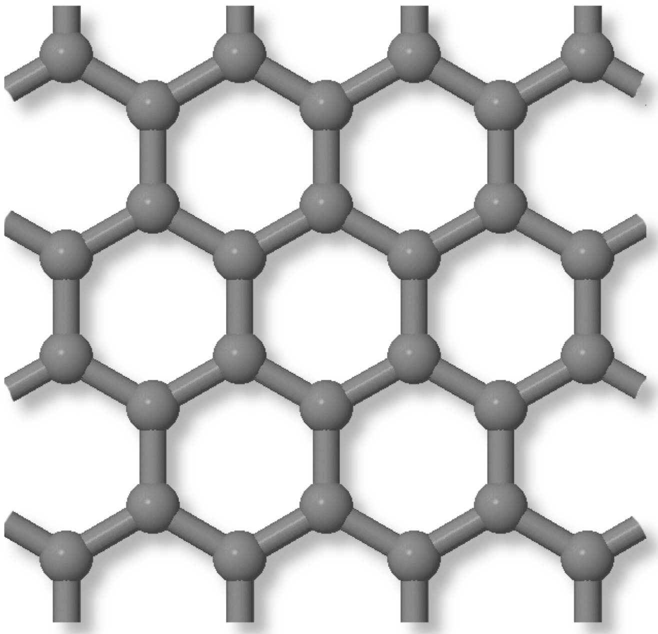

pristine

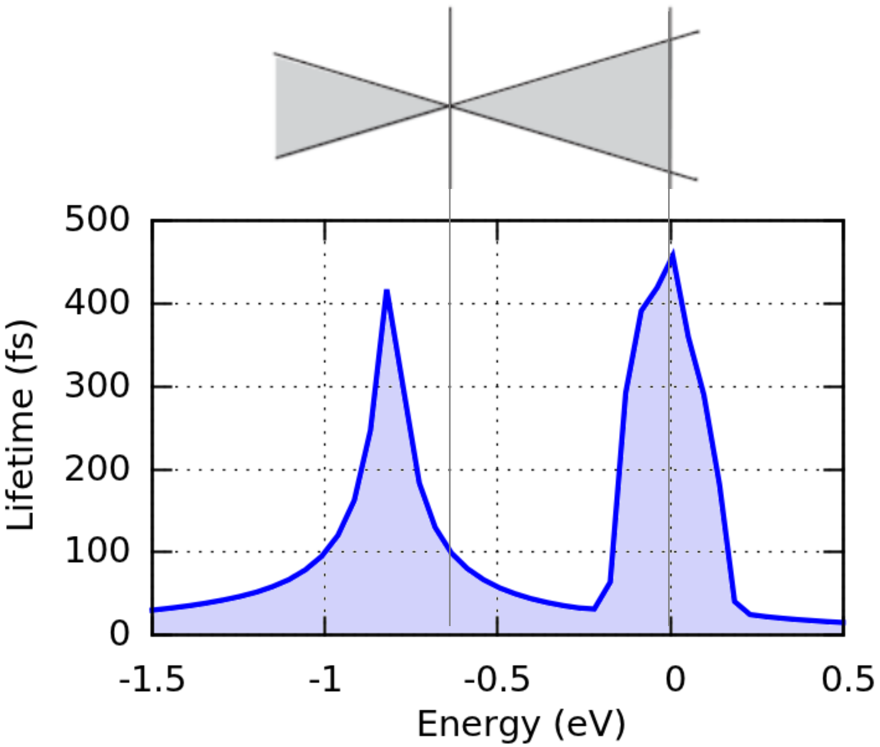
$4 \cdot 10^{13}$ electrons/cm$^{-2}$

CH Park, FG, ML Cohen, SG Louie, PRL 2007

# Example: graphene

$$\tau_{n\mathbf{k}} = \frac{\hbar}{2\mathrm{Im}\Sigma_{n\mathbf{k}}}$$






$4\cdot10^{13}$ electrons/cm$^{-2}$

CH Park, FG, ML Cohen, SG Louie, PRL 2007

UNIVERSITY OF OXFORD

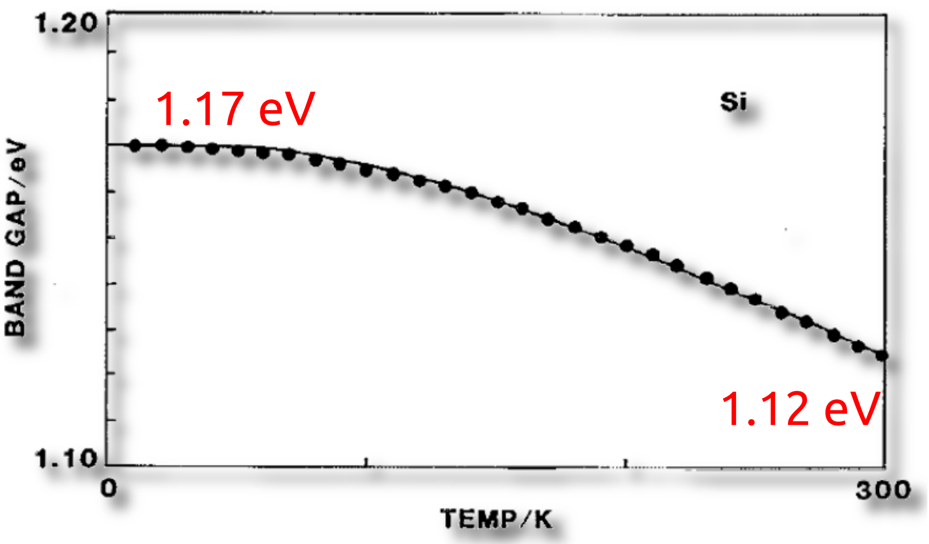
Metals

Insulators

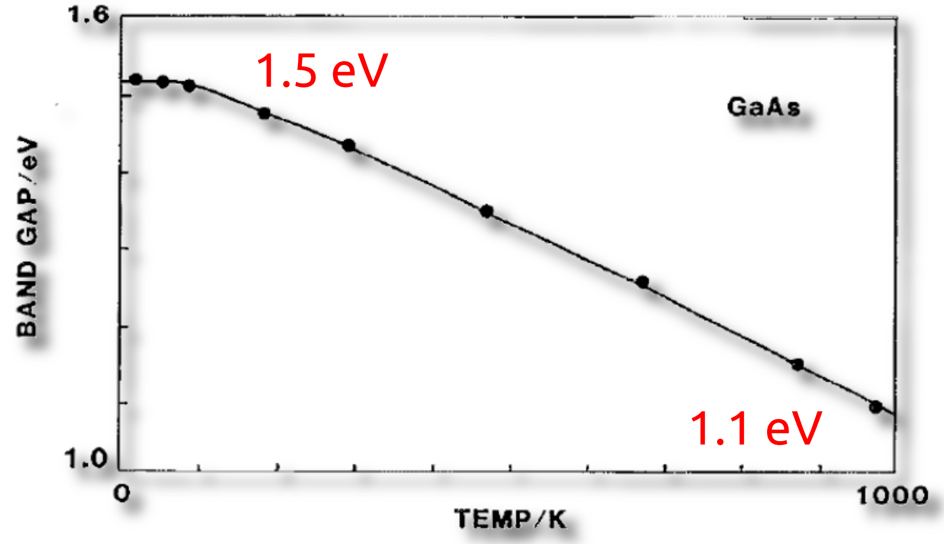
Superconductors

# **Temperature dependence** of band gaps

silicon




gallium arsenide




KP O'Donnel, X Chen, Appl Phys Lett 1991

REVIEWS OF MODERN PHYSICS, VOLUME 77, OCTOBER 2005

## Isotope effects on the optical spectra of semiconductors

Manuel Cardona*

*Max-Planck-Institut fuer Festkoerperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

M. L. W. Thewalt

*Physics Department, Simon Fraser University, Burnaby, B.C. V5A 1S6, Canada*

(Published 7 November 2005)

Since the end of the cold war, macroscopic amounts of separated stable isotopes of most elements have been available “off the shelf” at affordable prices. Using these materials, single crystals of many semiconductors have been grown and the dependence of their physical properties on isotopic composition has been investigated. The most conspicuous effects observed have to do with the dependence of phonon frequencies and linewidths on isotopic composition. These affect the electronic properties of solids through the mechanism of electron-phonon interaction, in particular, in the corresponding optical excitation spectra and energy gaps. This review contains a brief introduction to the history, availability, and characterization of stable isotopes, including their many applications in science and technology. It is followed by a concise discussion of the effects of isotopic composition on the vibrational spectra, including the influence of average isotopic masses and isotopic disorder on the phonons. The final sections deal with the effects of electron-phonon interaction on energy gaps, the concomitant effects on the luminescence spectra of free and bound excitons, with particular emphasis on silicon, and the effects of isotopic composition of the host material on the optical transitions between the bound states of hydrogenic impurities.

