CONDENSED MATTER THEORY: FROM MODELS TO FIRST PRINCIPLES

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IT WAS SUGGESTED THAT I

“REVIEW CMT WITH EMPHASIS ON ELECTRONIC STRUCTURE AND THE DEVELOPMENT OF COMPUTATIONAL METHODS TO CALCULATE AND PREDICT PROPERTIES OF REAL MATERIALS AND GIVE MODERN EXAMPLES (MY OWN WORK)”

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ALL MY REJECTION LETTERS FROM PRL

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NANOSCIENCE AND SUPERCONDUCTIVITY

PREHISTORY

EINSTEIN, DIRAC,
SOMMERFELD-BETHE, FERMI

EINSTEIN 1905

DETERMINATION OF MOLECULAR DIMENSIONS

BROWNIAN MOTION

SPECIAL RELATIVITY

PHOTOELECTRIC EFFECT

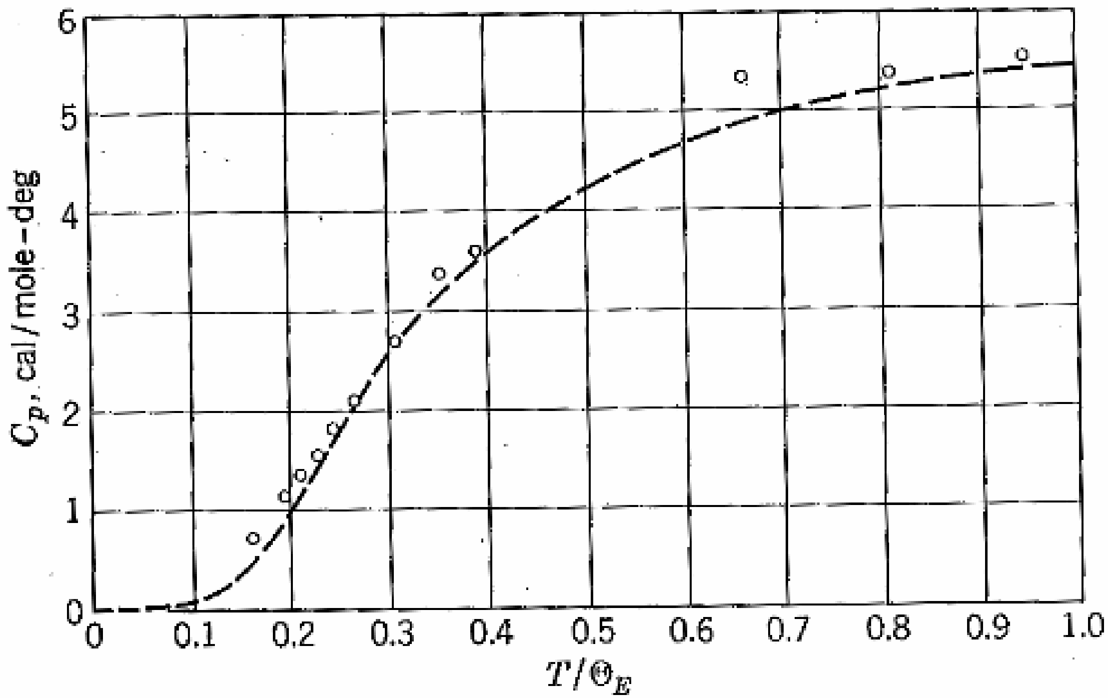


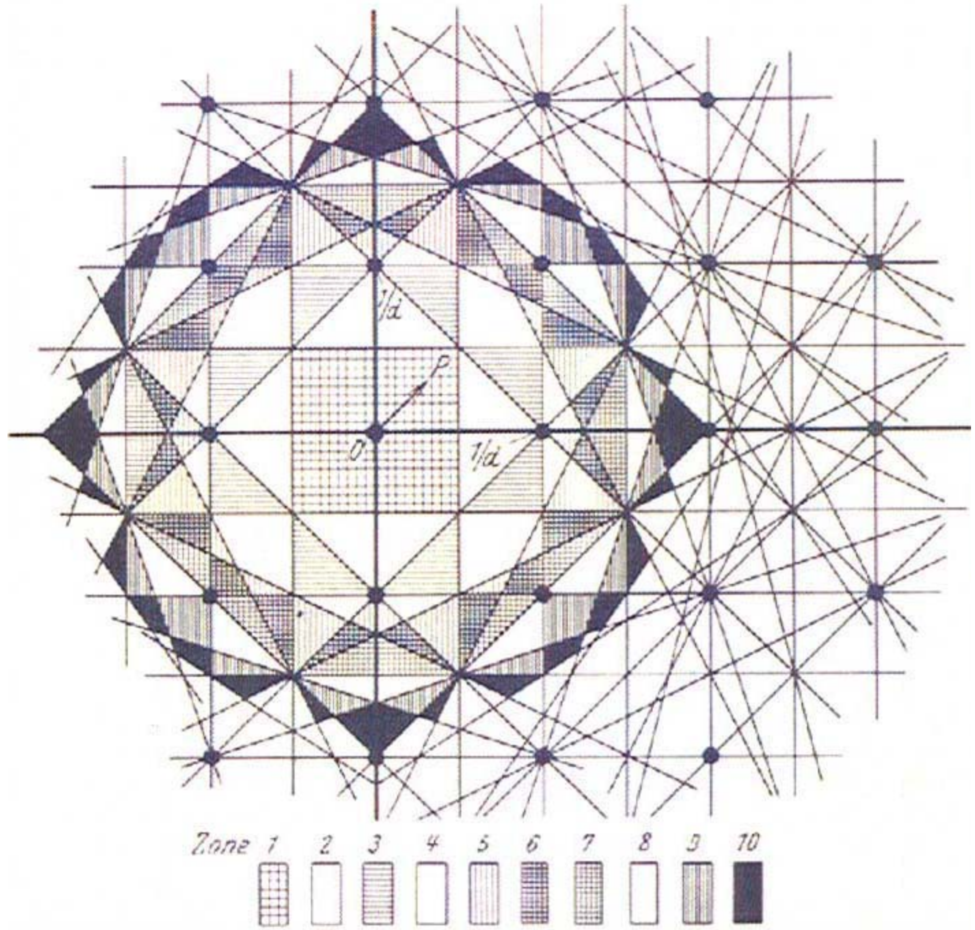
Figure 3 Comparison of experimental values of the heat capacity of diamond with values calculated on the Einstein model, using the characteristic temperature $\Theta_E = \hbar\omega/k_B = 1320°K$. [After A. Einstein, Ann. Physik **22**, 180 (1907).]

This figure is still in textbooks after a century.

Dirac (1929)

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact applicationof these laws leads to equations much too complicated to be soluble."

[Proc. Roy. Soc. (London) A123, 714]



BRILLOUIN ZONES
SOMMERFELD AND BETHE 1933

PSEUDOPOTENTIAL - FERMI 1934

All'esterno della buca, dove $V(r)$ si annulla, la u è dunque una funzione lineare di r. E siccome il valore di ψ lontano dalla buca

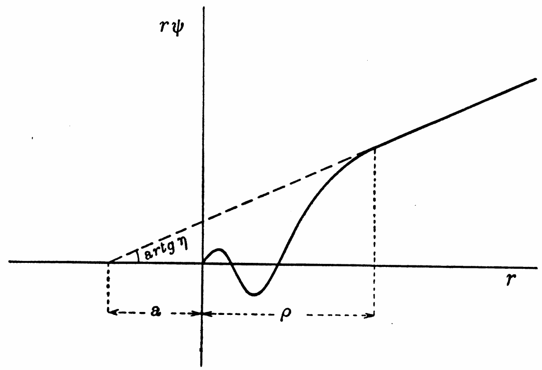


Fig. 1.

deve tendere approssimativamente al valore $\bar{\psi}$, si potrà porre, all'esterno della buca:

$$u(r) = (a + r)\bar{\psi} \tag{11}$$

dove a è una lunghezza, il cui significato è chiarito nella Fig. 1. In essa sono riportati in ascisse i valori di r e in ordinate quelli di u. La u, come risulta dalla (9), è nulla per $r = 0$, mentre, per r maggiore di ρ ha per grafico una retta. Prolunghiamo questa retta fino ad incontrare l'asse delle ascisse; a è la distanza del punto di intersezione dall'origine delle coordinate.

