Session L23: Focus Session: Search for New Superconductors II: Towards Theoretical Design

2:30 PM–5:30 PM, Tuesday, March 22, 2011
Room: D165

Abstract: L23.00004 : Why positive hole carriers and negatively charged planes are conducive to high temperature superconductivity

3:06 PM–3:42 PM

References: http://physics.ucsd.edu/~jorge/hole.html
1989 → 2011
Principal collaborator: Frank Marsiglio

J.E. Hirsch
(University of California San Diego)

The vast majority of superconducting materials have positive Hall coefficient in the normal state, indicating that hole carriers dominate the normal state transport. This was noticed even before BCS theory, and has been amply confirmed by materials found since then: the sign of the Hall coefficient is the strongest normal state predictor of superconductivity. In the superconducting state instead, superfluid carriers are always electron-like, i.e. negative, as indicated by the fact that the magnetic field generated by rotating superconductors is always parallel, never antiparallel, to the body's angular momentum (``London moment''). BCS theory ignores these facts. In contrast, the theory of hole superconductivity, developed over the past 20 years (papers listed in http://physics.ucsd.edu/$\sim $jorge/hole.html) makes charge asymmetry the centerpiece of the action. The Coulomb repulsion between holes is shown to be smaller than that between electrons, thus favoring pairing of holes, and this fundamental electron-hole asymmetry is largest in materials where the conducting structures have \textit{excess negative charge}, as is the case in the cuprates, arsenides and MgB$_{2}$. Charge asymmetry implies that superconductivity is driven by lowering of kinetic energy, associated with expansion of the carrier wavefunction and with \textit{expulsion of negative charge} from the interior to the surface of the material, where it carries the Meissner current. This results in a macroscopic electric field (pointing outward) in the interior of superconductors, and a macroscopic spin current flowing near the surface in the absence of external fields, a kind of macroscopic zero point motion of the superfluid (spin Meissner effect). London's electrodynamic equations are modified in a natural way to describe this physics. It is pointed out that a dynamical explanation of the Meissner effect \textit{requires} radial outflow of charge in the transition to superconductivity, as predicted by this theory and not predicted by BCS. The theory provides clear guidelines regarding where new higher T$_{c}$ superconductors will and will not be found.

The current search efforts for new high T_c superconductors

Under the street light **of BCS theory…**

Late at night, a drunk was on his knees beneath a street-light, evidently looking for something.

… why are you looking for your watch here if you lost it half a block up the street? "
The drunk said: "Because the light's a lot better here. "

The continuum of superconductivity in materials

Where is the BCS-non-BCS divide?????

Differences: | Differences: | Differences:

Elements — MgB_2 — Pnictides — Cuprates

Common features: | Common features: | Common features:

The continuum of superconductivity in materials

Where is the BCS-non-BCS divide?????

Differences: **Differences:** **Differences:**

Elements **MgB_2** **Pnictides** **Cuprates**

Common features: **Common features:** **Common features:**

BaKBiO?

Sr_2RuO_4?

Borocarbides?

Cobaltates?

Heavy fermion compounds?

Organic superconductors?

The continuum of superconductivity in materials

There is NO BCS-non-BCS divide!

Differences: **Differences:** **Differences:**

Elements **MgB_2** **Pnictides** **Cuprates**

Common features: **Common features:** **Common features:**

BaKBiO?

Sr_2RuO_4?

Borocarbides?

Cobaltates?

Heavy fermion compounds?

Organic superconductors?

How to find new high temperature superconductors:

1) **Observe that among known superconducting materials there are pervasive correlations even among very different classes.**

2) **Infer empirical rules from these observed correlations.**

3) **See whether or not newly found superconductors (found after these empirical rules were formulated) conform to the same rules.**

4) **Understand the essential physics that gives rise to these empirical rules. Build simplified models containing this physics.**

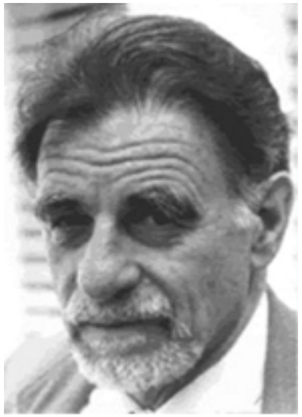
5) **Calculate from these models measurable properties, predict / compare with experiment.**

6) **BONUS: discover that this essential physics explains other long known experimental facts (not used in getting to this physics).**

7) **Formulate realistic models that contain this essential physics; do realistic calculations; predict new materials; make them…**

future

Alex Muller, 1988 (NEC Symposium, Japan)



$BaBi_{1-x}Pb_xO_3$ (T_c=13K) versus $Ba_{1-x}K_xBiO_3$ (T_c=29K):

"As the Tc of hole-containing $BaBiO_3$ is more than twice as high as that of the electron-containing compound, one might expect an enhancement of T_c for hole superconductivity over electron superconductivity in the cuprates if the latter are found."

Volume 134, number 7 PHYSICS LETTERS A 23 January 1989

HOLE SUPERCONDUCTIVITY

J.E. HIRSCH
Department of Physics, University of California, San Diego, La Jolla, CA 92093, USA

Received 13 December 1988; accepted for publication 14 December 1988
Communicated by A.A. Maradudin

We argue that a fundamental mechanism for superconductivity arises from the interaction of a hole with the outer electrons in atoms with nearly filled shells. This is the origin of high T_c superconductivity in oxides. This picture also provides an explanation for general trends in T_c and correlations with Hall coefficient observed in nature, and suggests where the highest T_c's will be found.

In this paper we discuss a new approach to understand the origin of superconductivity in the recently discovered oxide superconductors, with application to other materials as well. Although we are far from a quantitative theory we believe the considerations discussed here should play an essential role in reformulating our understanding of superconductivity in all materials with particular application to materials with high critical temperature. In

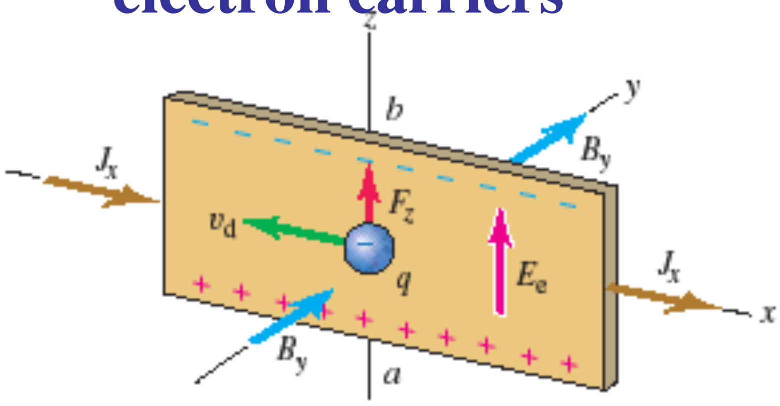
What is the recipe to make high T_c superconductors? To create structures with elements to the right on the periodic table (F, Cl, O, S, N, etc.) where conduction occurs via holes through the anion network.

We predict superconductivity through this mechanism for any anion network where conduction occurs through holes in the anion outer shell and the *direct hopping* between anions is appreciable.

Hall effect: R_H=Hall coefficient

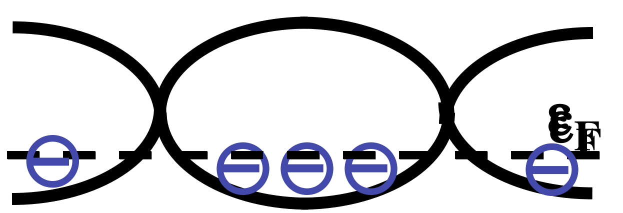
Lorentz force: $\vec{F} = q(\vec{E} + \frac{1}{c}\vec{v} \times \vec{B})$

electron carriers



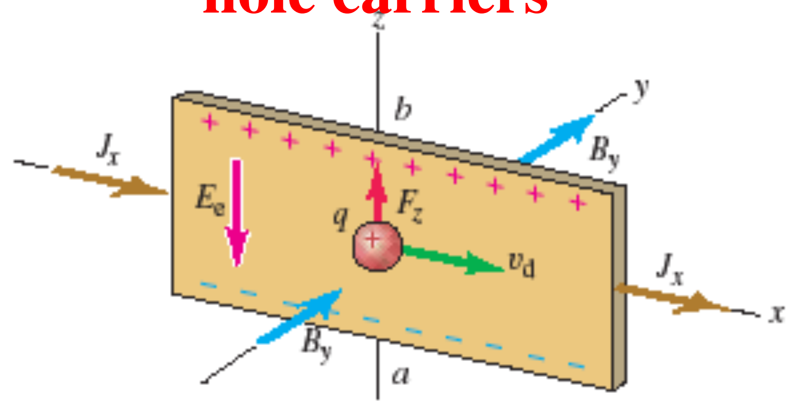
(a)

$R_H < 0$



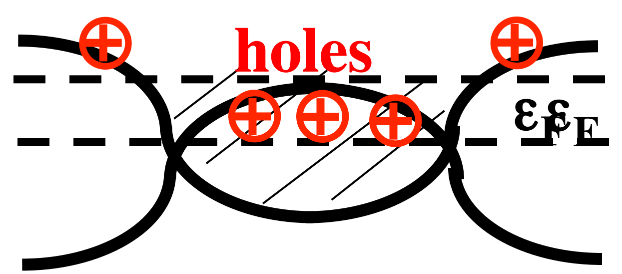
electrons

hole carriers



(b)

$R_H > 0$

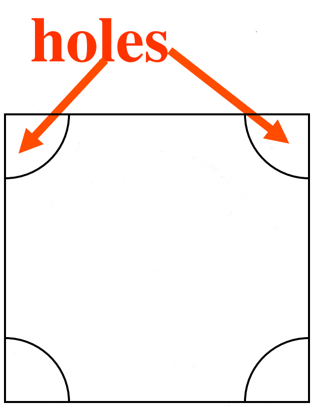


1932: Kikoin and Lasarew (Nature): Hall coefficient small in superconductors.