CONTENTS



*Electronic address: m.cardona@fkf.mpg.de

0034-6861/2005/77(4)/1173(52)/$50.00 1173 

Y Fan, Phys Rev 1951

E. Antoncik, Czechosl J Phys 1955

PB Allen, V Heine, J Phys C 1976

M Cardona et al, 1970–

CP Herrero, R Ramírez, ER Hernández, PRB 2006

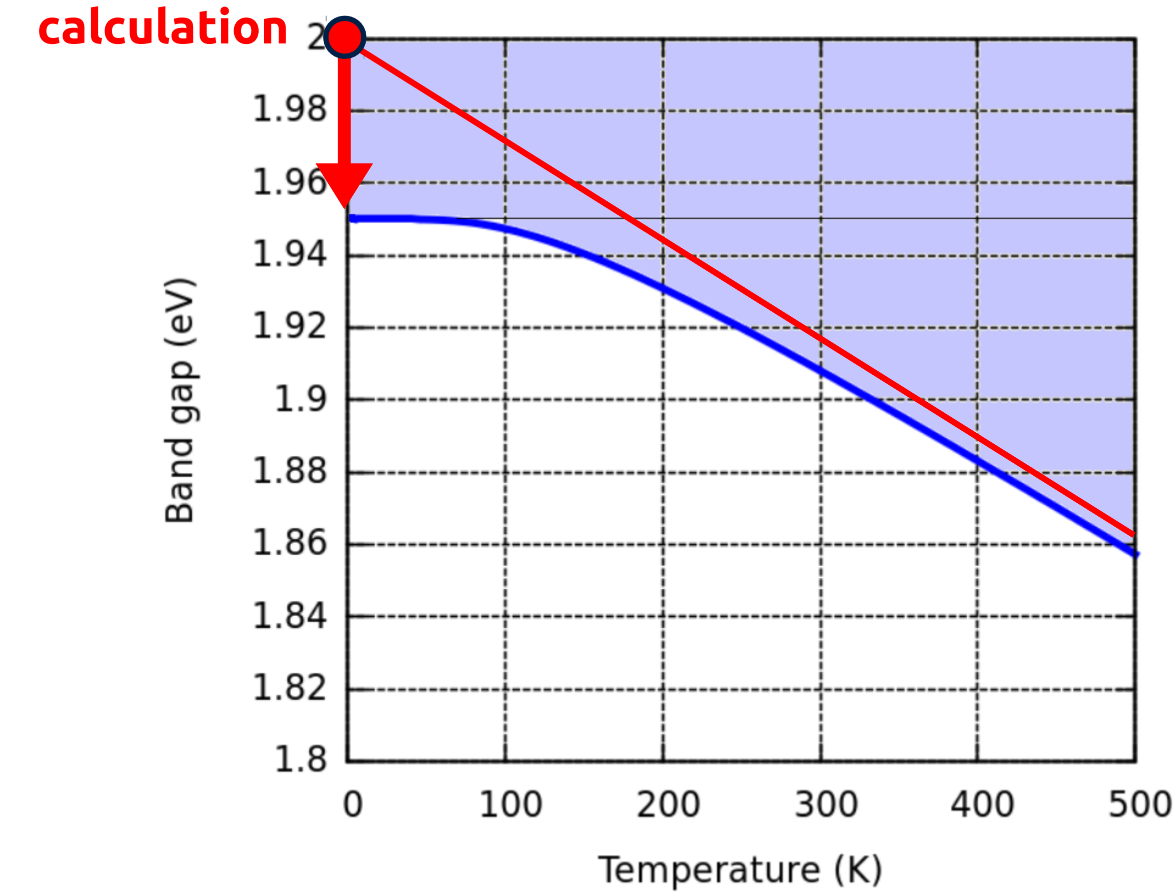
A Marini, PRL 2008

FG, SG Louie, ML Cohen, PRL 2010

X Gonze, P Boulanger, M Coté, Ann Phys 2010

E Cannuccia, A Marini, PRL 2011

$$\Delta E_g(T) = -(2n+1)\,\Delta E_g^0$$




M Cardona & MLW Thewalt, Rev Mod Phys 2005

$$V(u) = V^0 + \frac{\partial V}{\partial u} u + \frac{1}{2} \frac{\partial^2 V}{\partial u^2} u^2$$

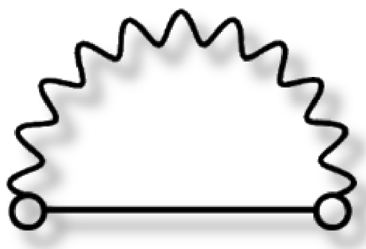
$$E_{n\mathbf{k}}(u) = E^0_{n\mathbf{k}} + \langle n\mathbf{k} | \bullet | n\mathbf{k} \rangle + \sum_{m\mathbf{q}} \frac{|\langle m\mathbf{k}+\mathbf{q} | \bullet | n\mathbf{k} \rangle|^2}{E^0_{n\mathbf{k}} - E^0_{m\mathbf{k}+\mathbf{q}}}$$

- Thermal average of displacements
- Harmonic
- Adiabatic
- Semiclassical

Allen & Heine, J Phys C 1976

$$\Delta\epsilon_{n\mathbf{k}} = \Delta^{\mathrm{SE}}\epsilon_{n\mathbf{k}} + \Delta^{\mathrm{DW}}\epsilon_{n\mathbf{k}}$$

Fan (self-energy)

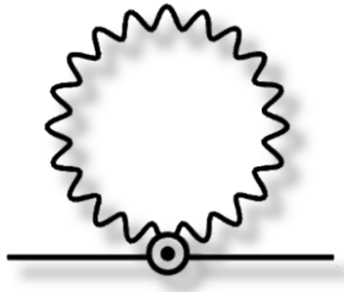


$$\Delta^{\mathrm{SE}}\epsilon_{n\mathbf{k}} = \sum_{m\neq n,\nu} \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} \frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}+\mathbf{q}}} |g_{mn,\nu}(\mathbf{k},\mathbf{q})|^2$$

the same term as for metals

$$\Delta\epsilon_{n\mathbf{k}} = \Delta^{\mathrm{SE}}\epsilon_{n\mathbf{k}} + \Delta^{\mathrm{DW}}\epsilon_{n\mathbf{k}}$$

Debye-Waller



$$\Delta^{\mathrm{DW}}\epsilon_{n\mathbf{k}} = -\sum_{m\neq n,\nu}\int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} \frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}} - \epsilon_{m\mathbf{k}}} [g^{\mathrm{DW}}_{mn,\nu}(\mathbf{k},\mathbf{q})]^2$$

essential for the theory to be translationally invariant

$$\Delta^{\rm DW}\epsilon_{n\mathbf{k}} = -\sum_{m\neq n,\nu}\int \frac{d\mathbf{q}}{\Omega_{\rm BZ}}\frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}}}[g^{\rm DW}_{mn,\nu}(\mathbf{k},\mathbf{q})]^2$$

$$[g^{\rm DW}_{mn,\nu}(\mathbf{k},\mathbf{q})]^2 = \frac{1}{2\omega_{\mathbf{q}\nu}}\sum_{\mu\mu'} t^{\nu}_{\mu\mu'}(\mathbf{q})h^{\star}_{mn,\mu}(\mathbf{k})h_{mn,\mu'}(\mathbf{k}),$$

$$t^{\nu}_{\kappa\alpha,\kappa'\alpha'}(\mathbf{q}) = u^{\star}_{\nu,\kappa\alpha}(\mathbf{q})u_{\nu,\kappa\alpha'}(\mathbf{q}) + u^{\star}_{\nu,\kappa'\alpha}(\mathbf{q})u_{\nu,\kappa'\alpha'}(\mathbf{q})$$

$$h_{mn,\mu}(\mathbf{k}) = \sum_{\nu} u^{-1}_{\mu\nu}(\mathbf{0})\,\omega^{1/2}_{\mathbf{0}\nu}\,g_{mn,\nu}(\mathbf{k},\mathbf{0}).$$

PHYSICAL REVIEW B VOLUME 26, NUMBER 3 1 AUGUST 1982

**Generalization of the theory of the electron-phonon interaction: Thermodynamic formulation of superconducting- and normal-state properties**

Warren E. Pickett
*Naval Research Laboratory, Washington, D.C. 20375*
(Received 25 January 1982)

A thermodynamic formulation for the electron self-energy is given which is applicable when the electronic spectrum possesses structure on the scale of phonon frequencies, provided only that the ratio of phonon phase velocity to electron Fermi velocity is small. Electron-phonon, Coulomb, and electron-defect interactions are included on an equal footing and it is shown that their different frequency dependencies lead to specific effects on the Eliashberg self-energy: (a) The Coulomb interaction contributes nothing of essence to the normal-state self-energy (in this isotropic approximation) but retains its usual depairing effect upon the superconducting gap function, (b) defects affect superconducting properties primarily through a broadening of the electronic spectrum, and (c) phonons contribute a thermal shift and broadening as well as the mass enhancement. A generalization to *intensive* electron-phonon, electron-electron, and electron-defect interaction constants is necessary to redevelop an intuition into the effects of these interactions. The change in the structure of the Eliashberg equation due to a nonconstant density of states (DOS) and the consequent interplay between static and thermal disorder is analyzed in detail, with a central feature being the change in frequency dependence of the self-energy compared to a constant DOS solution. The effect of DOS structure on the superconducting transition temperature $T_c$, which is manifested in the defect dependence of $T_c$, is analyzed in detail. Further it is proposed that an extension of the self-consistent Eliashberg approach be extended above $T_c$ to determine the normal-state self-energy and thereby the electronic contribution to thermodynamic quantities. Phonon broadening is shown to affect the spin susceptibility at finite temperature. Reinterpretation of several of the anomalous properties of *A*15 compounds in terms of the present theory is suggested. Several aspects of the theory are compared to experimental data for $Nb_3Sn$.

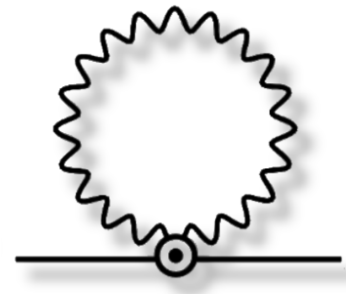
## I. INTRODUCTION

Deeply ingrained in the formal theory of the interacting electron-phonon (*e*-ph) system in metals are two simplifying approximations. The first is an extension of the adiabatic, or Born-Oppenheimer approximation[1] in which the light electrons are considered to respond instantaneously to the heavy ions (of mass *M*). Central to the theory of *e*-ph systems is Migdal's theorem,[2] which demonstrates that nonadiabatic effects can be obtained accurately by low-order Feynman-Dyson perturbation theory, to lowest order in an expansion parameter of the order of $(m/M)^{1/2} \ll 1$. The second simplification is the assumption of a constant density of states (CDOS) over a region $\pm\bar{\Omega}$ around the Fermi energy $E_F$, where $\bar{\Omega}$ is a few times of the mean phonon frequency. This approximation allows the DOS function $N(E)$ to be approximated by $N(E_F)$ in certain energy integrals. The two approximations in fact are related, and it often seems to be assumed that Midgal's theorem is inapplicable if $N(E)$ is not constant [to within $(m/M)^{1/2}$] over a range $\pm\bar{\Omega}$ around $E_F$. As will be shown in this paper, however, there exists an important regime within which the CDOS approximation may be relaxed in a straightforward manner while retaining Migdal's simplification. The resulting generalizations of the CDOS expressions often are not intuitively obvious, and the consequences involve a reinterpretation of many of the properties of this class of materials.

That structure in the DOS on the scale of $\bar{\Omega}$ should be expected in crystals containing several transition-metal atoms per unit cell can be deduced from general considerations.[3] Elemental transition metals are known to have peak structure in their DOS which may be only a few tenths of an eV wide. A compound with (for example) ten atoms per unit cell will have 10 times the number of bands in the same overall bandwidth, leading to structure on the order of hundredths of an eV.



Where is Debye-Waller in the theory of metals?