Tenendo conto di (9), (10) e (11) troviamo

$$\frac{8\pi^2 m}{h^2}\int V\psi d\tau = 4\pi\frac{8\pi^2 m}{h^2}\int V\, u r dr = 4\pi\int u'' r dr \tag{12}$$

$$= 4\pi \left| u' r - u \right|_0^r = -4\pi a\bar{\psi}$$

e siccome nell'unità di volume sono contenute n buche di potenziale, ricaviamo infine

$$\frac{8\pi^2 m}{h^2}\overline{\Sigma V_i \psi} = -4\pi a n\bar{\psi}. \tag{13}$$

Con ciò la (8) diventa

$$\Delta\bar{\psi} + \frac{8\pi^2 m}{h^2}(W_0 - U)\bar{\psi} = 0 \tag{14}$$

dove si è posto

$$W_0 = W + \frac{h^2 a n}{2\pi m}. \tag{15}$$

DENSITY FUNCTIONAL THEORY - DIRAC 1930

1940-1960

HERRING-SLATER-PHILLIPS

1957--PRL, BCS, but no accurate/detailed Si E(k)

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BUT BY…

1965--14 accurate semiconductor E(K)’s-EPM

1970--optical structure of semiconductors solved

1980’s--structural properties, superc.,surf.,high P

1990-2008 --complex materials, nanostructures, and a variety of properties

“I'm often asked whether doing physics research using computers is ‘mindless research.’ My answer is that I can do ‘mindless research’ without a computer.”

M. L. Cohen (1970)

For calculating materials properties**: “If given the choice between the computers of today together with the physical concepts of the 1970's—*or*—the computers of the 1970's along with current concepts, I'd choose the latter.”**

J. R. Chelikowsky (2000)

CONCEPTUAL BASIS

ONE CAN ARGUE FOR TWO MODELS OR "MENTAL PICTURES" OF A SOLID:

"INTERACTING ATOMS"

and

"ELEMENTARY EXCITATIONS"

MODELS

INTERACTING ATOMS MODEL

A solid is a collection of strongly interacting atoms.

The particles are electrons and nuclei interacting via EM interactions.

(associated with reductionism)

ELEMENTARY EXCITATION MODEL

particles are mainly:

quasiparticles and collective excitations

[probe-response]

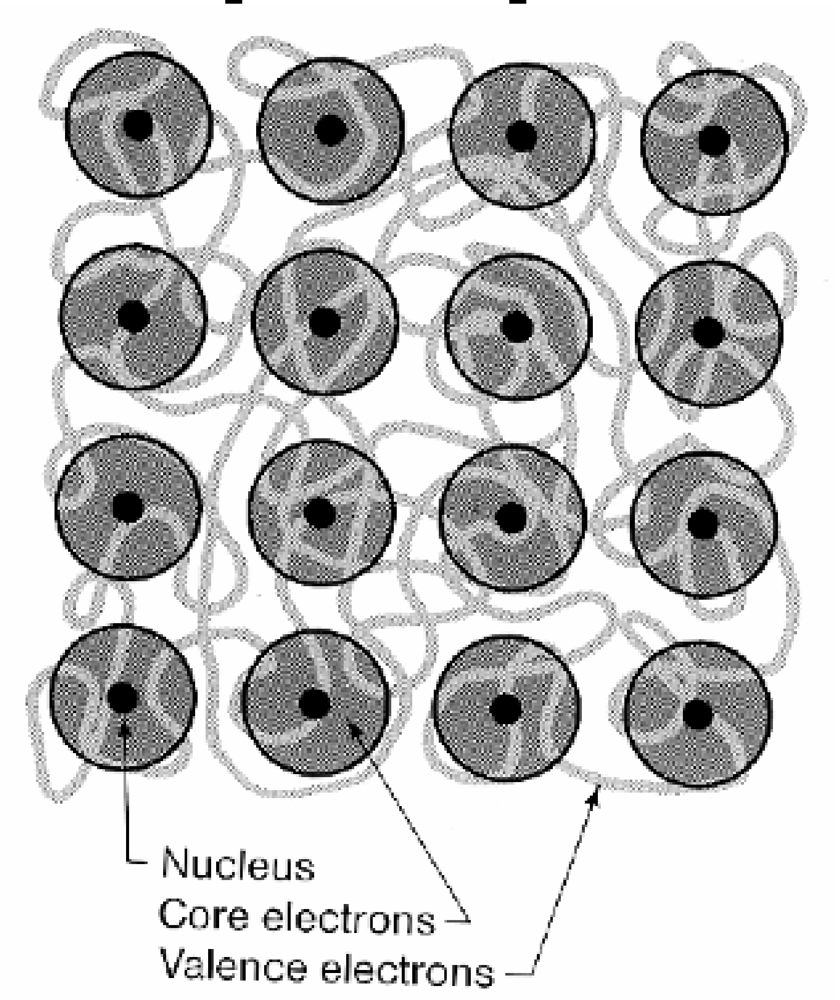
(emergent behavior)

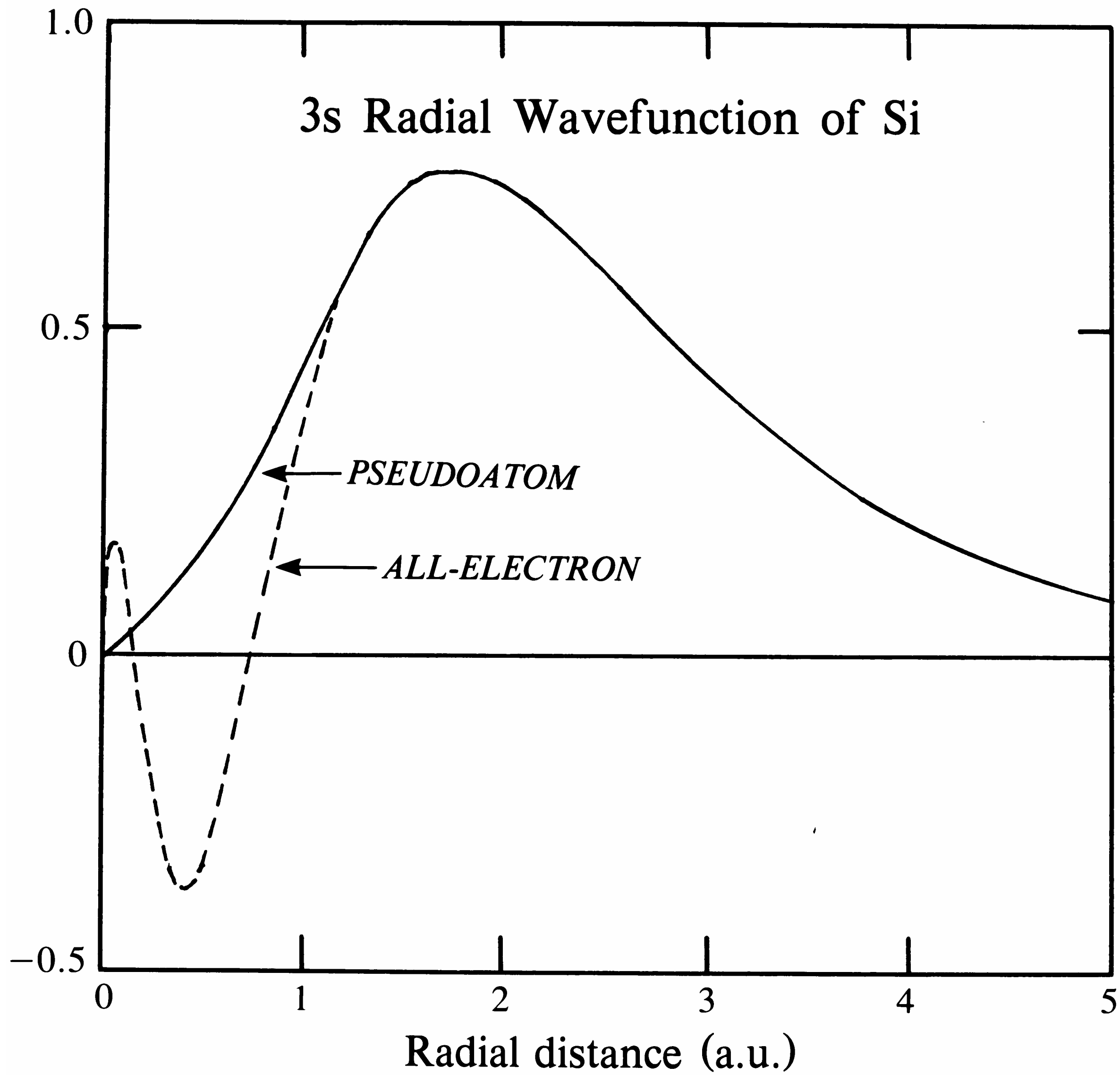
quasiparticles: quasielectrons (like polarons), holes, superconducting quasiparticles,…