1948

On the other hand, we have found an empirical rule that indicates a correlation between superconductivity and lattice structure; namely, those metals are superconductive for which the Fermi surface, supposed to be a sphere, lies in very close proximity to one set of the corners formed by the boundary planes of a Brillouin zone. The following table shows the different ratios of the radius of the Fermi surface and the distance from the origin to those corners, for most of the superconductive elements and for some of the non-superconductive elements.

Lattice type	Superconductive elements		Non-superconductive elements
Body-centred cubic	V, Ta, βZr	1·03 and 0·98	Li, Na, K, Rb, Cs, $\leqslant$0·75
Face-centred cubic	Al, βLa, βTl, Th, Pb(?)	1·008	Ca, Sr $\leqslant$0·88; Au, Ag, Cu $\leqslant$0·7
Close packed hexagonal	Zn	0·927	
	Cd	0·925	
	αTl	1·10	
	αLa	1·098	



MAX BORN
KAI CHIA CHENG
(1948)

1957

There may be small regions in momentum space, for instance, where the electrons behave as positively charged particles, that is, places where the conductivity is by holes and other regions where they behave normally. There is some indication that this is the case because it has been noticed that the Hall effect is very small when the material has a tendency to be superconductive. The Hall effect is very small when the positive and negative carriers cancel. Thus some people think that this, in conjunction with the lattice vibrations, may have something to do with superconductivity. Of course, that makes the problem more complicated, because it would mean that if Frohlich and Bardeen could solve their model exactly, they still would not find superconductivity, since it would still involve only negative carriers.

R. Feynman, Rev.Mod.Phys.29, 205 (1957)

1962

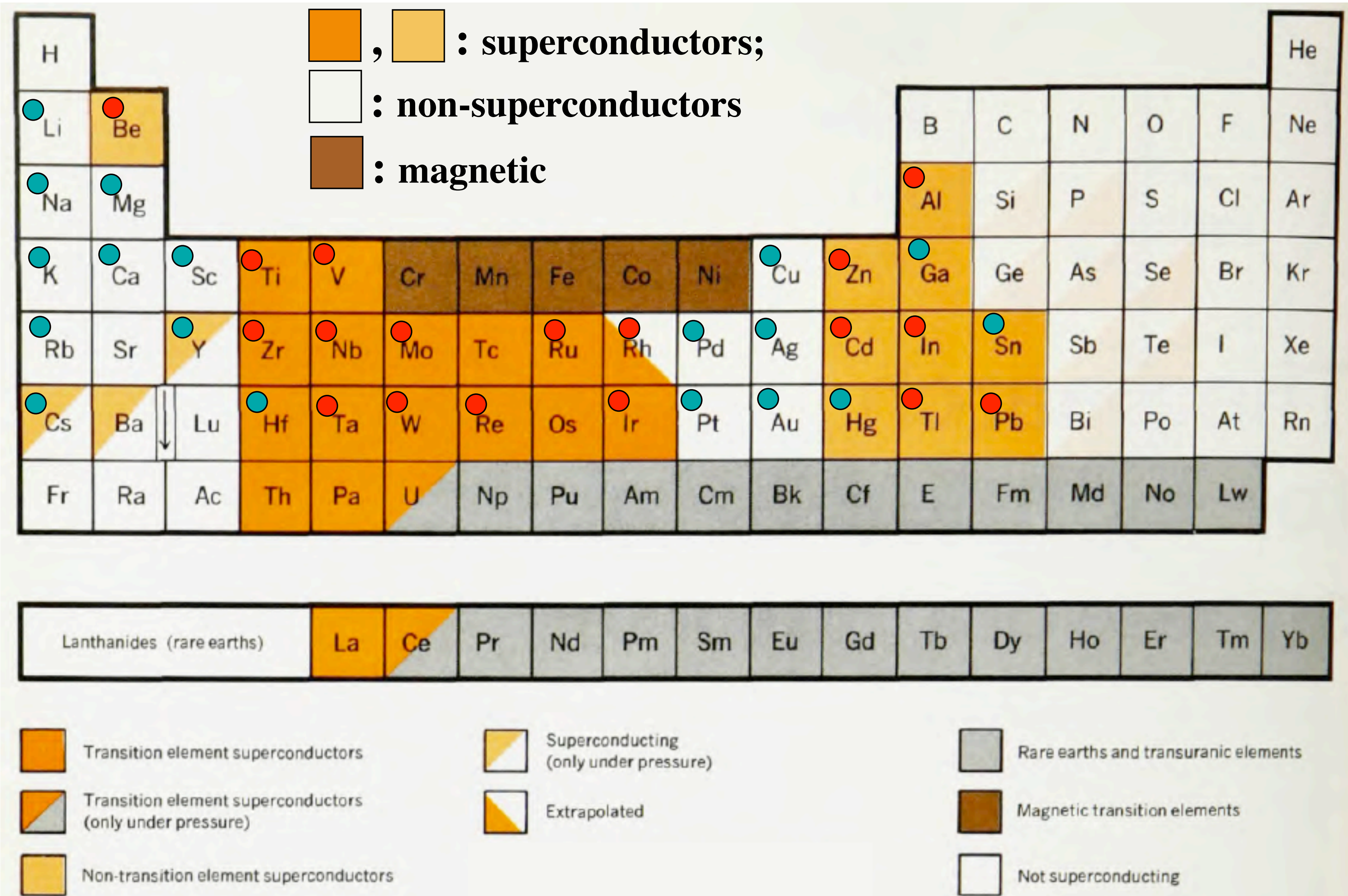
A POSSIBLE CRITERION OF SUPERCONDUCTIVITY

Chapnik, I.M. Sov. Phys. Dokl. 6, 988 (1962)

it is presumed that hole conduction is necessary for the occurrence of superconductivity

Negative Hall coefficient=electron carriers

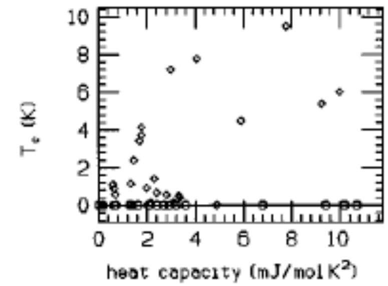
Positive Hall coefficient=hole carriers

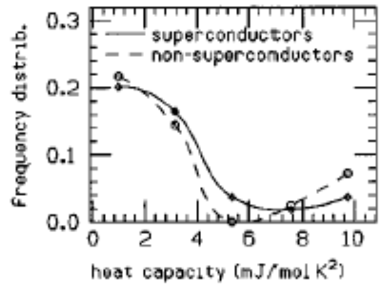


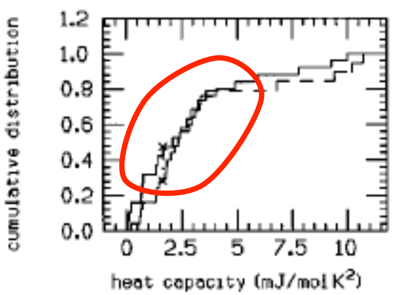
Correlations between normal-state properties and superconductivity

PHYSICAL REVIEW B VOLUME 55, NUMBER 14 p. 9007 1 APRIL 1997-II

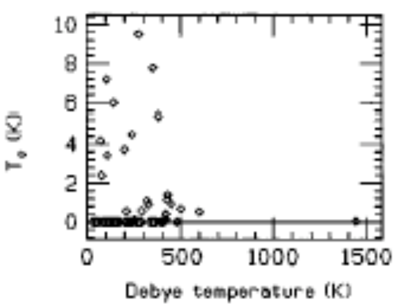
(Elements)