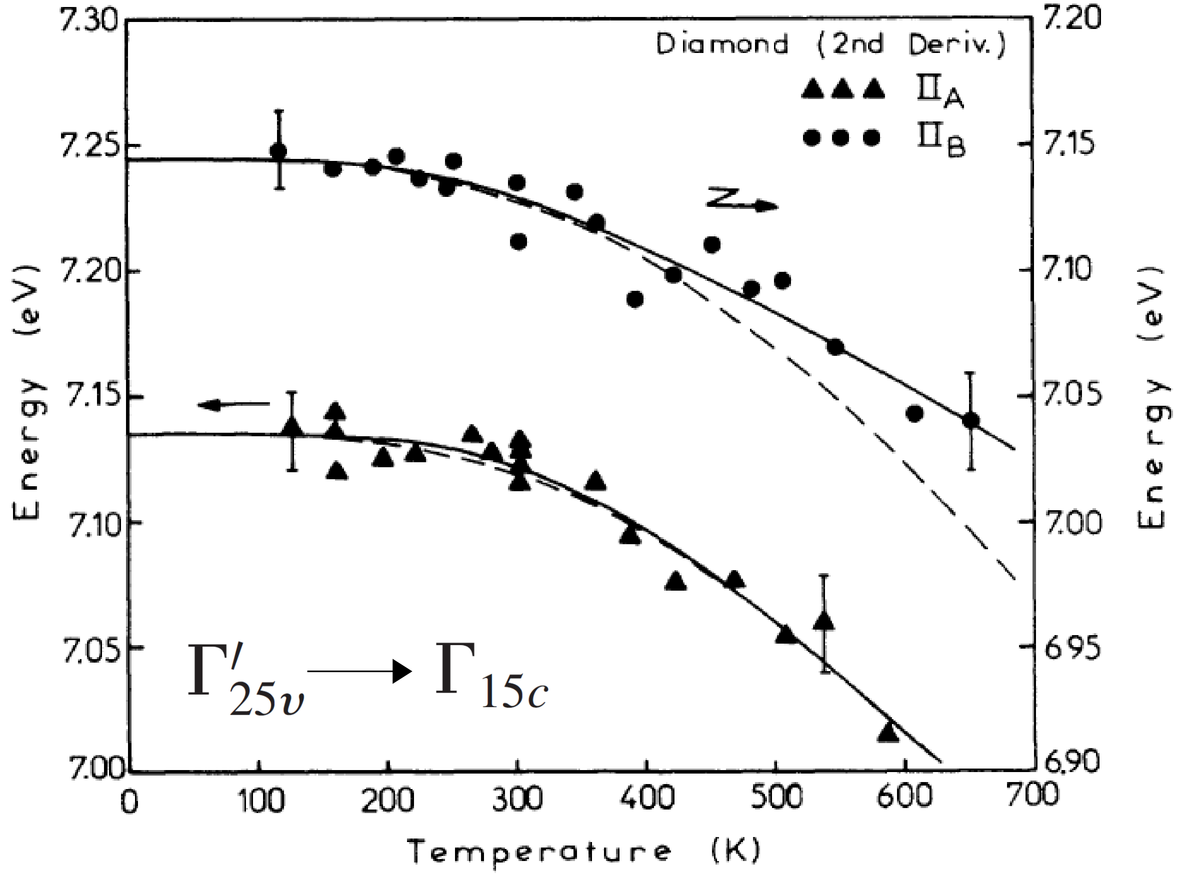


In this form of the Hamiltonian Ψ describes *band electrons*, for which the electron-static lattice and electron-electron interactions have been included in a mean-field sense. For the electron-lattice interaction the remaining coupling is given, to second order in the ion displacement, by the electron-phonon Hamiltonian $H_{e\text{-ph}}$. The second-order term, which has not been displayed explicitly, is required to keep the theory translationally invariant.[16]

UNIVERSITY OF OXFORD

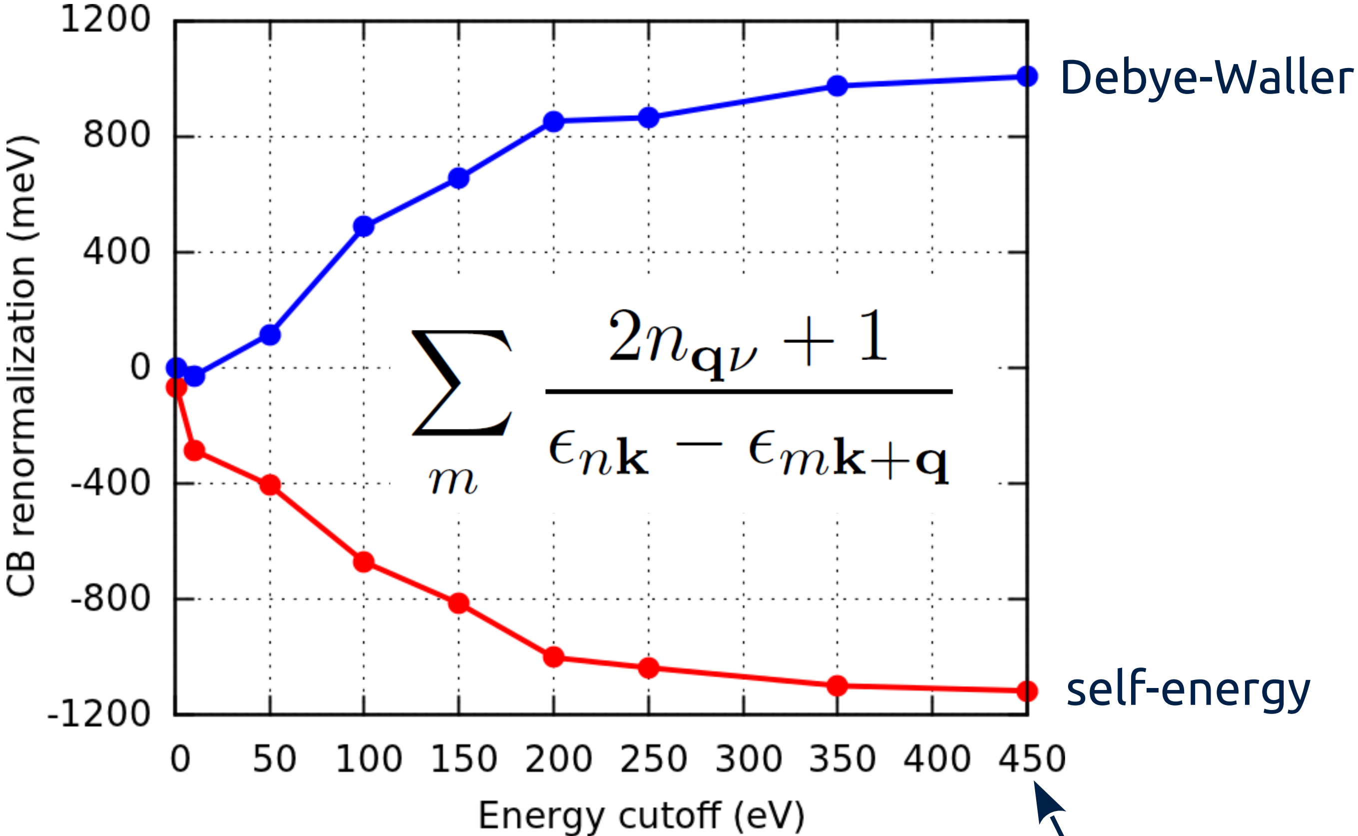
**Diamond**

- Negligible thermal expansion
- Negligible excitonic effects




Logothetidis, Petalas, Polatoglou & Fuchs, PRB 1992

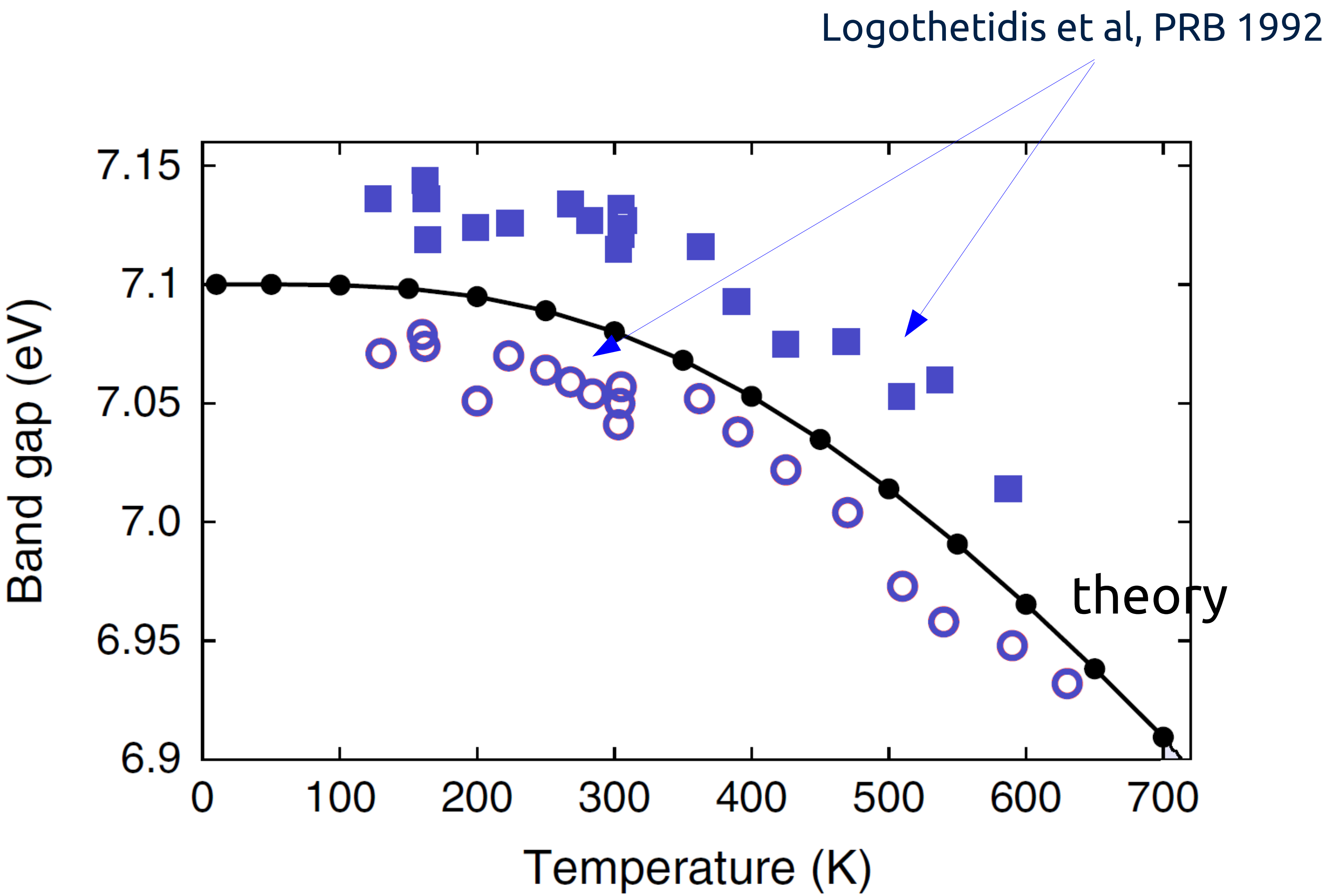
# Slow **convergence** over unoccupied states