collective excitations: phonons, plasmons, magnons,…

Standard Model

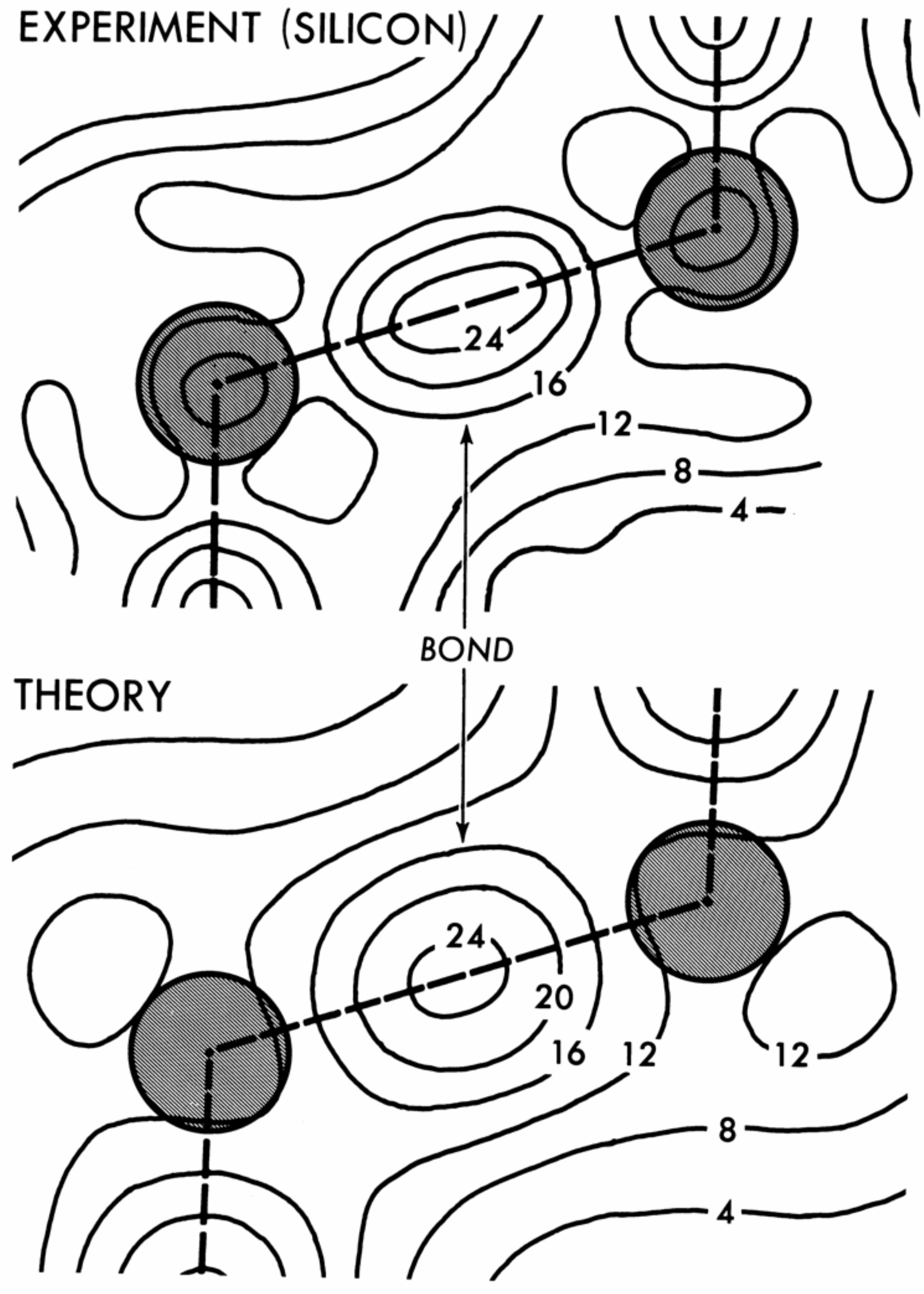
Plane Wave Pseudopotential Method [PWPM]

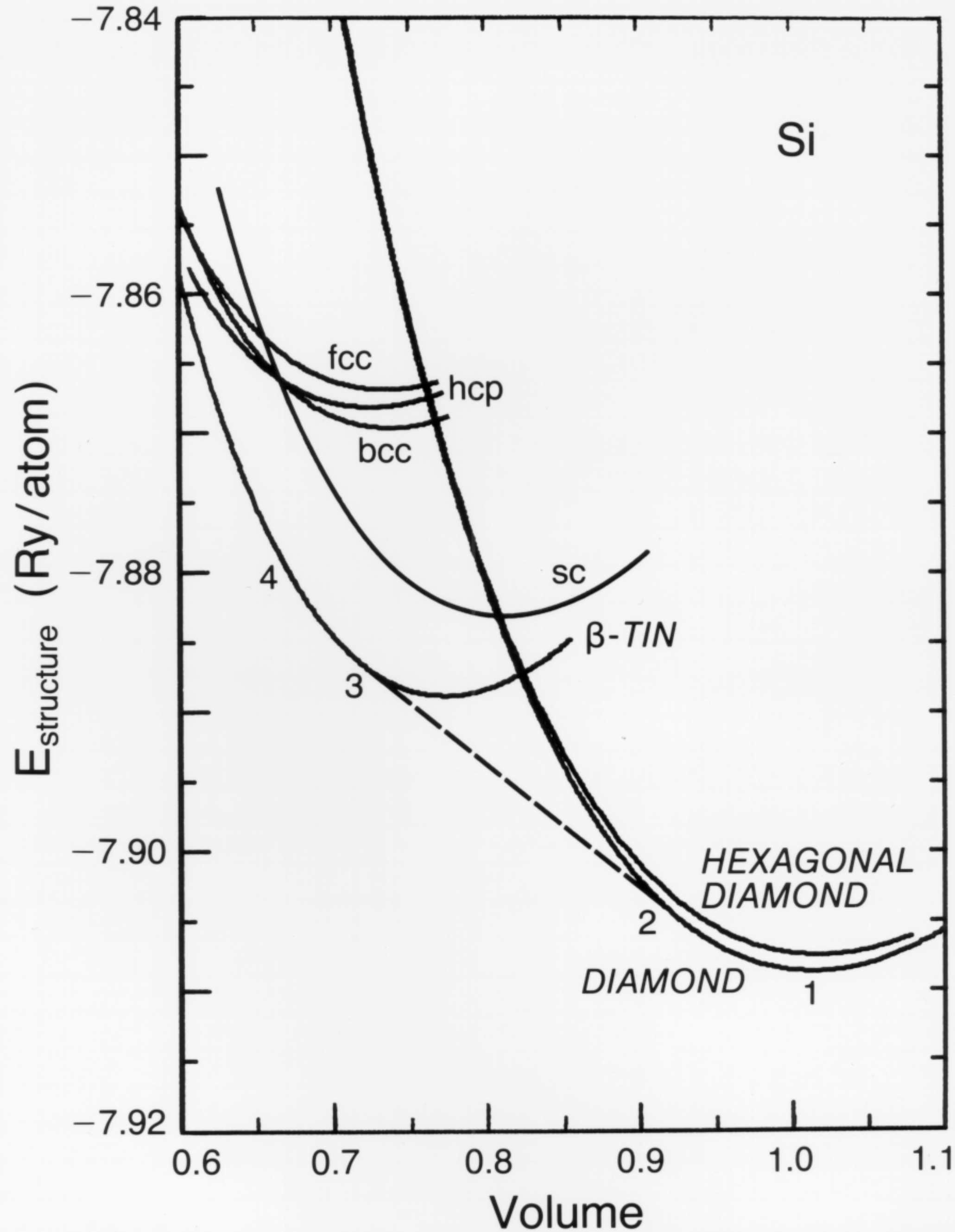




3s Radial Wavefunction of Si
1.0
0.5
0
−0.5
PSEUDOATOM
ALL-ELECTRON
0
1
2
3
4
5
Radial distance (a.u.)

Charge Density of Si





Si
fcc
hcp
bcc
sc
β-TIN
4
3
2
1
HEXAGONAL DIAMOND
DIAMOND
$E_{structure}$ (Ry/atom)
Volume
−7.84
−7.86
−7.88
−7.90
−7.92
0.6
0.7
0.8
0.9
1.0
1.1

Static Structural Properties

	lattice constant (Angstroms)	bulk modulus (GPa)
Si		
calc.	5.45	98
expt.	5.43	99
% diff.	0.4%	-1%
Ge		
calc.	5.66	73
expt.	5.65	77
% diff.	0.1%	-5%
C		
calc.	3.60	441
expt.	3.57	443
% diff.	0.8%	-1%