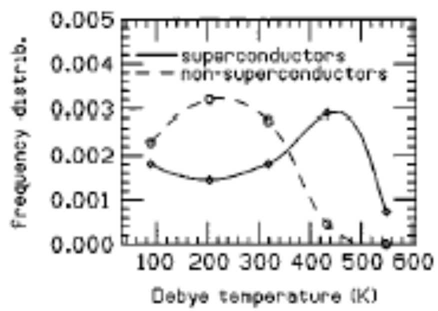


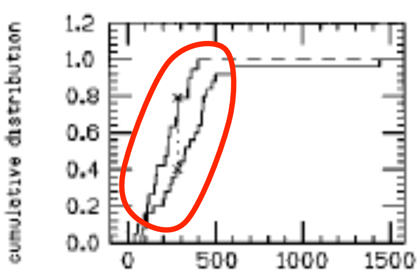




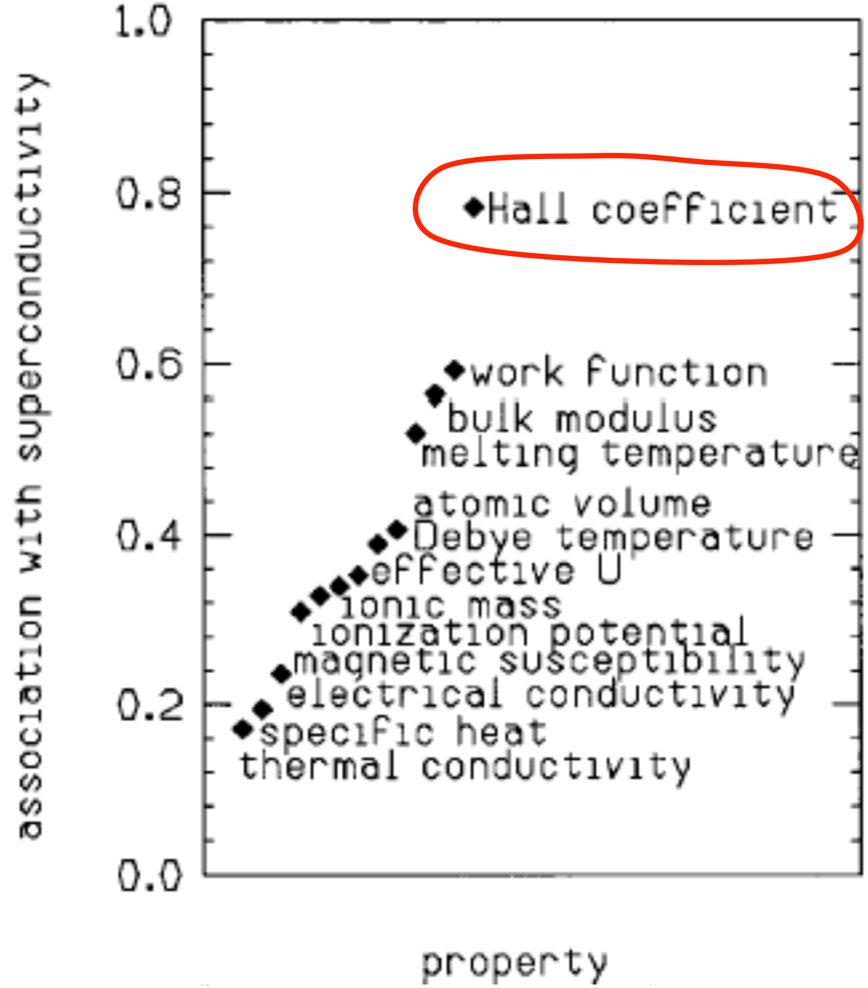
Heat capacity

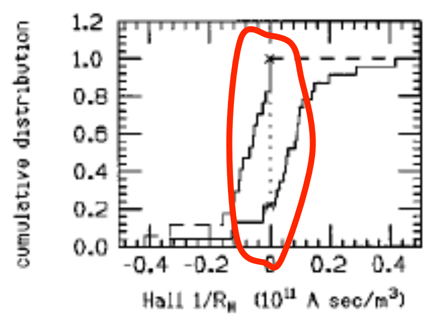






Debye temperature





Hall coefficient

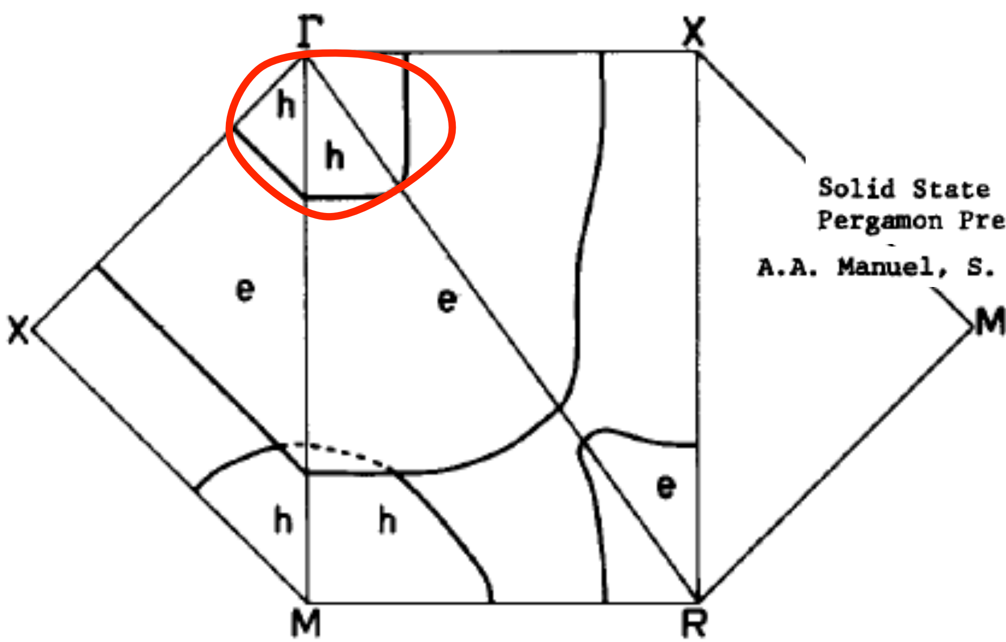
A15' s

Fermi surfaces in Nb_3Sn through positron annihilation

L Hoffmann†, A K Singh†, H Takei‡ and N Toyota‡

dimensional reconstruction of the occupation density. The extracted Fermi surfaces (FS) reveal the presence of a cube-shaped hole pocket, responsible for the high superconducting transition temperature ($T_c = 18$ K), which seems to be a feature of all FS of high-T_c A15 compounds.

DETERMINATION OF THE FERMI SURFACE OF V_3Si



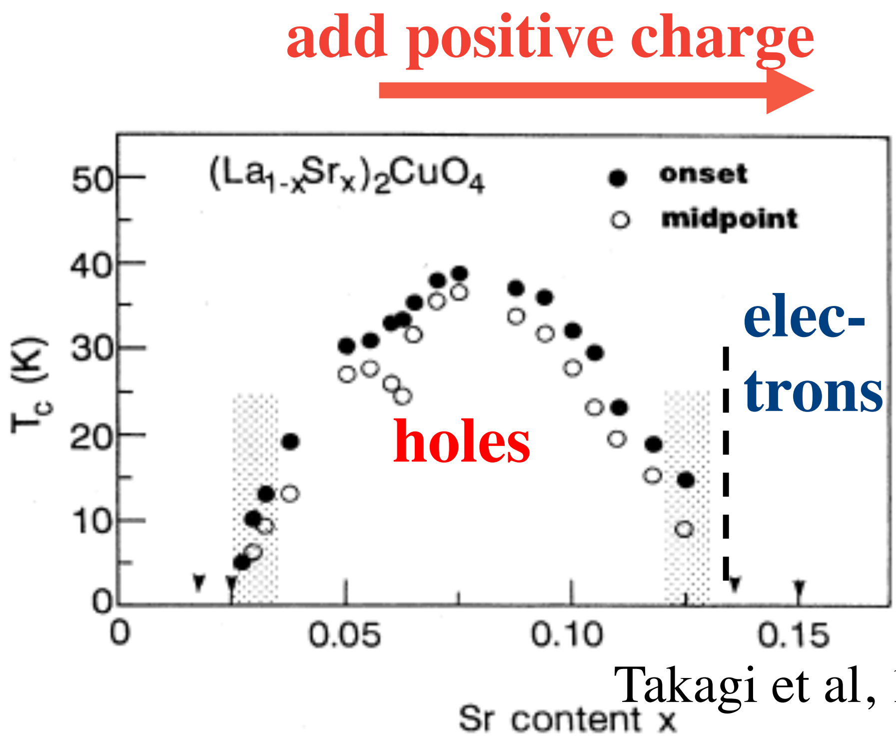
Solid State Communications, Vol.31, pp.955-959.
Pergamon Press Ltd. 1979. Printed in Great Britain.

A.A. Manuel, S. Samoilov, R. Sachot, P. Descouts, M. Peter

Fig 5. Sections of the Fermi Surface of V_3Si consistent with the

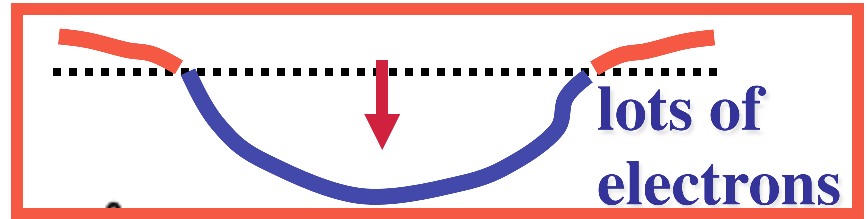
High T_c cuprates

Hall coefficient



Takagi et al, 1989

FIG. 3. Sr content x dependence of the superconducting transition temperature T_c. T_c was determined by the Meissner measurements shown in Fig. 4. The midpoint temperature were defined as half of the low-temperature saturated value.