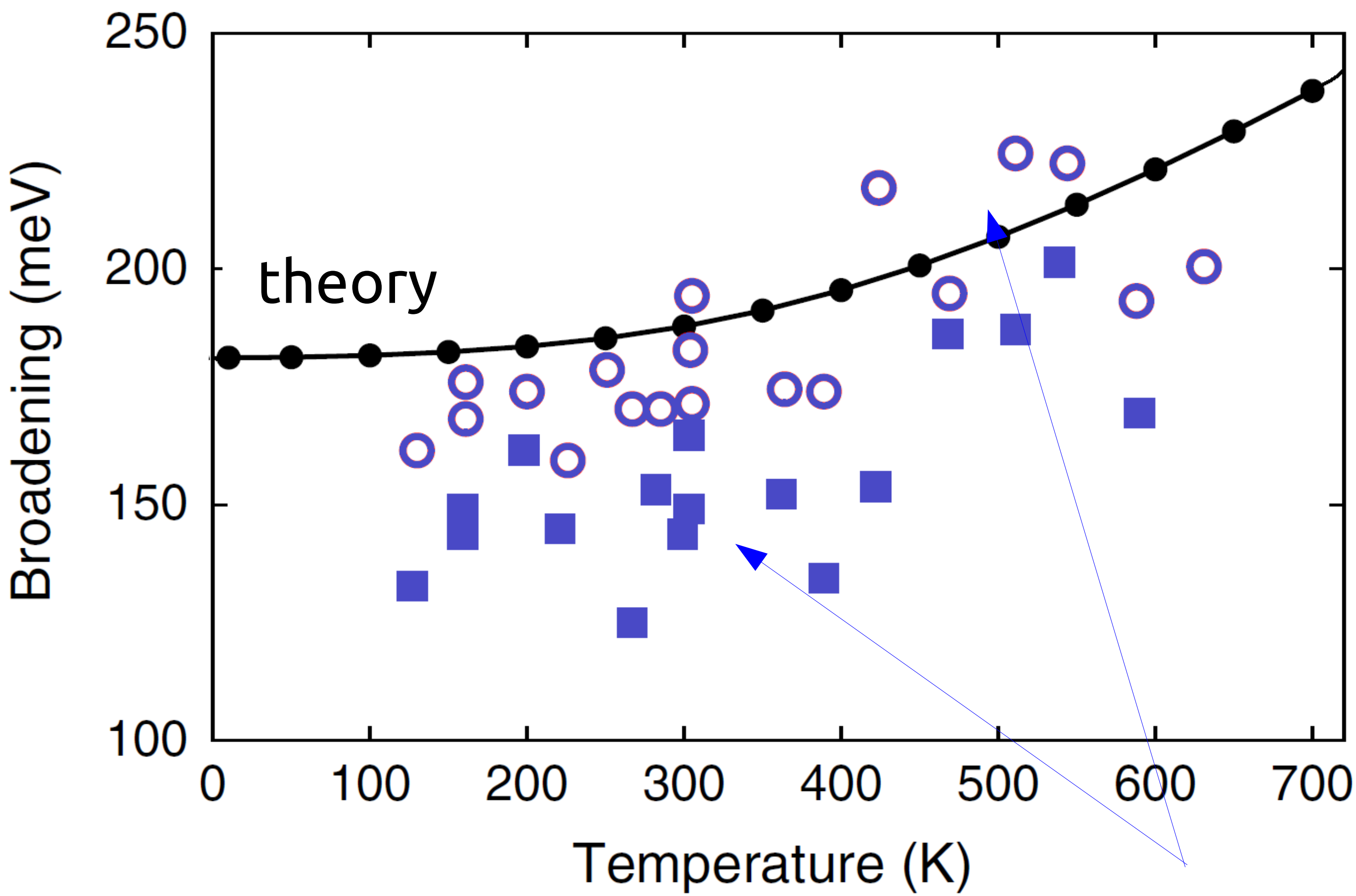

$$\sum_m \frac{2n_{\mathbf{q}\nu}+1}{\epsilon_{n\mathbf{k}}-\epsilon_{m\mathbf{k}+\mathbf{q}}}$$

>300 bands

UNIVERSITY OF OXFORD

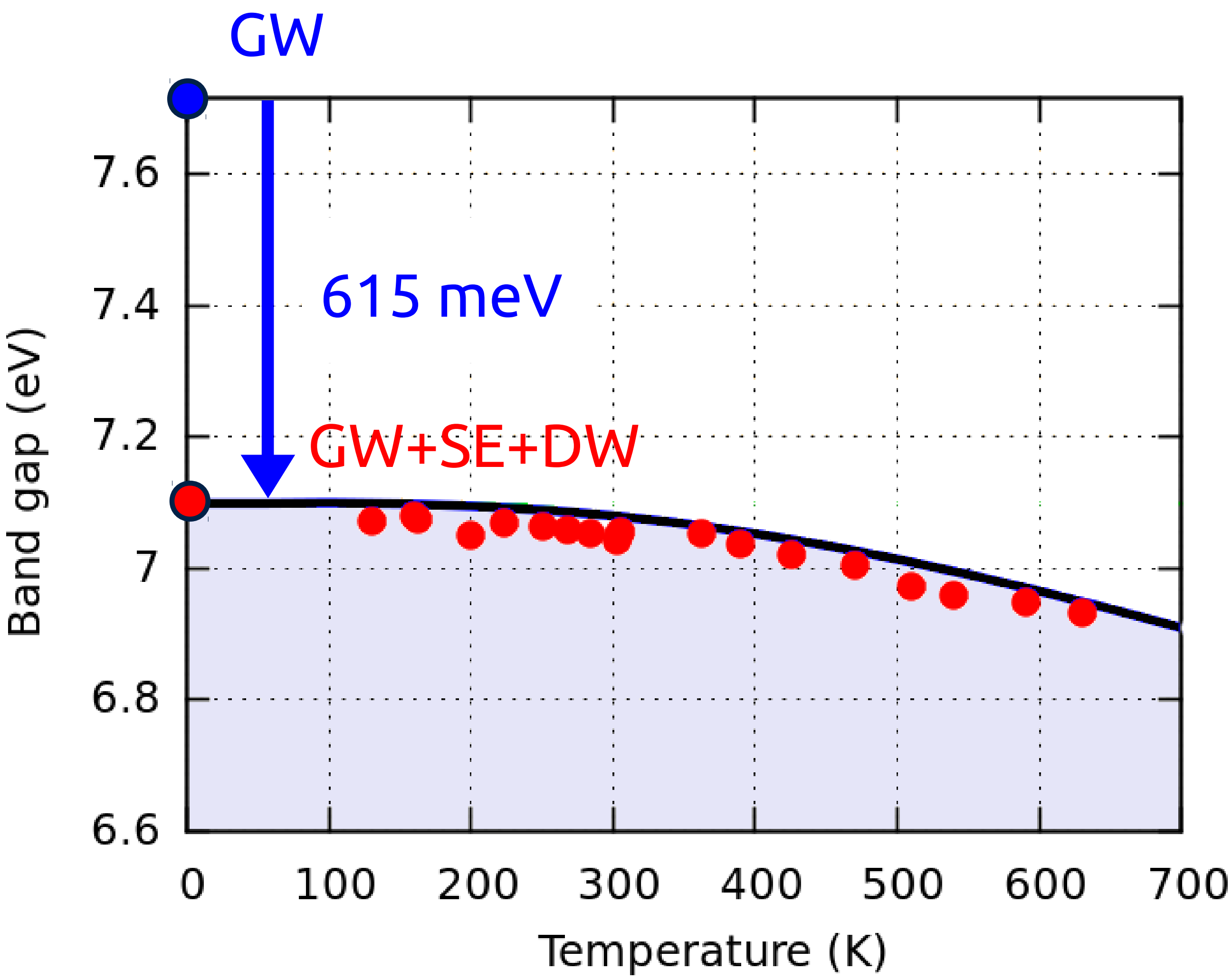


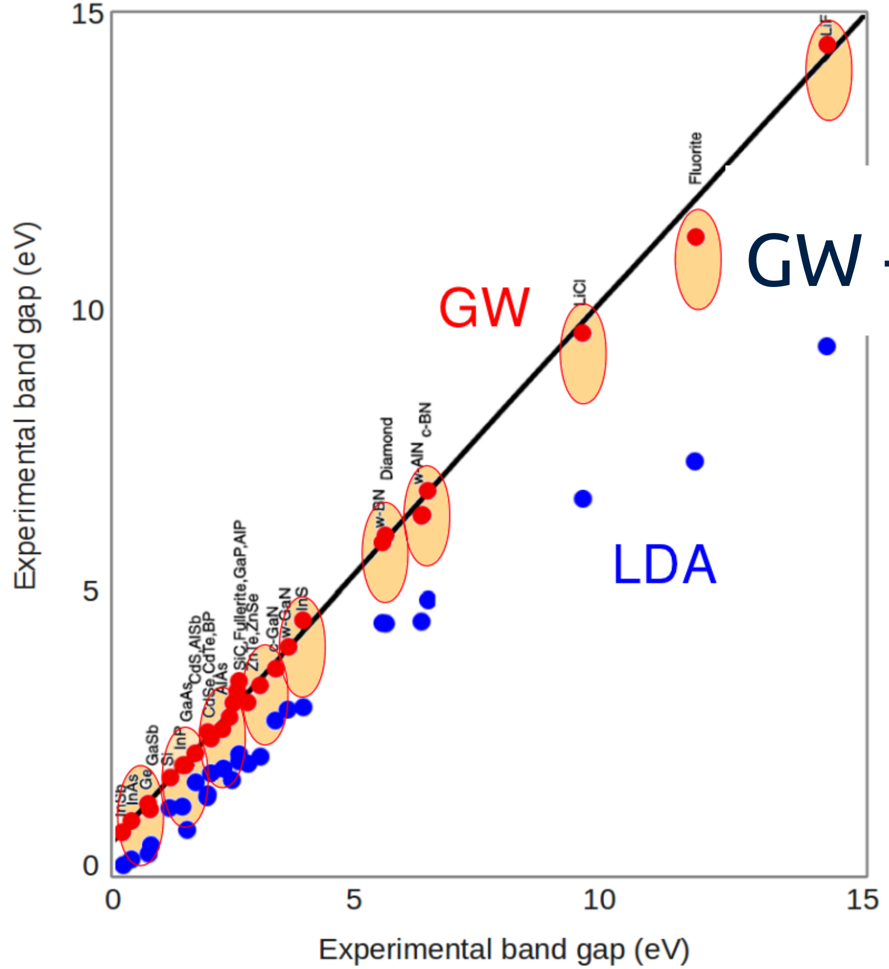

FG, SG Louie & ML Cohen PRL 2010




Logothetidis et al, PRB 1992

FG, SG Louie & ML Cohen PRL 2010


GW
615 meV
GW+SE+DW
7.6
7.4
7.2
7
6.8
6.6
Band gap (eV)
0
100
200
300
400
500
600
700
Temperature (K)