YIN + COHEN

Plane Wave Pseudopotential Method

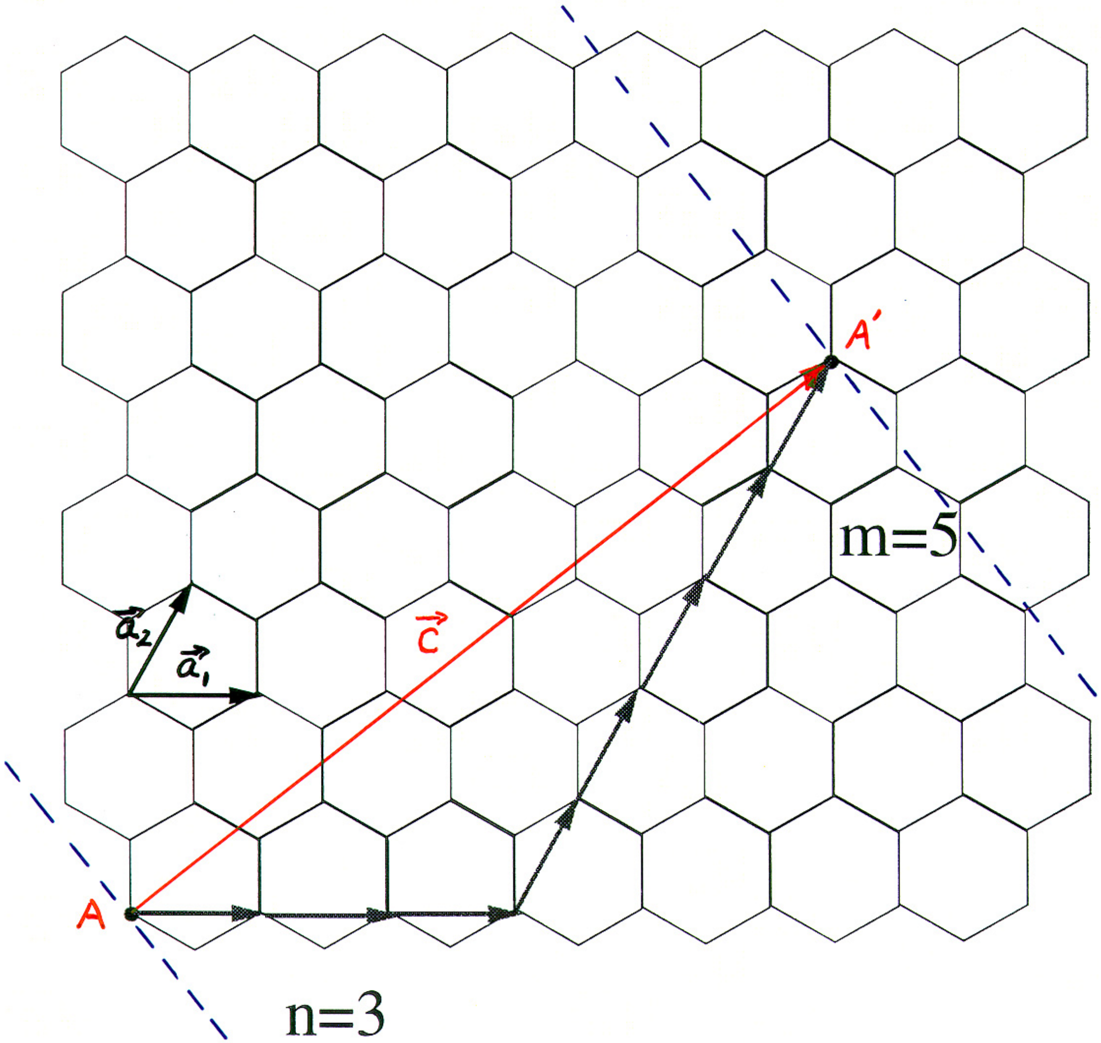
(Standard Model of Solids)

For a broad class of solids, clusters, and molecules, this method describes ground-state and excited-state properties such as:

- **electronic structure**
- **crystal structure and structural transitions**
- **structural and mechanical properties**
- **vibrational properties**
- **electron-lattice interactions**
- **superconductivity**
- **optical properties**

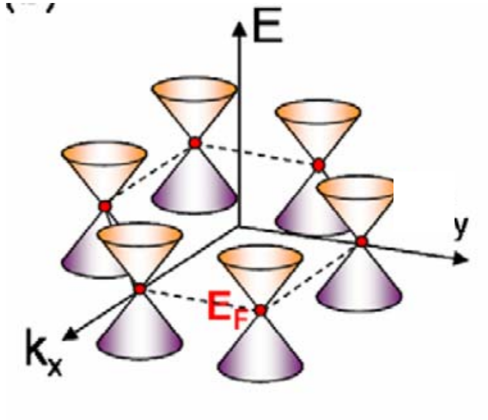
CONFINEMENT
REDUCED DIMENSONALITY
SYMMETRY

Nanotubes are indexed by the circumferential periodicity.

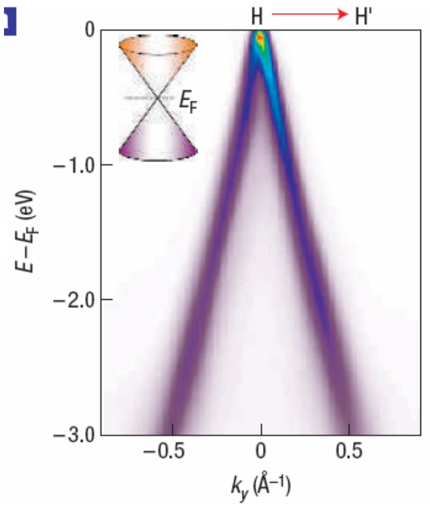


The (3,5) nanotube.

2-D graphene as physical realization of (2+1)D QED



Single particle energy dispersion



ARPES, S. Y. Zhou *et al*, Nature Phys.**2**, 595 (2006)

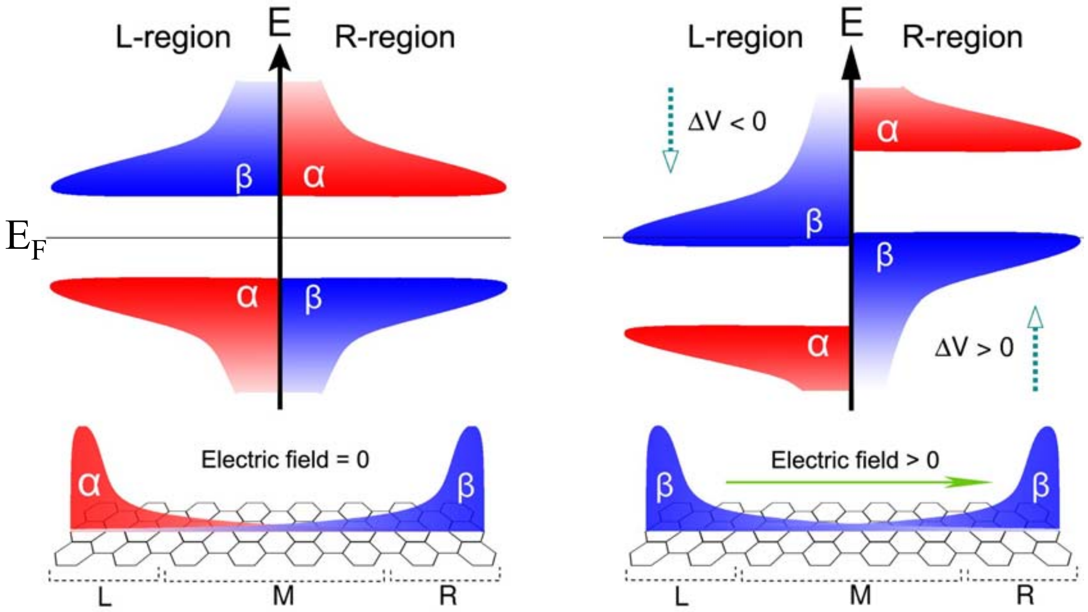
Massless Dirac equation with c^{*}~c/300~10^6m/s