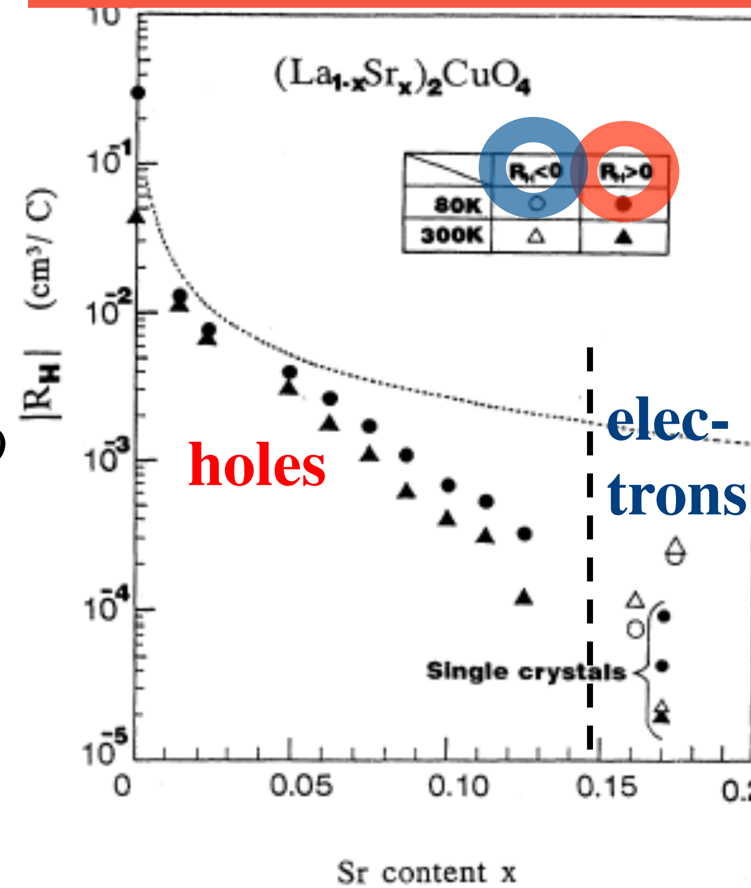
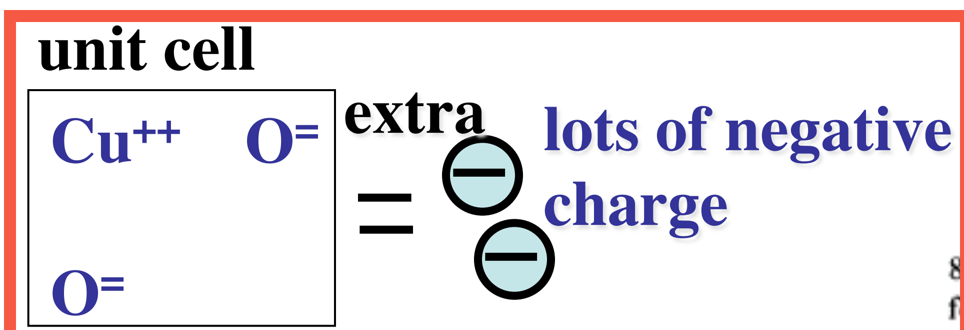
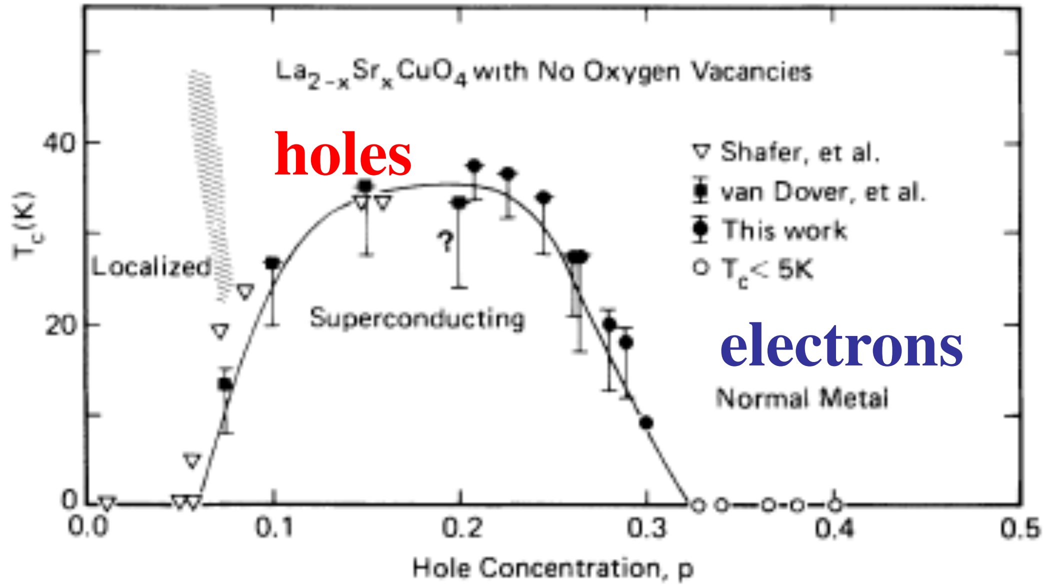


FIG. 5. Sr content x dependence of the Hall coefficient R_H at 80 K (circles) and 300 K (triangles). The sign of R_H is positive for $x<0.15$ and negative for $x>0.15$, respectively. The data for single crystals with $x=0.17$ are also plotted.





Torrance et al PRL 61, 1127 (1988)

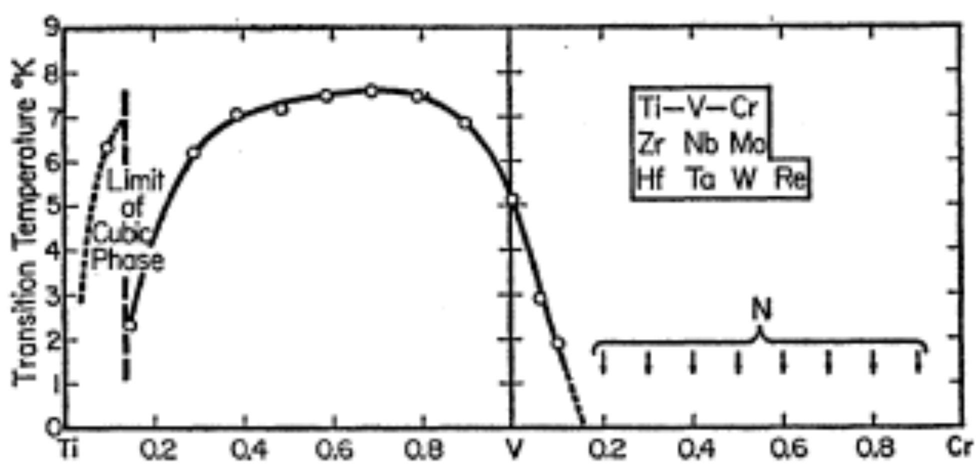
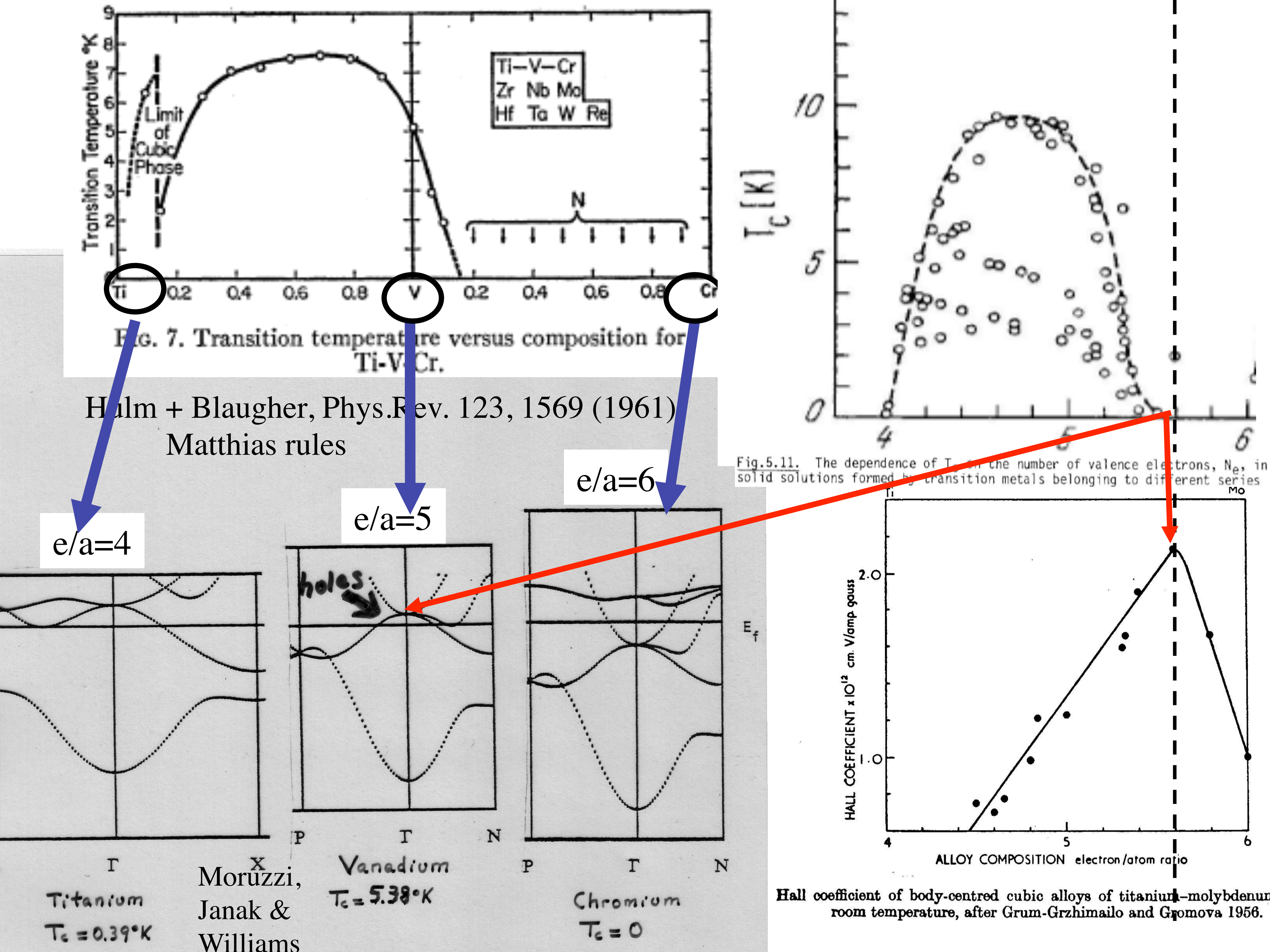


FIG. 7. Transition temperature versus composition for Ti-V-Cr.