GW + **e-ph** ?

data from: SG Louie, Topics in computational materials science 1997

# Open questions

Dynamical theory inconsistent with translational invariance

Linewidth to be used in energy denominators

$$\Sigma_{n\mathbf{k}} \sim \frac{1}{\omega - \epsilon_{m\mathbf{k}+\mathbf{q}} \pm \omega_{\mathbf{q}\nu} + i\delta}$$

Off-diagonal Debye-Waller (Gonze)

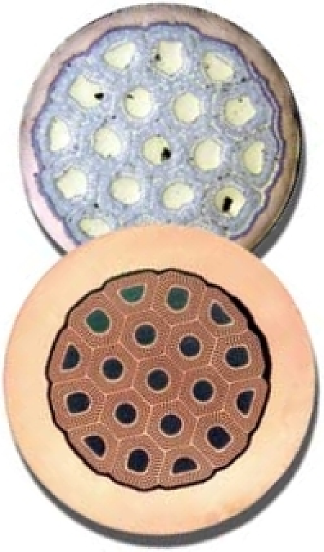
Hedin-Lundqvist formulation missing DW term

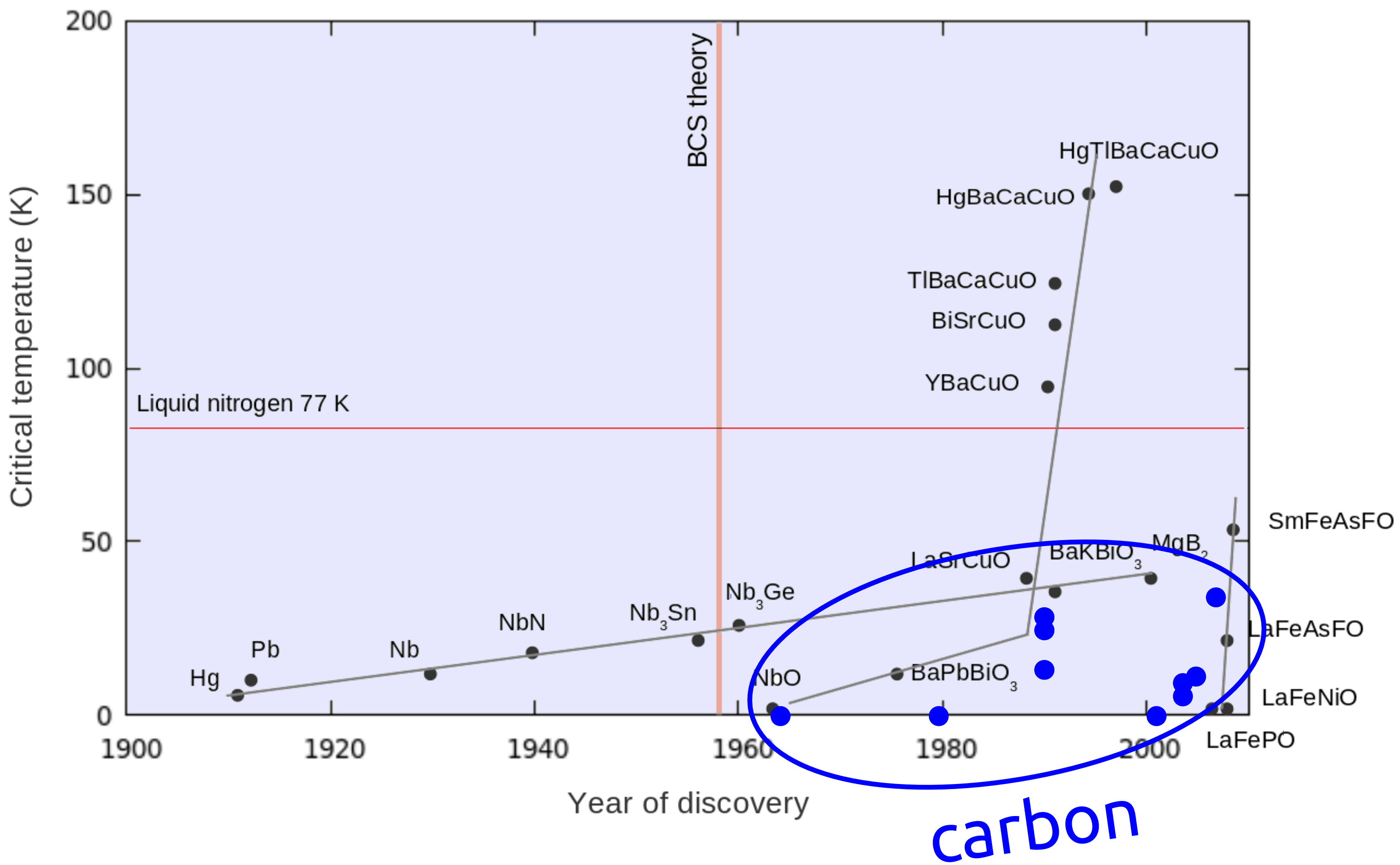
$$\Sigma_{\mathrm{ph}}(\mathbf{x},\mathbf{x}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega' G(\mathbf{x},\mathbf{x}',\omega+\omega')\, W_{\mathrm{ph}}(\mathbf{r},\mathbf{r}',\omega')e^{i\omega'\delta}$$

Metals

Insulators

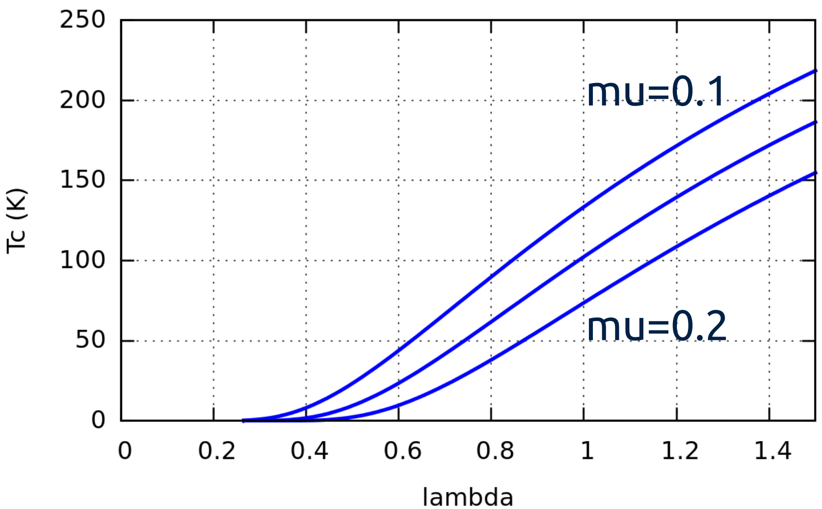
Superconductors

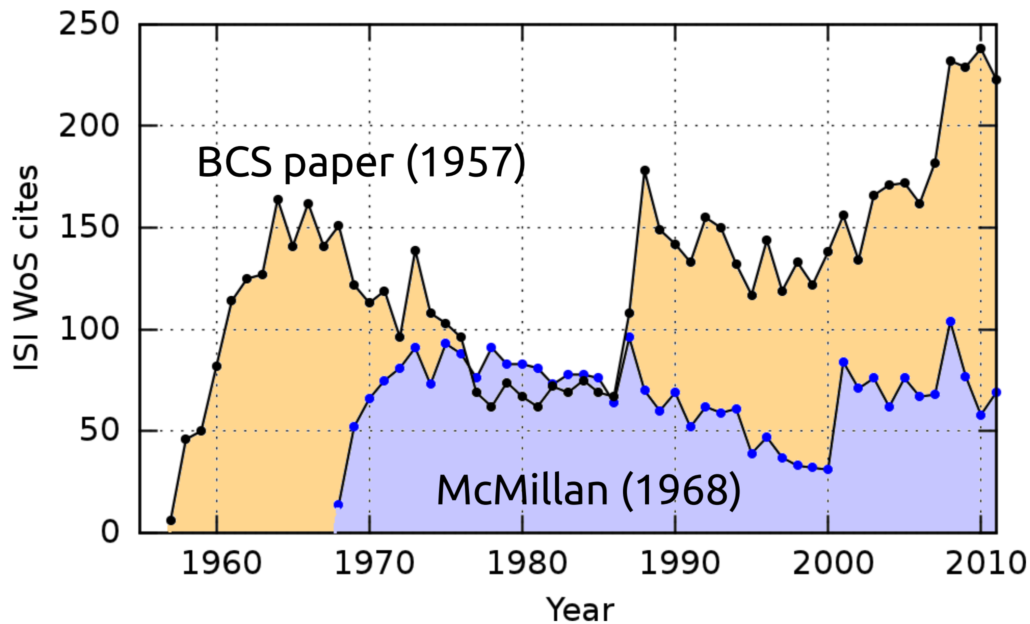



200
150
100
50
0
Critical temperature (K)
1900
1920
1940
1960
1980
2000
Year of discovery
BCS theory
Liquid nitrogen 77 K
Hg
Pb
Nb
NbN
Nb3Sn
Nb3Ge
NbO
BaPbBiO3
LaSrCuO
BaKBiO3
MgB2
YBaCuO
BiSrCuO
TlBaCaCuO
HgBaCaCuO
HgTlBaCaCuO
SmFeAsFO
LaFeAsFO
LaFeNiO
LaFePO
carbon