Quantum Hall effect in graphene obseved

Electric field induced half-metallic states in graphene nanoribbons

Effect of Transverse Electric Field on Edge States

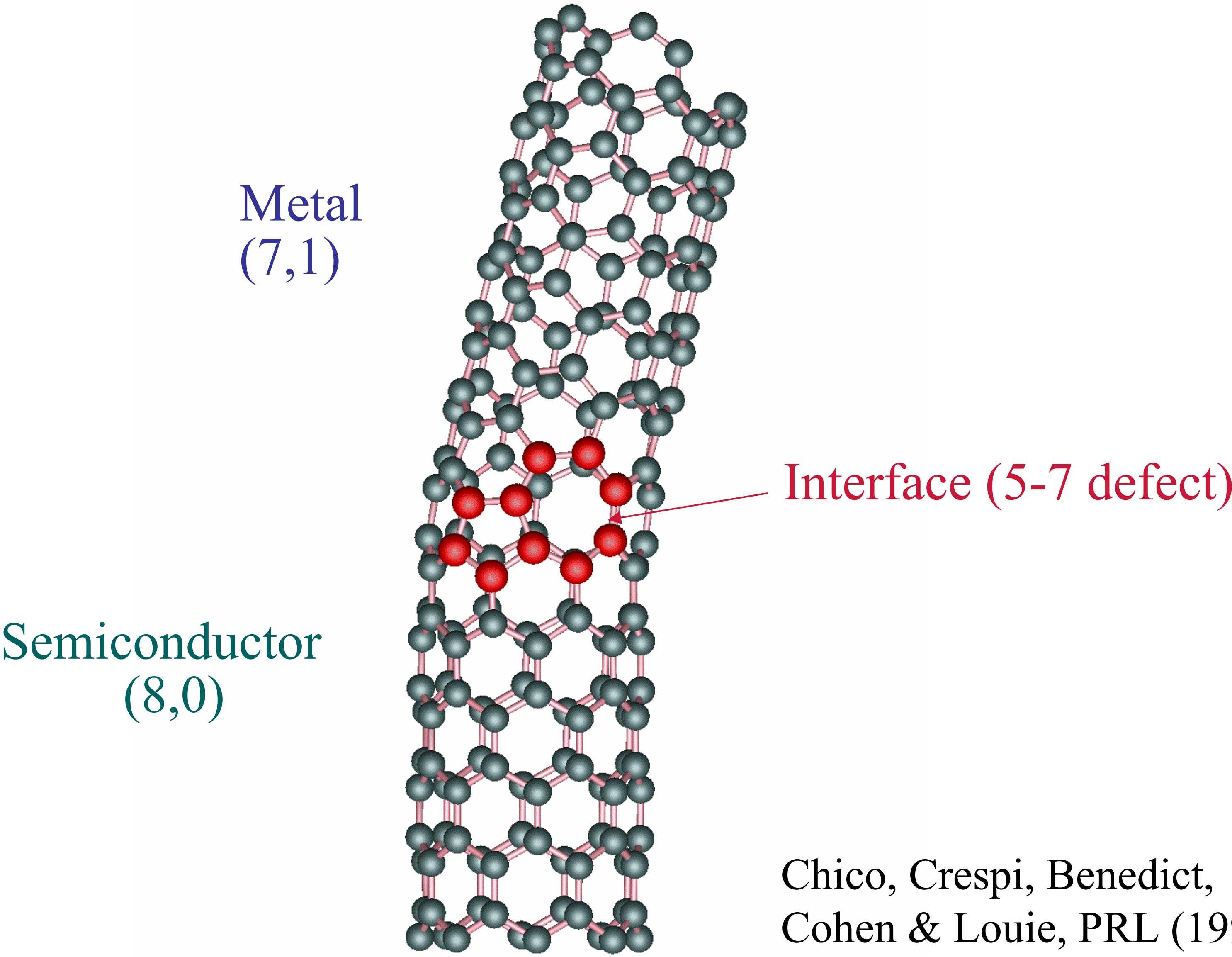
no field



with field

- Spin polarization of carriers is 100%.
- It is tunable and reversible!
- Electric field is more effective on wider nanoribbons ($E_c \sim 1/w$)

(8,0)/(7.1) Nanotube Schottky Barrier



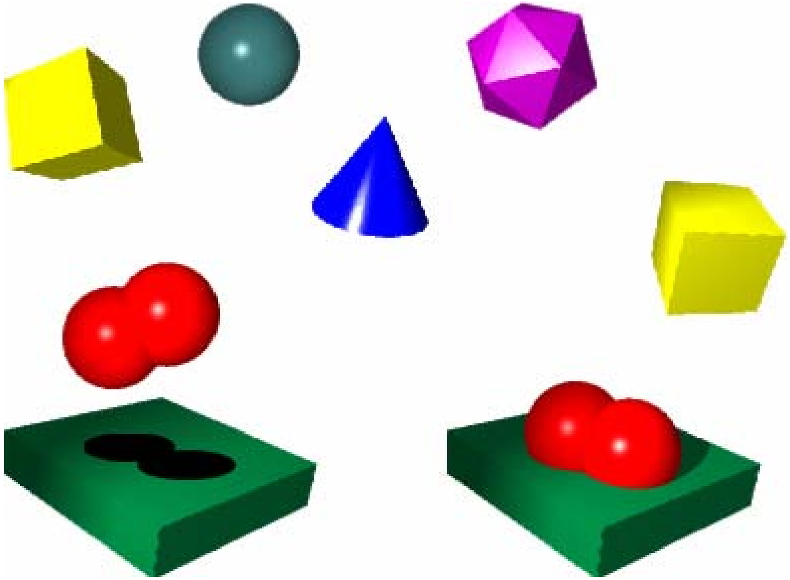
Chico, Crespi, Benedict, Cohen & Louie, PRL (1996)

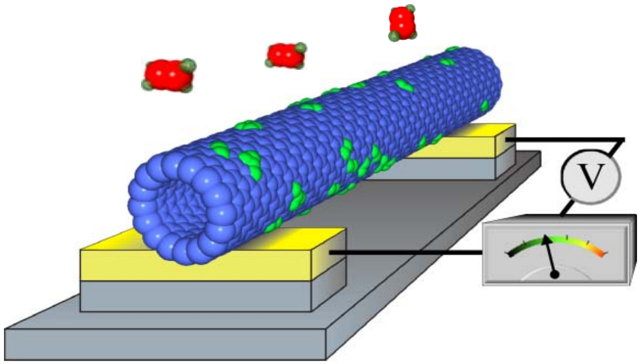
Sensor Concept: Sensing Specific Analytes

Architecture:

integration of three layers

1. **Recognition layers or recognition molecules to achieve analyte specificity**
2. **NTFET as transducer**
3. **Si CMOS architecture**

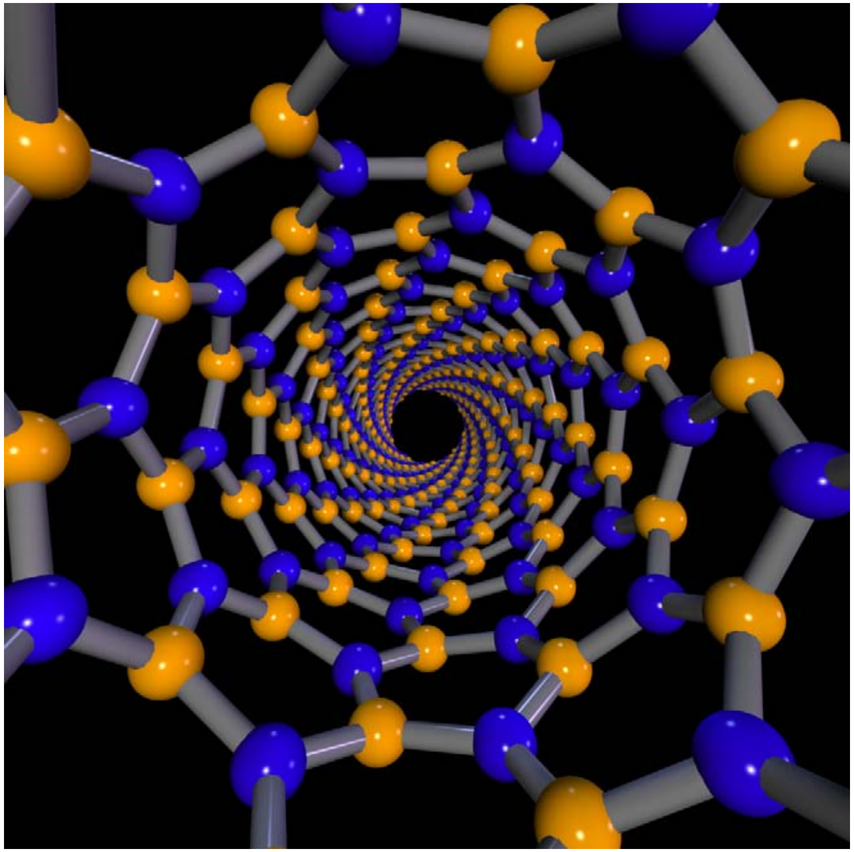




Boron Nitride Nanotubes

Predicted by theory
Semiconductors
Electronic properties independent of tube chirality

Zettl, Cohen, Louie, et al., *Science (1995)*



CLASSES OF SUPERCONDUCTORS

BCS : conventional metals, C60, some organics, doped semiconductors, MgB2,…

“BCS” EXOTIC: copper oxides, heavy fermion metals, some organics,…

CAN BCS THEORY PREDICT T_c?

$$T_c \propto T_D \, e^{-\frac{1}{NV}} \sim 11K$$

$T_D \sim 300K$, $NV \sim 0.3$

IF "NV" → 0.03 $T_c \to 10^{-12}$

NEED TO KNOW "NV" VERY ACCURATELY

TO PREDICT T_c

DOPED SEMICONDUCTOR

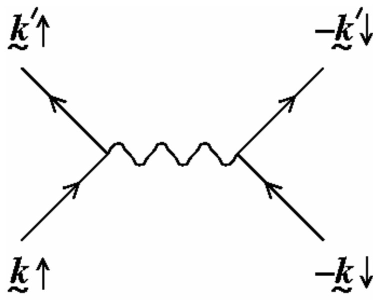
$SrTiO_3$

FIRST SUPERCONDUCTING OXIDE

(COHEN 1963; SCHOOLEY ET AL 1964)