Hulm + Blaugher, Phys.Rev. 123, 1569 (1961)



Transition Temperature °K
Limit of Cubic Phase
Ti–V–Cr
Zr Nb Mo
Hf Ta W Re
N
Ti
V
Cr
FIG. 7. Transition temperature versus composition for Ti-V-Cr.
Hulm + Blaugher, Phys.Rev. 123, 1569 (1961)
Matthias rules
T_c [K]
Fig.5.11. The dependence of T_c on the number of valence electrons, N_e, in solid solutions formed by transition metals belonging to different series
e/a=4
e/a=5
e/a=6
holes
E_f
Γ
X
P
N
Titanium
T_c = 0.39°K
Moruzzi, Janak & Williams
Vanadium
T_c = 5.38°K
Chromium
T_c = 0
Ti
Mo
HALL COEFFICIENT x 10^{12} cm. V/amp gauss
ALLOY COMPOSITION electron/atom ratio
Hall coefficient of body-centred cubic alloys of titanium-molybdenum at room temperature, after Grum-Grzhimailo and Gromova 1956.

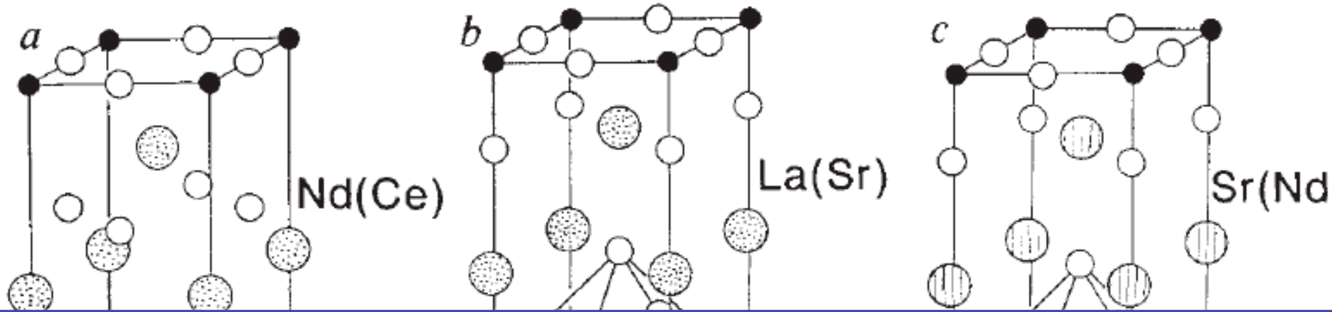
Electron-doped cuprates

letters to nature

Nature **337**, 345 - 347 (26 January 1989); doi:10.1038/337345a0

A superconducting copper oxide compound with electrons as the charge carriers

Y. TOKURA*, H. TAKAGI† & S. UCHIDA†



With regard to the "electron-doped" oxide superconductors,[21] our model has a specific prediction: oxygen hole carriers will be found in all the samples that go superconducting.

(JEH 1989)

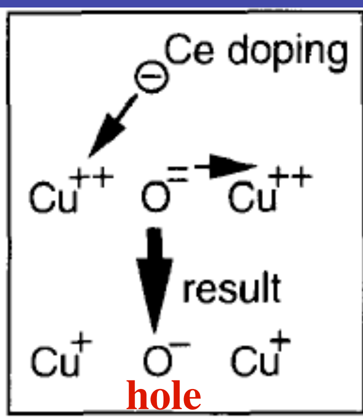
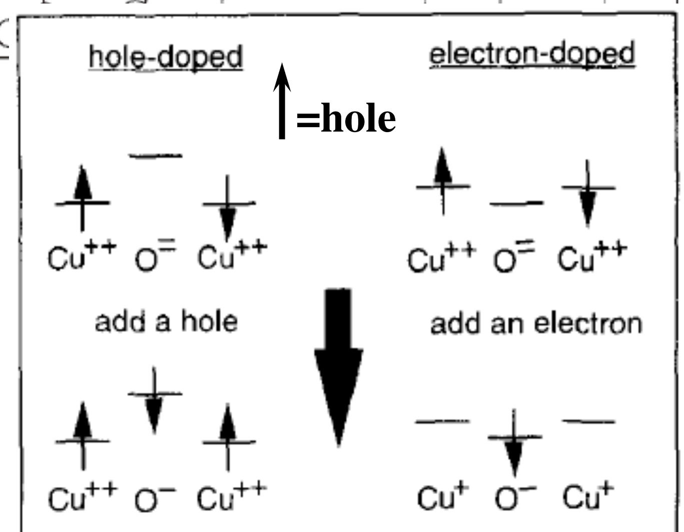


Fig. 1. Schematic depiction of how holes are created by electron doping. The electron added to Cu^{2+} repels an electron from O^{2-} to the neighboring Cu^{2+}, leaving behind a hole in oxygen (O^{-}).

Physica C243, 319 (1995)



Electron-doped cuprates have hole carriers

VOLUME 73, NUMBER 9 PHYSICAL REVIEW LETTERS 29 AUGUST 1994

Anomalous Transport Properties in Superconducting $Nd_{1.85}Ce_{0.15}CuO_{4\pm\delta}$

Wu Jiang, S. N. Mao, X. X. Xi,* Xiuguang Jiang, J. L. Peng, T. Venkatesan,† C. J. Lobb, and R. L. Greene
Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742
(Received 4 February 1994)

We report a comprehensive study of the in-plane transport properties of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ epitaxial thin films and crystals by both increasing and decreasing δ with Ce content fixed at $x \approx 0.15$. We find a remarkable correlation between the appearance of superconductivity and (1) a positive magnetoresistance in the normal state, (2) a positive contribution to the otherwise negative Hall coefficient, and (3) an anomalously large Nernst effect. These results strongly suggest that both holes and electrons participate in the charge transport for the superconducting phase of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$.

PHYSICAL REVIEW B 76, 024506 (2007)

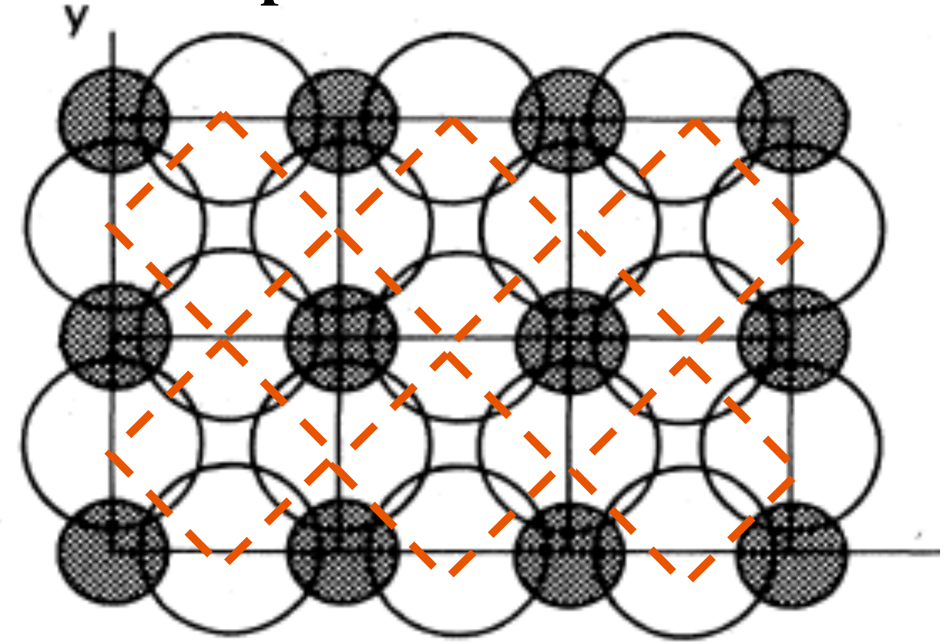
Hole superconductivity in the electron-doped superconductor $Pr_{2-x}Ce_xCuO_4$

Y. Dagan*
School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel Aviv, 69978, Israel

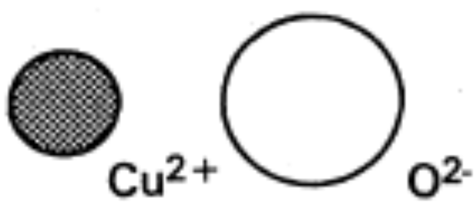
R. L. Greene
Center for Superconductivity Research Physics Department, University of Maryland, College Park, Maryland 20743, USA
(Received 4 February 2007; revised manuscript received 5 June 2007; published 11 July 2007)