# How can we calculate Tc ? McMillan equation

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1-0.62\lambda)} \right]$$

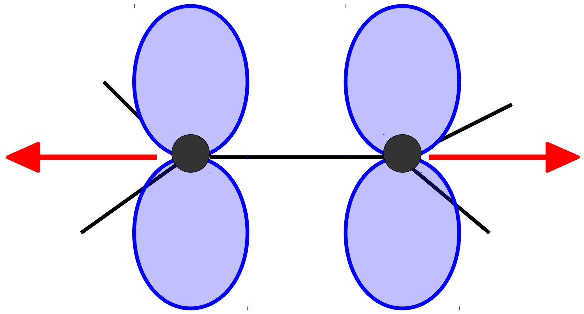


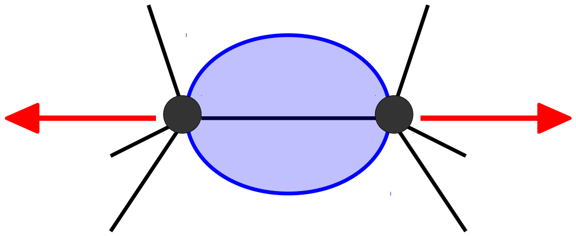

$\lambda$ from **mass-enhancement** in the normal state

Kindergarten picture: $\lambda = N_{\mathrm{F}} V_{\mathrm{ep}}$

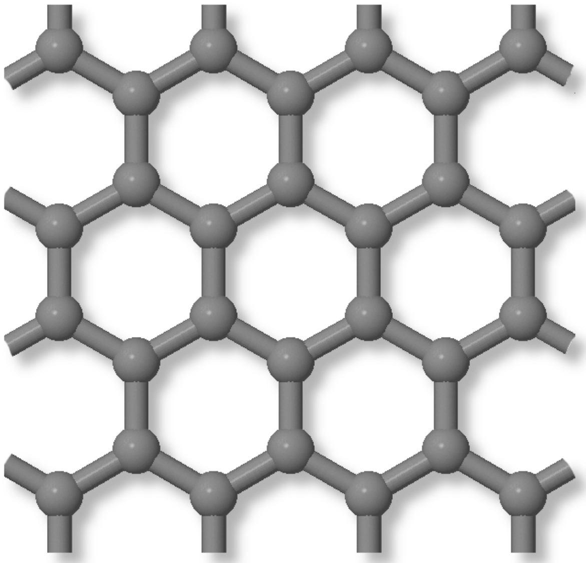
sp2 carbon

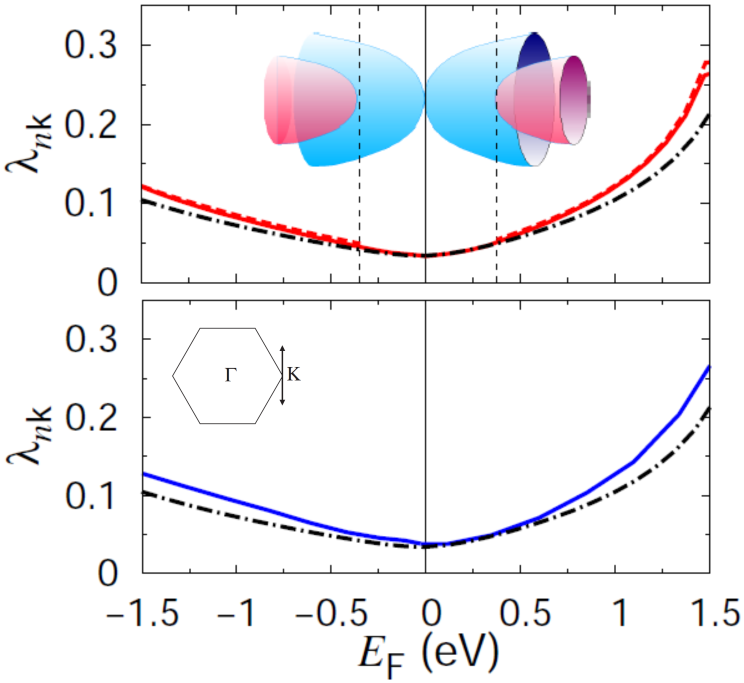


sp3 carbon



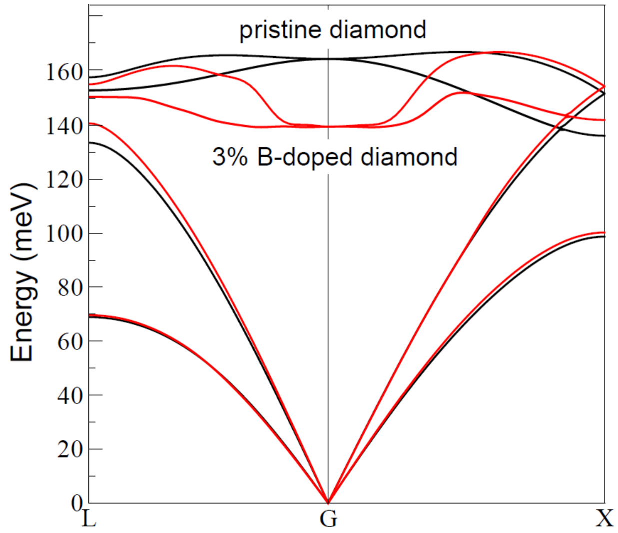
# sp2 carbon: graphene

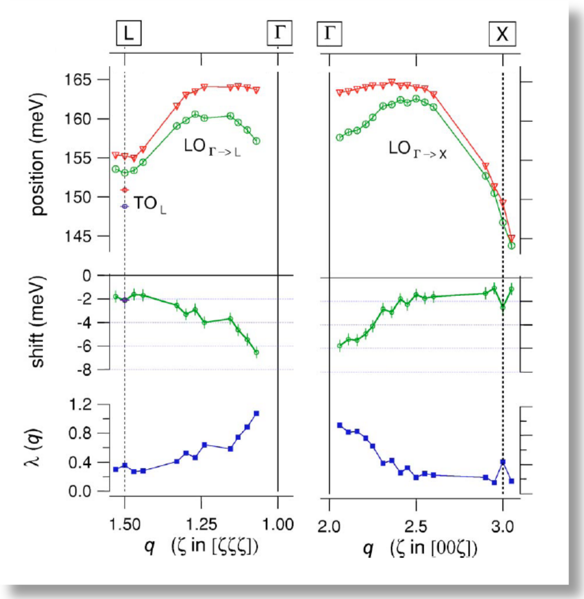





$$\lambda \sim 0.1 - 0.2$$

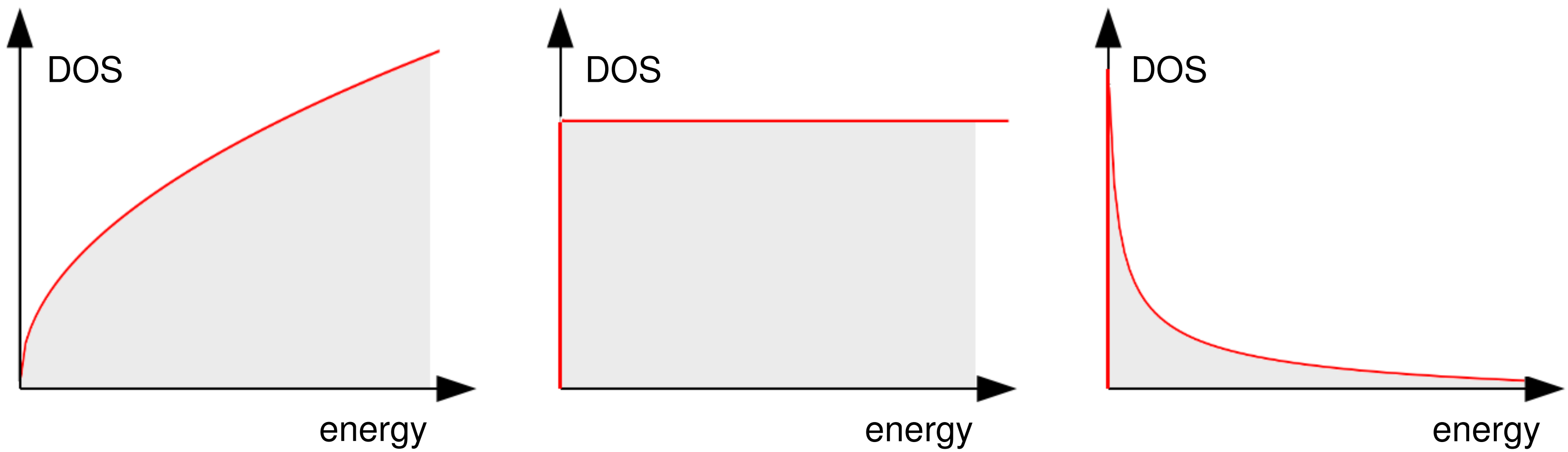
# sp3 carbon: diamond




M Hoesch et al, PRB 2007

$$\lambda \sim 0.2 - 0.3$$




3D

2D

1D

L Boeri, J Kortus
& OK Andersen PRL 2003

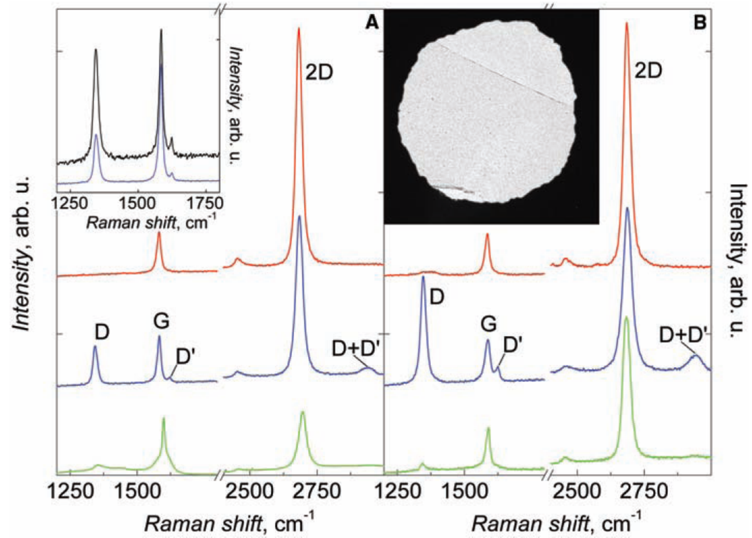
sp3 carbon & large DOS → low-dimensional diamond?