Superconductivity in the Eliashberg Formalism

BCS Theory



Electron pairing
via phonon exchange

Main ingredient: momentum– and frequency-dependent Eliashberg function

$$\alpha^2 F(\vec{k},\vec{k}',\omega) \equiv N(\varepsilon_F) \sum_j \left| g^j_{\vec{k}\vec{k}'} \right|^2 \delta(\omega - \omega_{j\vec{q}})$$

where $N(\varepsilon_F)$ = density of states per spin at Fermi level

$g_{\mathbf{kk'}}$ = electron-phonon matrix element

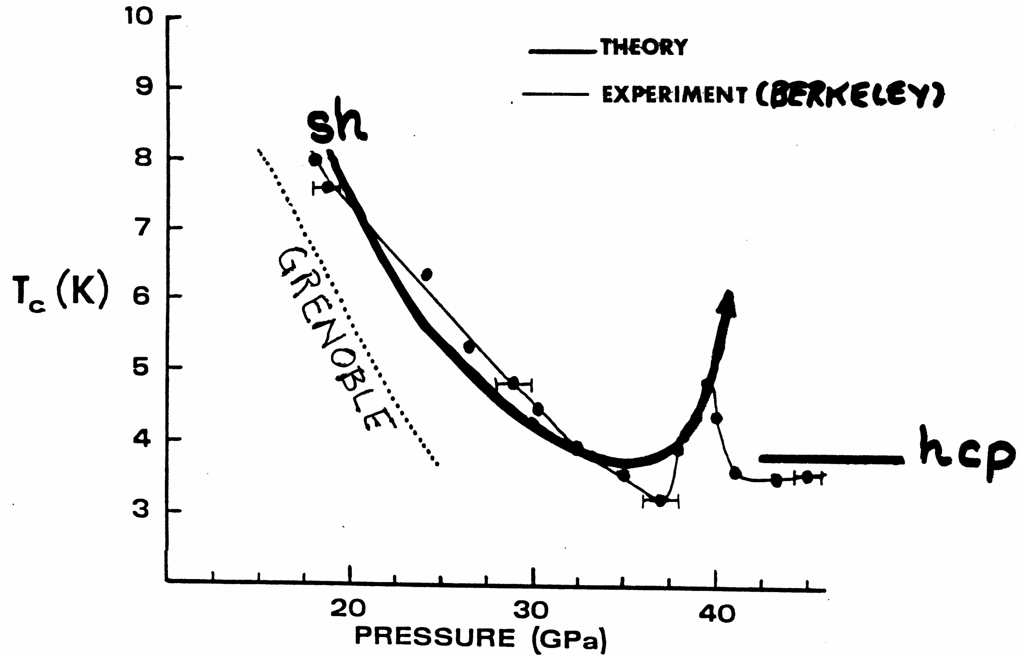
$\omega_{j\mathbf{q}}$ = frequency of phonon in jth branch with **q**=**k**-**k'**

Equivalently:

$$\lambda(\vec{k},\vec{k}',n) \equiv \int_0^\infty d\omega\, \alpha^2 F(\vec{k},\vec{k}',\omega) \frac{2\omega}{\omega^2 + (2n\pi T)^2}$$

$\lambda = \langle \lambda(k, k', 0) \rangle$

sh and hcp SILICON T_c (PRESSURE)



THEORY
CHANG, DACOROGNA & COHEN

EXP.
GRENOBLE : MIGNOT, CHOUTEAU & MARTINEZ
BERKELEY : ERSKINE & YU

Transition Temperature and Isotope Effect

	harmonic		anharmonic		experiment
	isotropic	anisotropic	isotropic	anisotropic	
T_c	28 K	55 K	19 K	39 K	39 K
α_B	0.42	0.46	0.25	0.32	0.26,0.30
α_{Mg}	0.04	0.02	0.05	0.03	0.02
λ	0.73		0.61		0.58, 0.62
ω_{ph}	62.7 meV		75.9 meV		75.9, 76.9

$\mu^*(\omega_c) = 0.12.$

Anharmonicity --> small α_B

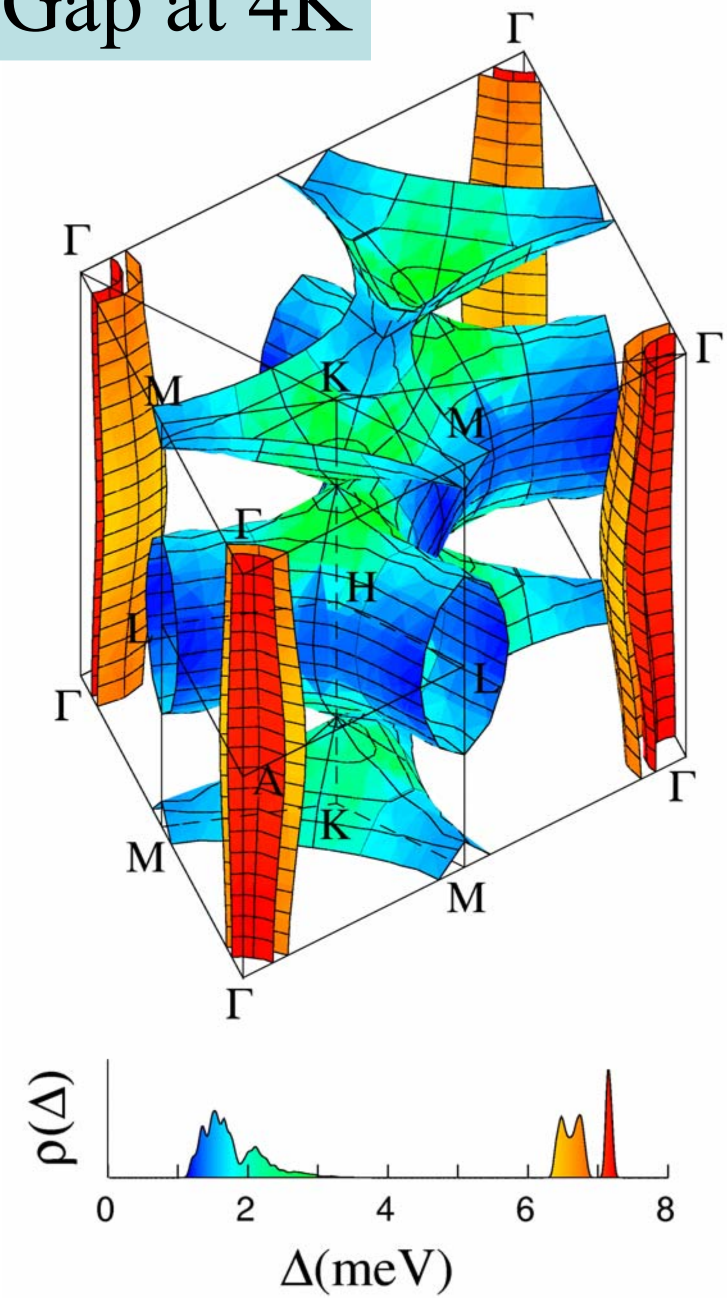
λ : averaged electron-phonon coupling.

ω_{ph} : frequency of the in-plane B–B stretching modes (E_{2g}) at Γ.

For $0.10 \leq \mu^*(\omega_c) \leq 0.14$, $41\ \text{K} \geq T_c \geq 37\text{K}$

Superconducting Gap at 4K

- $\Delta(\mathbf{k})$ on Fermi surface at T=4 K
- Large gap on cylindrical σ–sheets
- 2 dominant sets of gap values