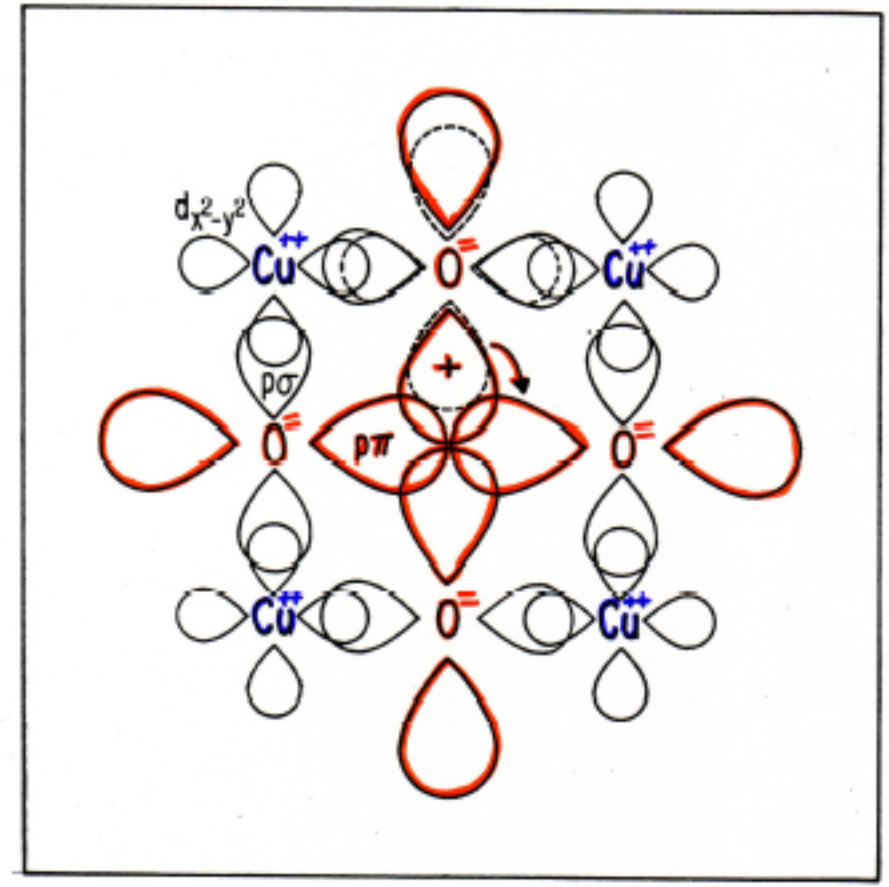
We measure the resistivity and Hall angle of the electron-doped superconductor $Pr_{2-x}Ce_xCuO_4$ as a function of doping and temperature. The resistivity ρ_{xx} at temperatures $100\ K < T < 300\ K$ is mostly sensitive to the electrons. Its temperature behavior is doping independent over a wide doping range and even for nonsuperconducting samples. On the other hand, the transverse resistivity ρ_{xy}, or the Hall angle θ_H, where $\cot(\theta_H) = \rho_{xx}/\rho_{xy}$, is sensitive to both holes and electrons. Its temperature dependence is strongly influenced by doping, and $\cot(\theta_H)$ can be used to identify optimum doping (the maximum T_c) even well above the critical temperature. These results lead to a conclusion that in electron doped cuprates holes are responsible for the superconductivity.

Cuprates

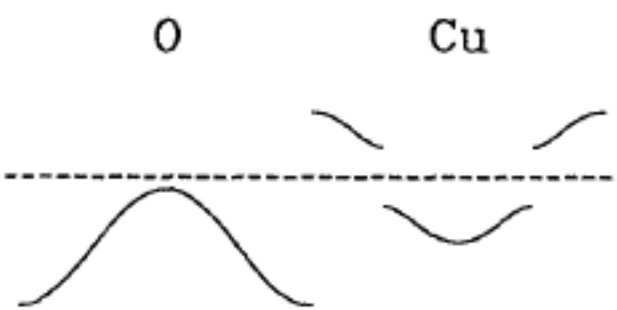


W. Pickett (1989 RMP)

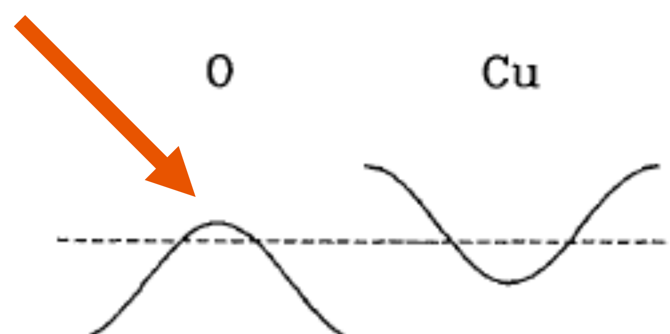




S.Tang, J.H. (1989)



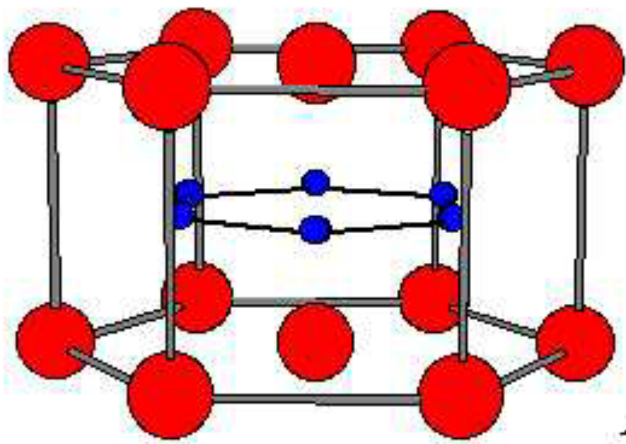
undoped



F.Marsiglio, J.H. (1991)