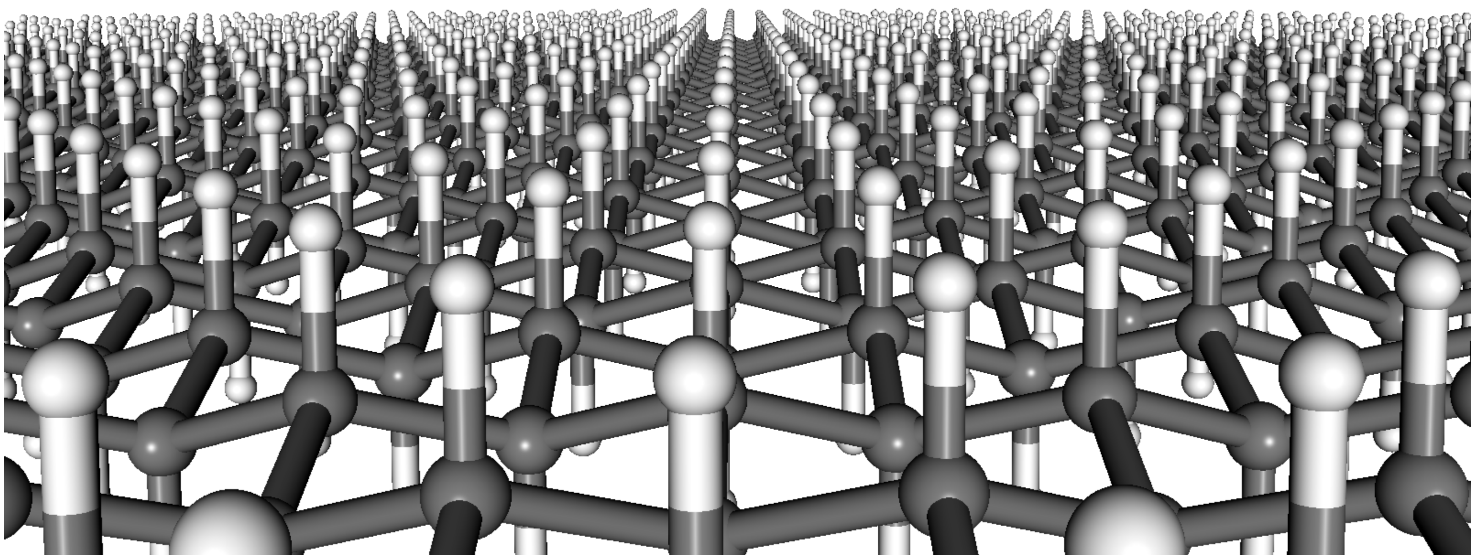
# sp3 carbon: graphane

JO Sofo & al, PRB 2007

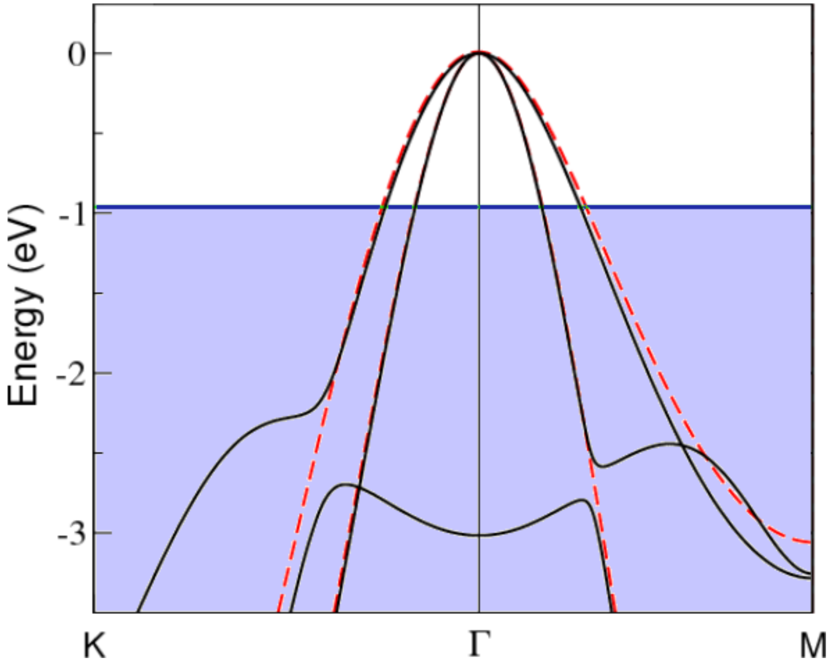
## Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

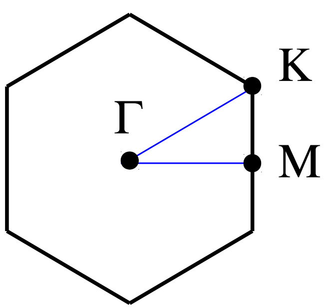
D. C. Elias,[1*] R. R. Nair,[1*] T. M. G. Mohiuddin,[1] S. V. Morozov,[2] P. Blake,[3] M. P. Halsall,[1] A. C. Ferrari,[4] D. W. Boukhvalov,[5] M. I. Katsnelson,[5] A. K. Geim,[1,3] K. S. Novoselov[1]†