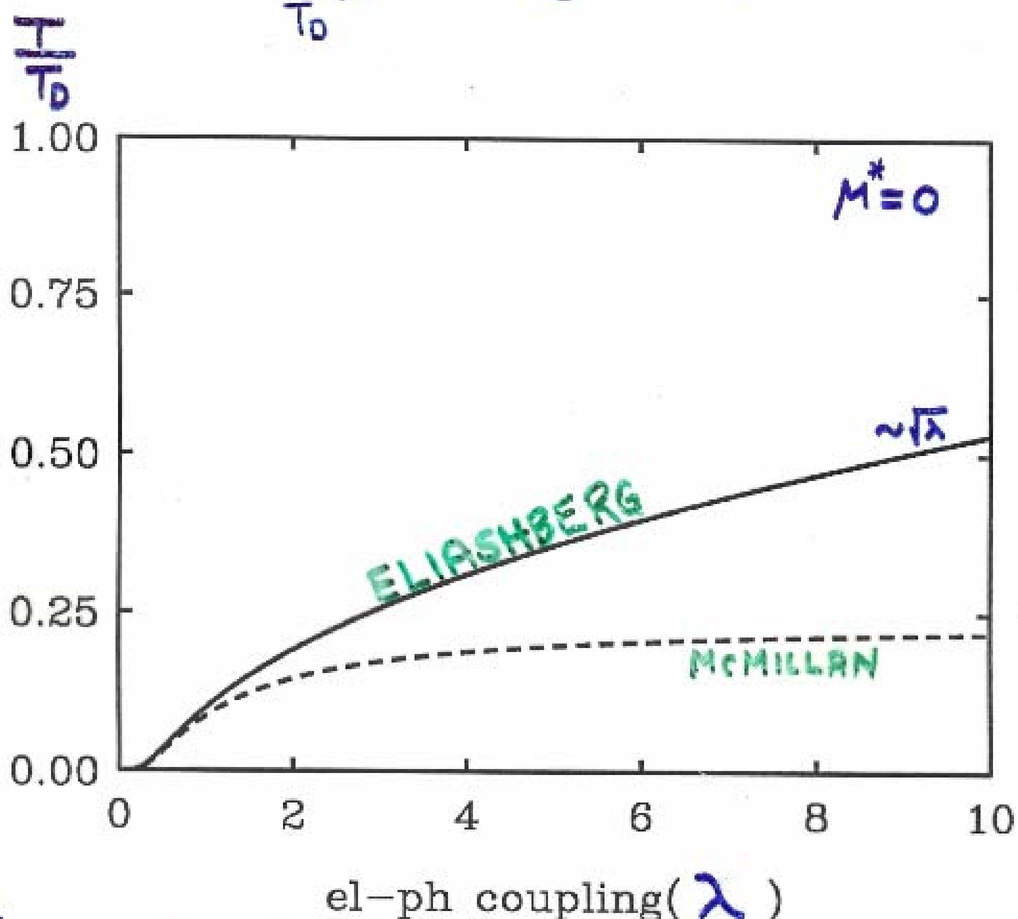
RAISING Tc

WE TRIED TO USE THEORY TO SUGGEST HOW TO INCREASE THE TRANSITION TEMPERATURE OF MAGNESIUM DIBORIDE SIGNIFICANTLY BUT FAILED!

THIS RESULT IS CONSISTENT WITH EXPERIMENTS UP TO NOW.

McMILLAN 1968

$$\frac{T_c}{T_D} \approx 0.69\, e^{-\frac{1}{\lambda^* - \mu^*}}$$



Kresin-Barbee-Cohen

$$\frac{T_c}{\langle \omega \rangle} = 0.26\,(e^{2/\lambda} - 1)^{-1}$$

ELECTRON-PHONON COUPLING

$$\lambda\left\langle \omega^2 \right\rangle = \sum_i \frac{\eta_i}{M_i}$$

SO λ CAN BE VIEWED AS THE RATIO OF AN ELECTRONIC SPRING CONSTANT η AND A LATTICE SPRING CONSTANT

Superconductivity in diamond

E. A. Ekimov[1], V. A. Sidorov[1], E. D. Bauer[2], N. N. Mel'nik[3], N. J. Curro[2], J. D. Thompson[2] & S. M. Stishov[1]

[1]*Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russia*
[2]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*Lebedev Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia*

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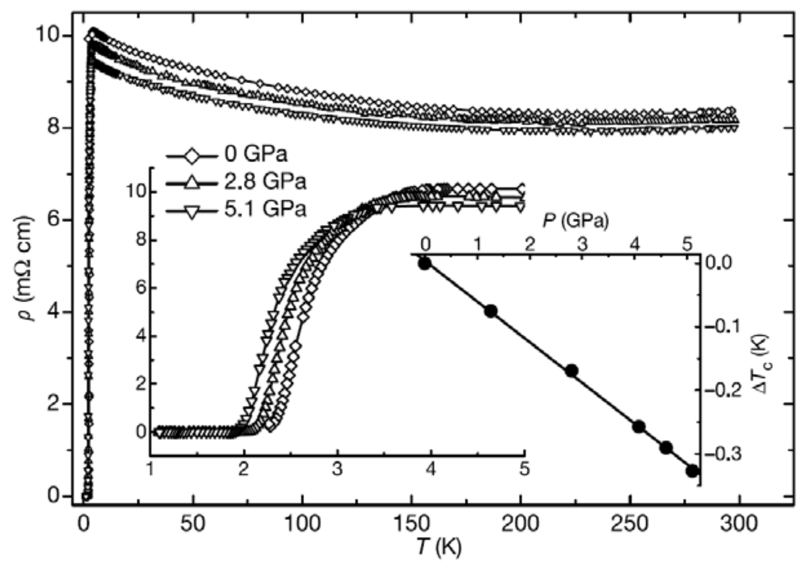


Bloch to Wannier Representation

$$g(\mathbf{k},\mathbf{q}) = \sum_{\mathbf{R}_\mathrm{e},\mathbf{R}_\mathrm{p}} \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}_\mathrm{e}}\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}_\mathrm{p}}\, u_\mathbf{q}\, U_{\mathbf{k}+\mathbf{q}}\, g(\mathbf{R}_\mathrm{e},\mathbf{R}_\mathrm{p})\, U^\dagger_\mathbf{k}$$

Bloch

Wannier

$$g(\mathbf{k},\mathbf{q}) = \sum_{\mathbf{R}_\mathrm{e},\mathbf{R}_\mathrm{p}} \mathrm{e}^{i\mathbf{k}\cdot\mathbf{R}_\mathrm{e}}\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{R}_\mathrm{p}}\, u_\mathbf{q}\, U_{\mathbf{k}+\mathbf{q}}\, g(\mathbf{R}_\mathrm{e},\mathbf{R}_\mathrm{p})\, U_\mathbf{k}^\dagger$$

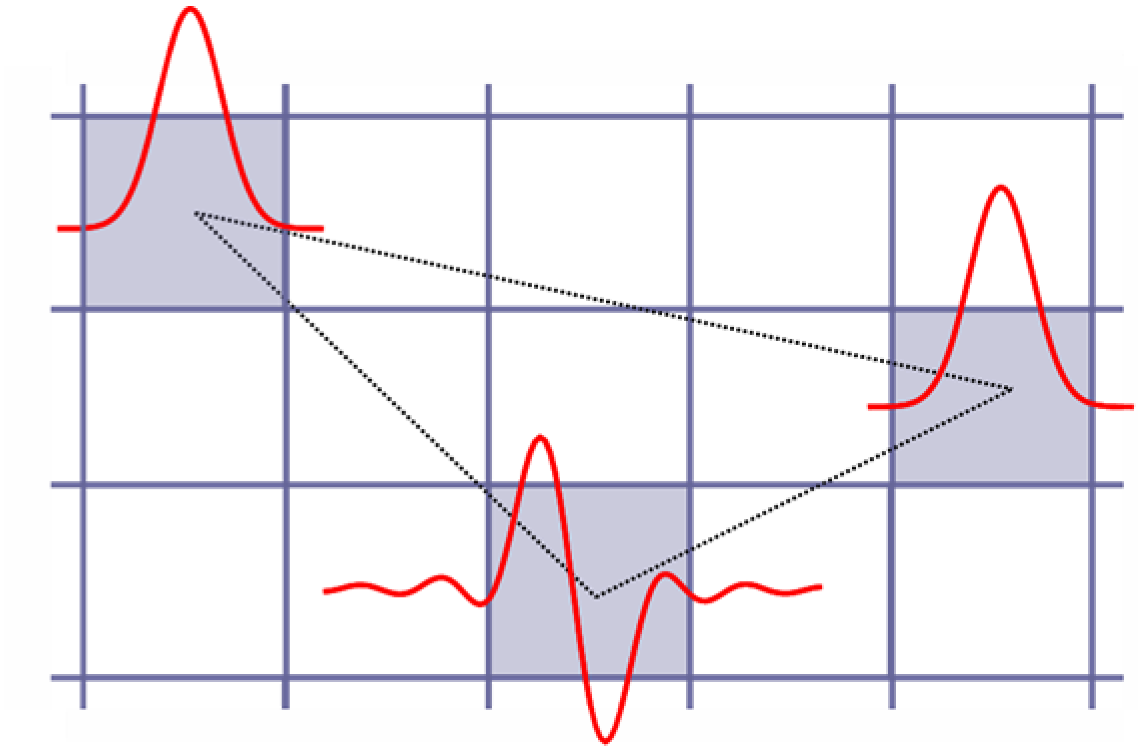
Bloch

Wannier

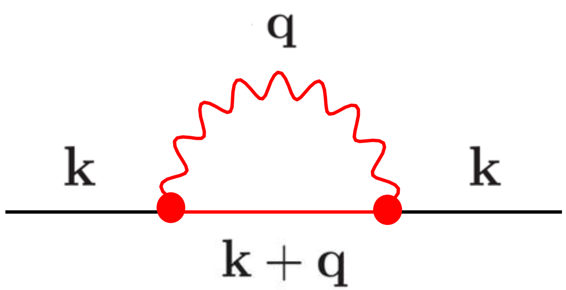
$$\langle m\mathbf{0}_\mathrm{e}|\, \Delta_{\kappa\alpha,\mathbf{R}_\mathrm{p}} V(\mathbf{r}) |n\mathbf{R}_\mathrm{e}\rangle$$