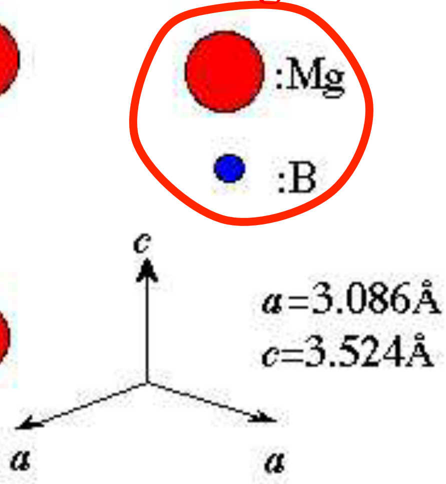
doped

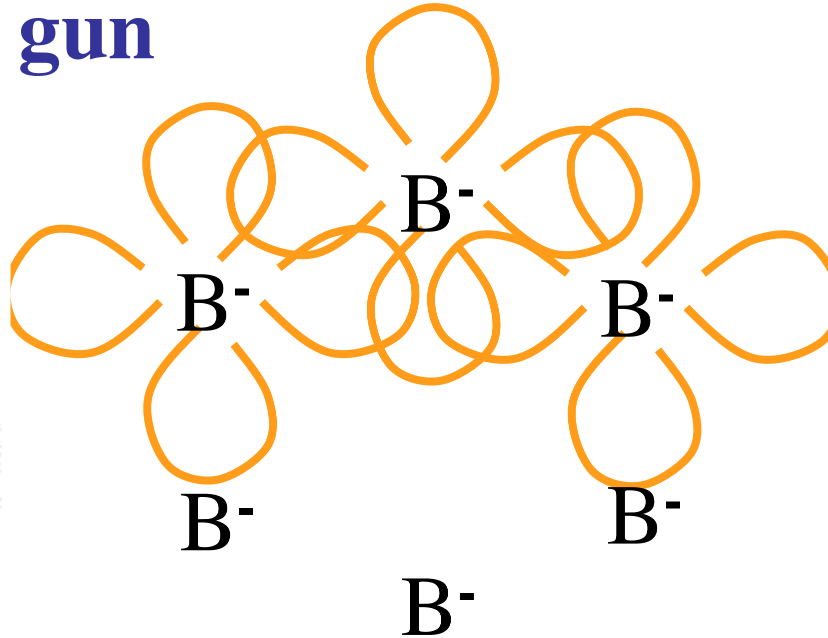
MgB_2 (T_c=39K): a smoking gun

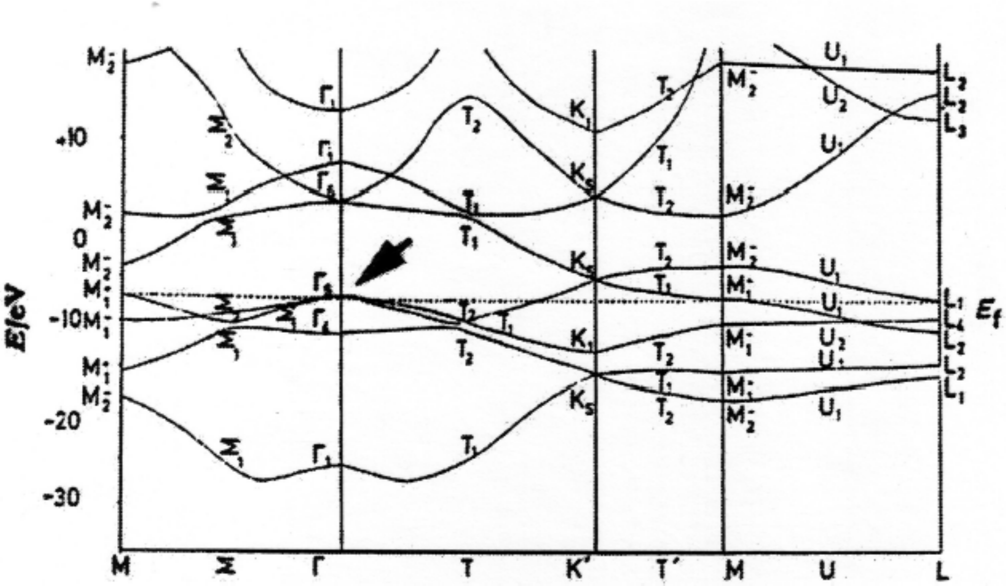


Akimitsu et al, 2001

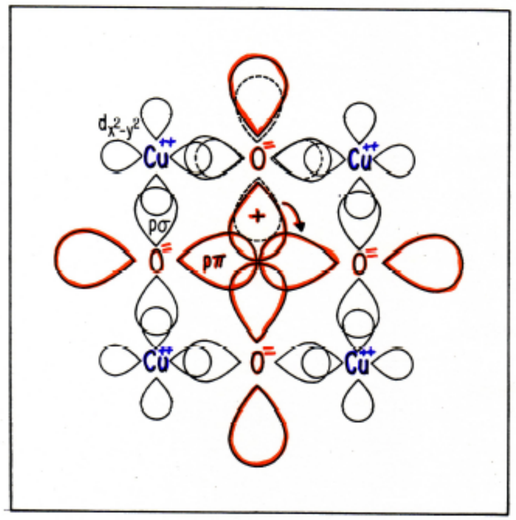
Wrong sizes





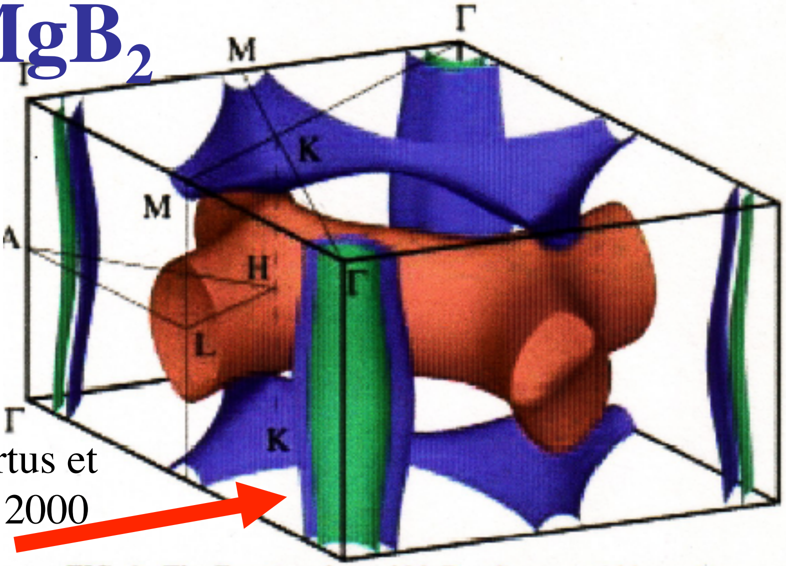


Armstrong et al, '79



- **Negatively charged ions: B^-**
- **Conduction by holes**

MgB_2



Kortus et Al, 2000

FIG. 3. The Fermi surface of MgB_2. Green and blue cylinders (hole-like) come from the bonding $p_{x,y}$ bands, the blue tubular network (hole-like) from the bonding p_z bands, and

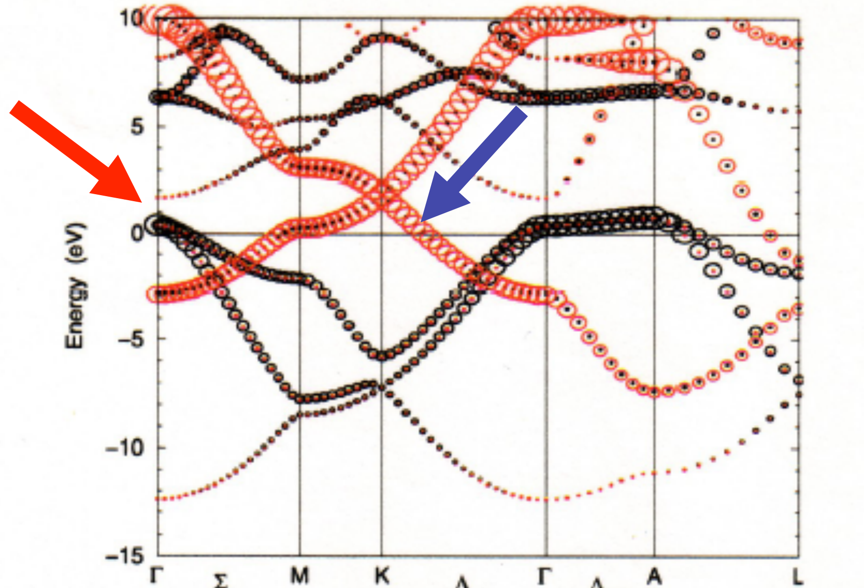
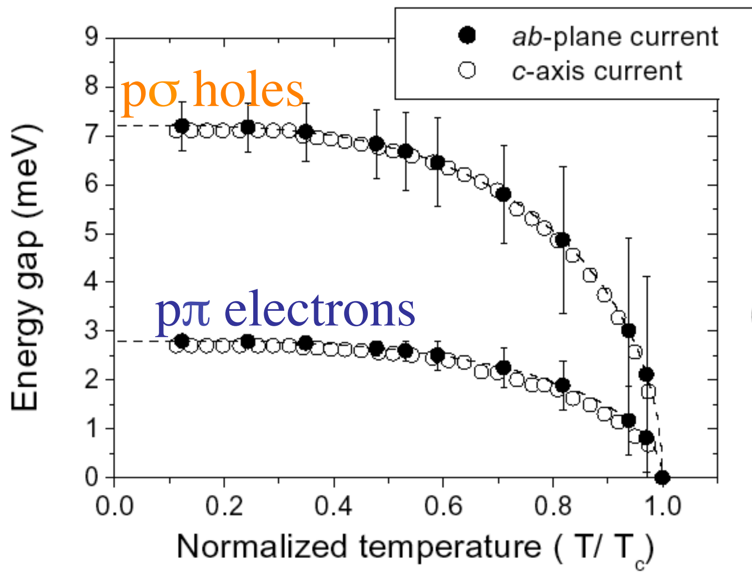
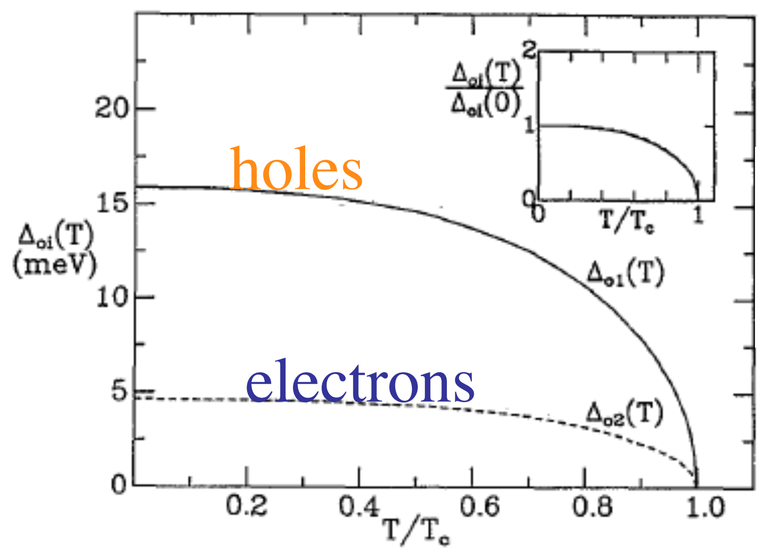
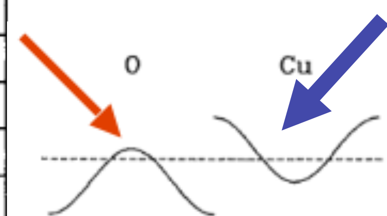


FIG. 1. Bandstructure of MgB_2 with the B p-character. The radii of the red (black) circles are proportional to the B p_z (B $p_{x,y}$) character.