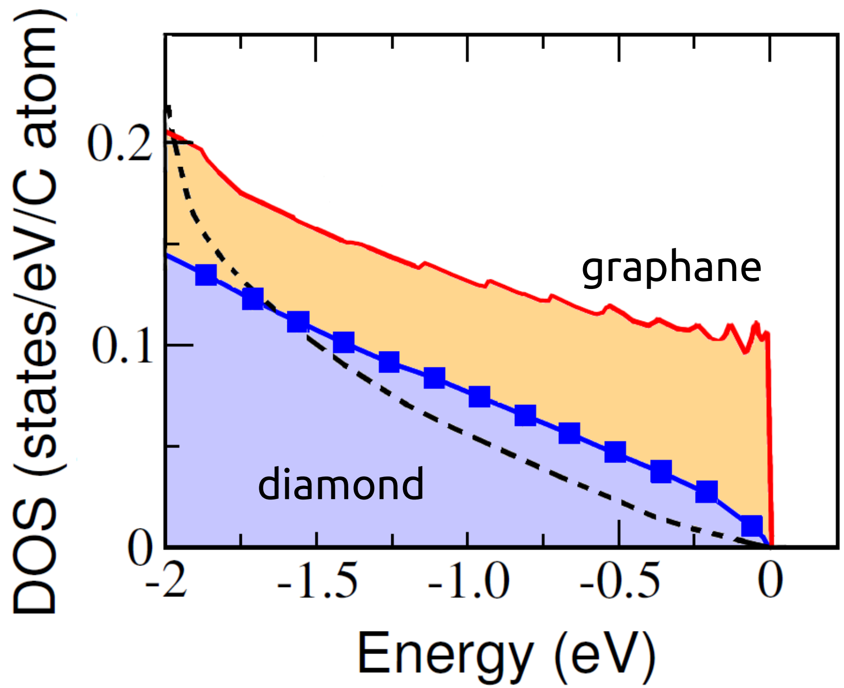


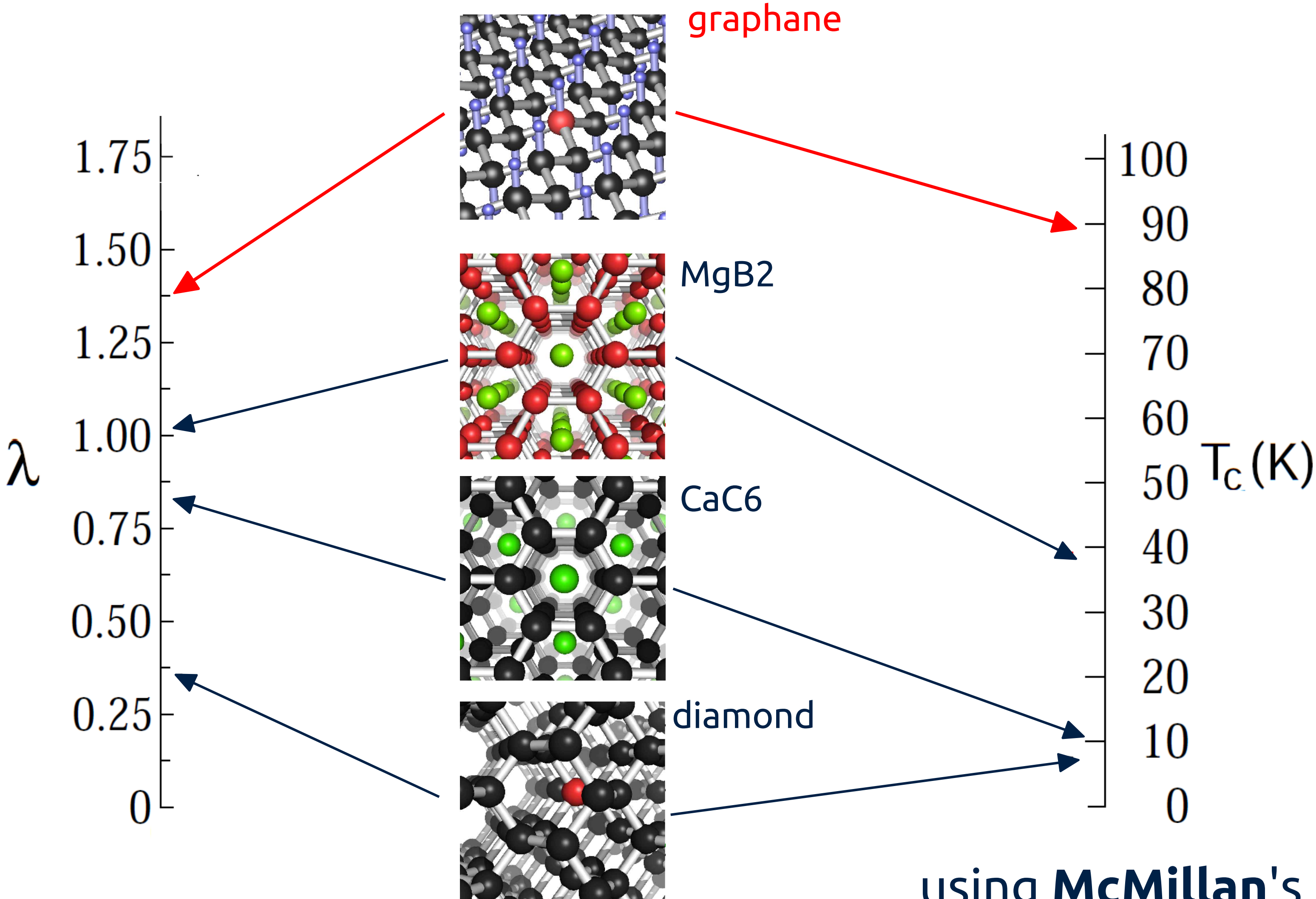



p-doped graphane / band structure





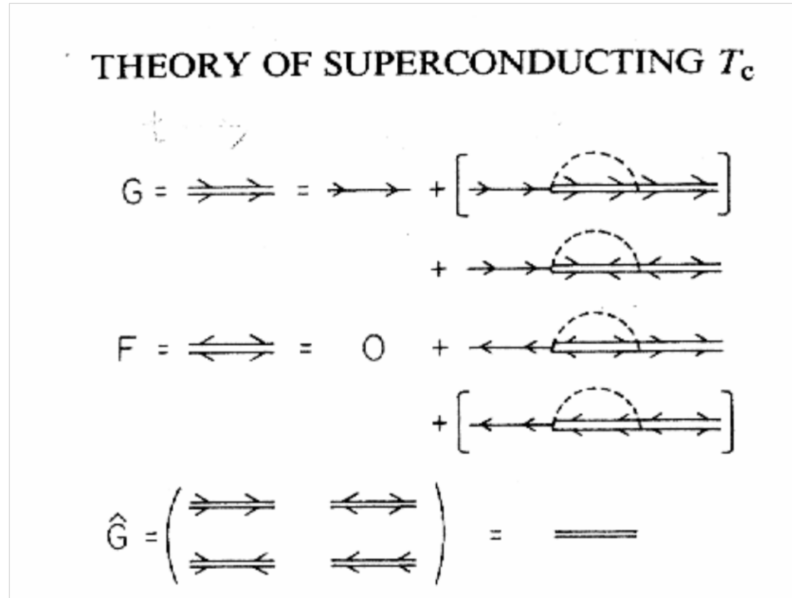

using **McMillan**'s

G Savini, AC Ferrari & FG, PRL (2010)

# Beyond McMillan's ? Anisotropic Eliashberg

PB Allen & B Mitrovic, Solid State Physics 1982

- Details of electron-phonon physics




$$
\begin{aligned}
\hat{\Sigma}(\mathbf{k}, i\omega_n) \quad &= -k_{\mathrm{B}}T \sum_{\mathbf{k}'n'} \hat{\tau}_3 \hat{G}(\mathbf{k}', i\omega_{n'})\hat{\tau}_3 \sum_{\nu} |g_{\mathbf{k}\mathbf{k}'\nu}|^2 D_\nu(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}) \\
&\quad -k_{\mathrm{B}}T \sum_{\mathbf{k}'n'} \hat{\tau}_3 \hat{G}(\mathbf{k}', i\omega_{n'})\hat{\tau}_3 W(\mathbf{k}-\mathbf{k}')
\end{aligned}
$$

See also: ME: HJ Choi et al, Nature 2001' SCDFT: M Luders et al, PRB 2005; MAL Marques et al, PRB 2005

# **Eliashberg** equation for the **superconducting gap**

$$\Delta(\mathbf{k}, i\omega_n) = \frac{\pi k_{\mathrm{B}} T}{N(\epsilon_{\mathrm{F}})} \sum_{\mathbf{k}' n'} \delta(\epsilon_{\mathbf{k}'} - \epsilon_{\mathrm{F}}) \left[\lambda(\mathbf{k}, \mathbf{k}', n - n') - \mu^* \theta(\omega_{\mathrm{c}} - |\omega'_n|)\right] \frac{\Delta(\mathbf{k}', i\omega_{n'})}{[\omega^2_{n'} + \Delta^2(\mathbf{k}', i\omega_{n'})]^{1/2}}$$

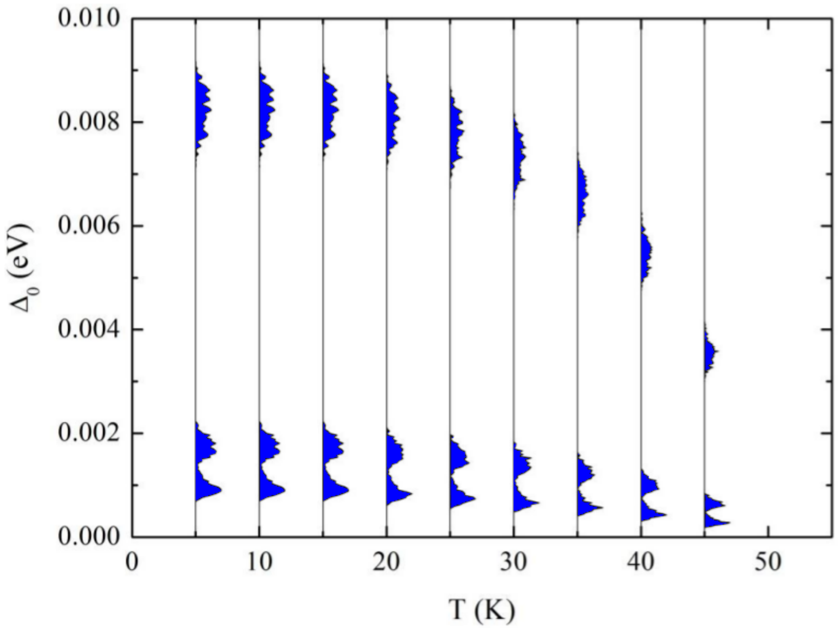
EPW.org.uk

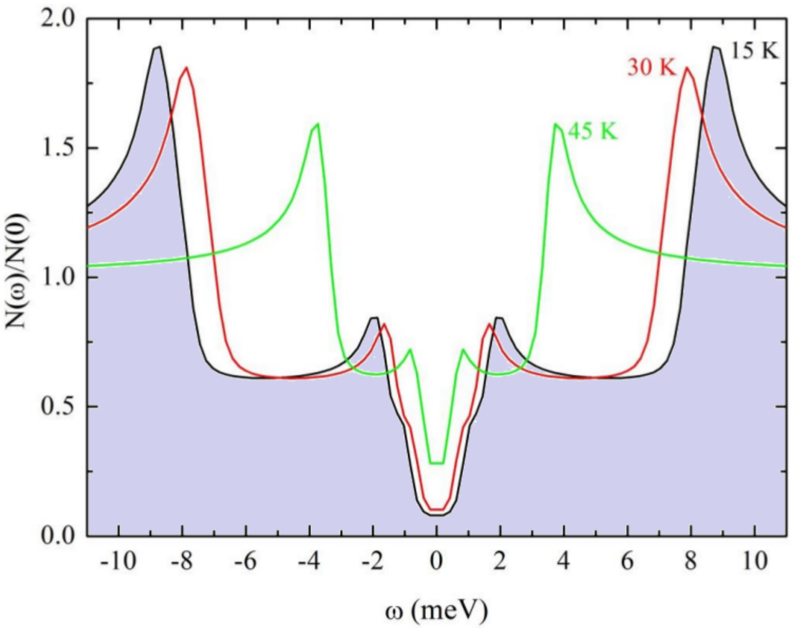
(Renorm factor Z set to 1 in this slide for clarity)

UNIVERSITY OF OXFORD

Roxana Margine

# $MgB_2$



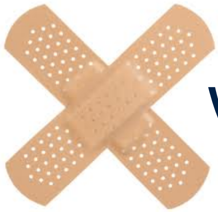

ER Margine & FG, in preparation

# Open questions

Off-diagonal matrix elements for degenerate bands

Only bands near the Fermi level

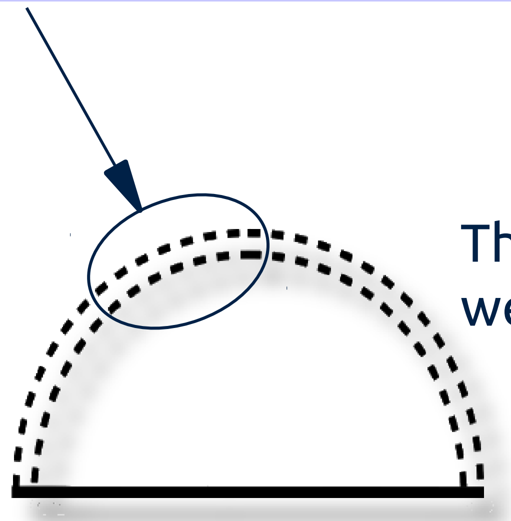
Nearly-constant density-of-states at the Fermi level



what about the Coulomb parameter $\mu^*$ ?

**Dynamically-screened** Coulomb interaction

$$W(\mathbf{r},\mathbf{r}';\omega) = \int d\mathbf{r}''\, v(\mathbf{r},\mathbf{r}'')\epsilon^{-1}(\mathbf{r}'',\mathbf{r}';\omega)$$

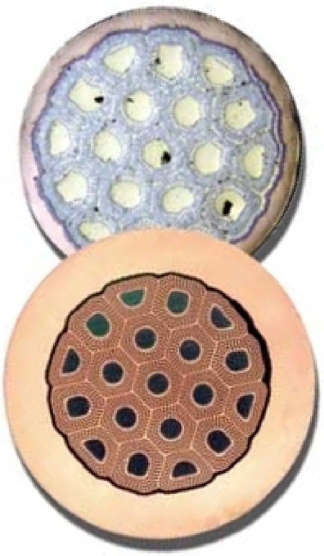


The same quantity that
we calculate in SternheimerGW

Metals

Insulators

Superconductors



# SOFTWARE

UNIVERSITY OF OXFORD

EPW.org.uk


EPW

DOWNLOAD AND INSTALL

Most recent snapshot of the code available here:
EPW-2.3.6.tar.gz
(Standardization of examples - 21 Dec 2011)

EPW-2.3.3 has been downloaded 51 times.
EPW-2.3.4 has been downloaded 227 times.
EPW-2.3.4-patched has been downloaded 205 times.
EPW-2.3.5 has been downloaded 48 times.
EPW-2.3.6 has been downloaded 65 times.

To install EPW:

1) download version 4.0.3 of Quantum-ESPRESSO here:
http://www.pwscf.org/downloads/PWversion/4.0.3/espresso-4.0.3.tar.gz

SEARCH
Go
PROJECT
About
Documentation
FAQ
Contact
Highlights
SOURCE CODE
Download and Install

EPW-2.3.6 with QE-4.0.3

QUANTUM ESPRESSO

WANNIER90

UNIVERSITY OF OXFORD


EPSRC

Engineering and Physical Sciences Research Council

MARIE CURIE ACTIONS