Wannier Representation

$$\langle m\mathbf{0}_{\mathrm{e}}| \qquad \Delta_{\kappa\alpha,\mathbf{R}_{\mathrm{p}}} V(\mathbf{r}) \qquad |n\mathbf{R}_{\mathrm{e}}\rangle$$



Electron Self-energy

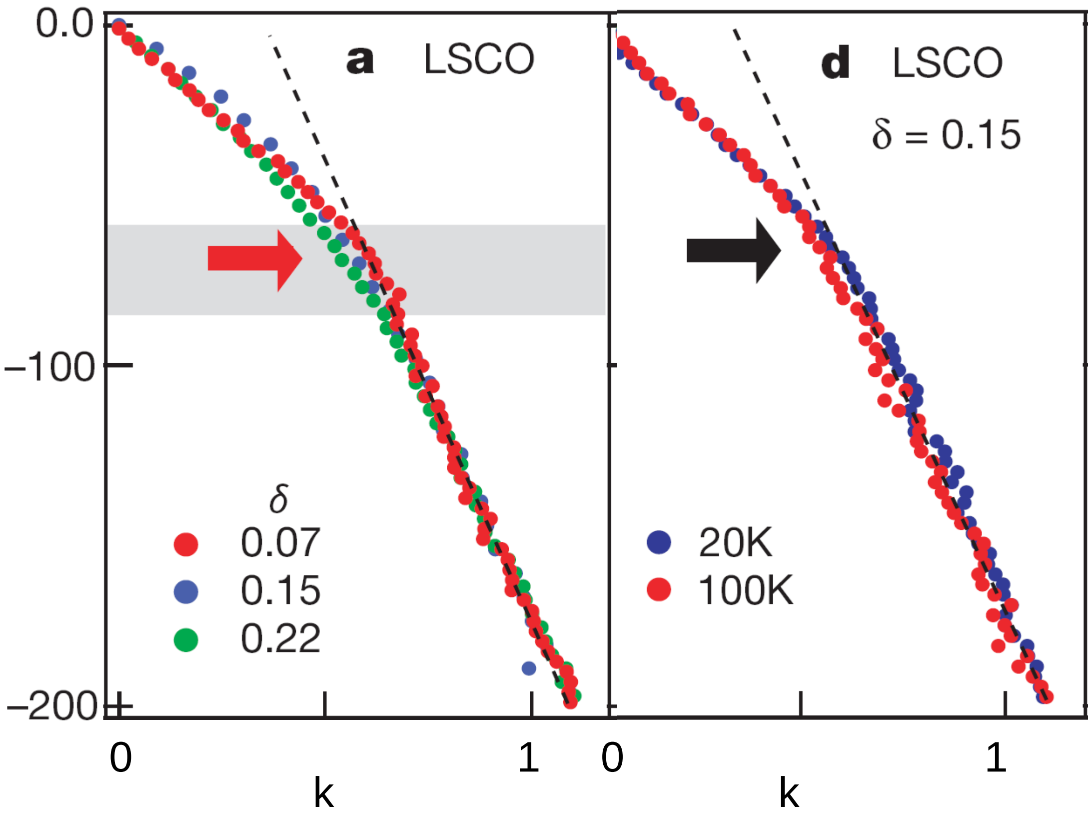


$$\Sigma = i \int \frac{d\,2}{(2\pi)^4} \, |g(1,2)|^2 \, D(1-2) \, G(2)$$

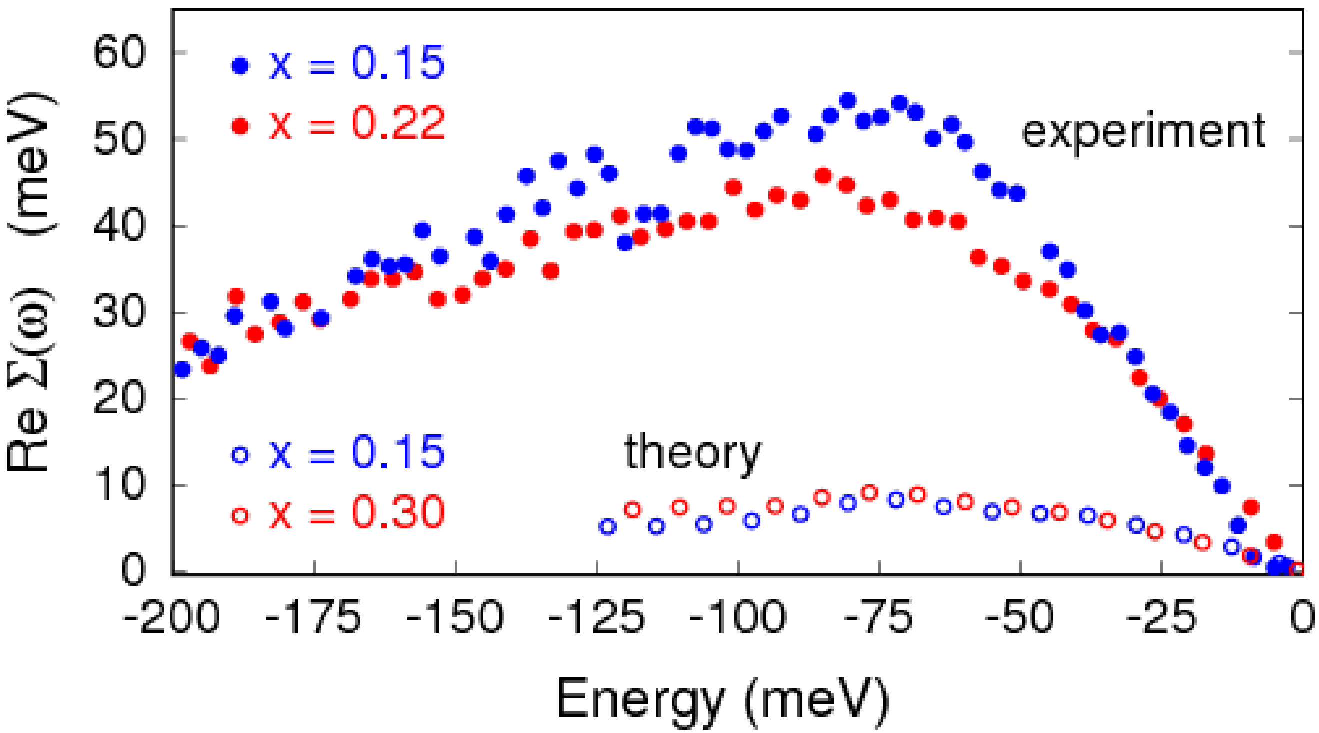
YIELDS A MASS ENHANCEMENT AND ASSOCIATED "KINK" AT THE FERMI SURFACE."KINKS" HAVE BEEN OBSERVED IN ARPES DATA AND INTERPRETETED AS SIGNATURES OF STRONG ELECTRON-PHONON COUPLING.

Electron-Phonon Interaction in the Photoemission Spectrum of $La_{2-x}Sr_xCuO4$ from First Principles

"Kink" (for example, Lanzara et al, Nature) 2001



By measuring the change in slope, the electron-phonon coupling is estimated



x = 0.15
x = 0.22
experiment
x = 0.15
x = 0.30
theory
Re Σ(ω) (meV)
Energy (meV)
60
50
40
30
20
10
0
-200
-175
-150
-125
-100
-75
-50
-25
0

CONCLUSION

BASED ON THE WANNIER FORMALISM FOR CALCULATING ELECTRON-PHONON SELF-ENERGIES, THE COUPLING IS 1/7 OF WHAT IS NEEDED TO REPRODUCE THE OBSERVED ARPES “KINKS”

EINSTEIN’S VIEW

Title of 1905 photoelectric effect paper:

"Concerning the generation and transformation of light from a heuristic point of view”

heuristic = model (an emergent view)

EMERGENCE

HENRI BERGSON (1859-1941)

“all we sense are images”

EINSTEIN’S VIEW

Title of 1905 photoelectric effect paper:

"Concerning the generation and transformation of light from a heuristic point of view”

heuristic = model (an emergent view)

a(reductionism) + b(emergence)

WHERE BOTH a AND b WERE FUNCTIONS OF TIME

Standard Model = “ interacting atoms” model + “elementary excitations” model

(reductionism + emergent behavior)

Standard Model =
“ interacting atoms” model +
“elementary excitations” model

(reductionism + emergent behavior)

Theorists can explain and predict ground and excited state properties of many condensed matter systems, but experimentalists still make the decisions on “what’s right”. They also make the major new discoveries (for now).

HAPPY 50TH BIRTHDAY TO PHYSICAL REVIEW LETTERS AND MANY THANKS TO THE PEOPLE WHO HAVE MADE IT SUCH A SUCCESS!

END