Gonnelli et al, cond-mat/0209472 (2002)
(Martinez-Samper et al, cond-mat/0209387 (2002))



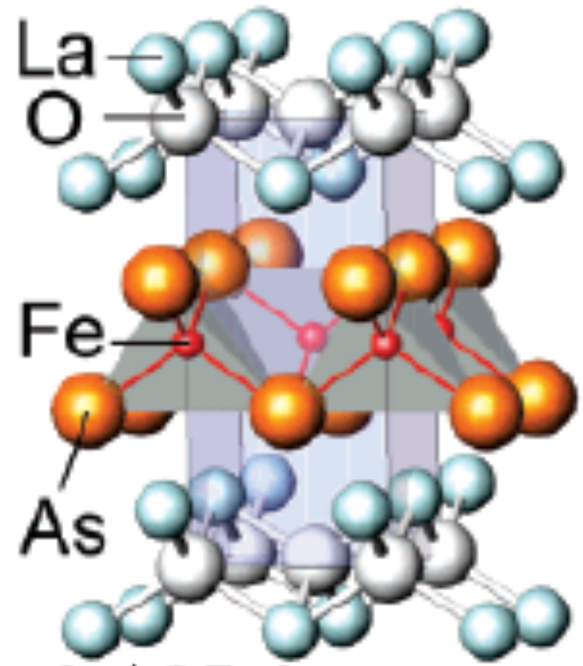


F.M.,J.H., Phys.Rev.B43, 424 (1991)

FeAs compounds: T_c^{max}=56K

Iron-Based Layered Superconductor $La[O_{1-x}F_x]FeAs$ ($x = 0.05-0.12$) with $T_c = 26$ K

Yoichi Kamihara,*,† Takumi Watanabe,‡ Masahiro Hirano,†,§ and Hideo Hosono†,‡,§



* **Dominant charge transport in FeAs layers**

* **Excess negative charge per unit cell:**

$$Fe^{2+}As^{3-} = \ominus$$

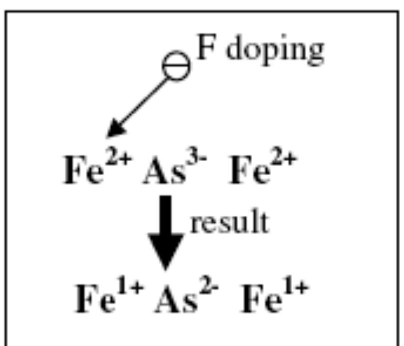
* **Hole carriers?**

Superconductivity at 25 K in hole-doped $(La_{1-x}Sr_x)OFeAs$

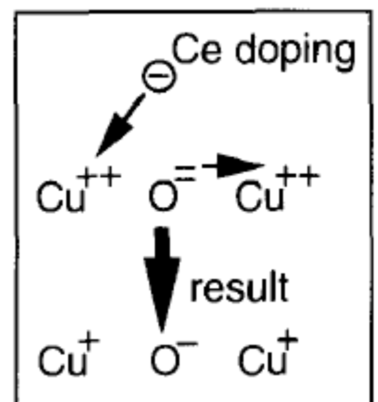
EPL, 82 (2008) 17009

Hai-Hu Wen[a], Gang Mu, Lei Fang, Huan Yang and Xiyu Zhu

Electron-doped arsenides



F. Marsiglio, J.H, Physica C 468, 1047 (2008)



Electron-doped cuprates

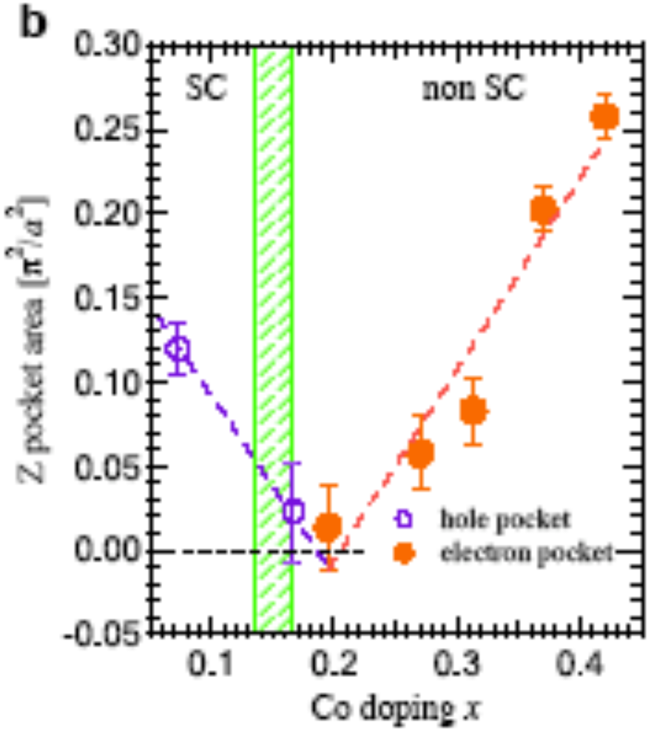
Fig. 2. Schematic depiction of how holes are created by electron doping. The electron added to Fe^{2+} repels an electron from As^{3-} to the neighboring Fe^{2+}, leaving behind a hole in arsenic (As^{2-}).

Fig. 1. Schematic depiction of how holes are created by electron doping. The electron added to Cu^{2+} repels an electron from O^{2-} to the neighboring Cu^{2+}, leaving behind a hole in oxygen (O^-).

Importance of Fermi surface topology for high temperature superconductivity in electron-doped iron arsenic superconductors

arXiv:1011.0980 (2010)

Chang Liu, A. D. Palczewski, Takeshi Kondo, R. M. Fernandes, E. D. Mun, H. Hodovanets, A. N. Thaler, J. Schmalian, S. L. Bud'ko, P. C. Canfield, and A. Kaminski



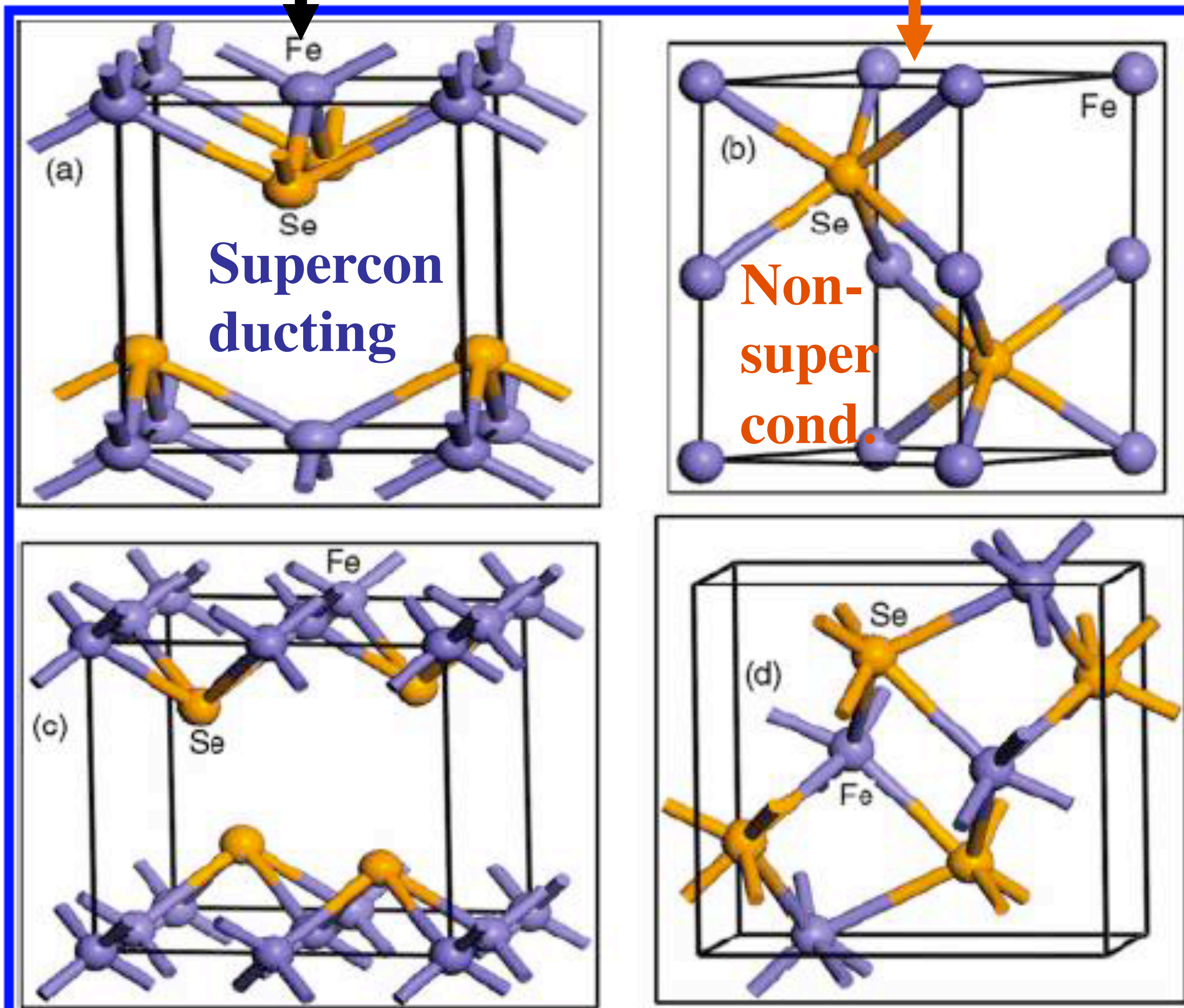
disappear around $x = 0.2$. Changes in thermoelectric power occur at similar x-values. Beyond this doping level the central pocket changes to electron-like and superconductivity does not exist. Our observations reveal the crucial importance of the underlying Fermiology in this class of materials. A necessary condition for superconductivity is the presence of the central hole pockets rather than perfect nesting between central and corner pockets.

FeSe: another smoking gun
enormous increase of T_c with pressure:

T_c=8K → T_c=37K → T_c=0

Pressure: ambient → ~9GPa → >10GPa

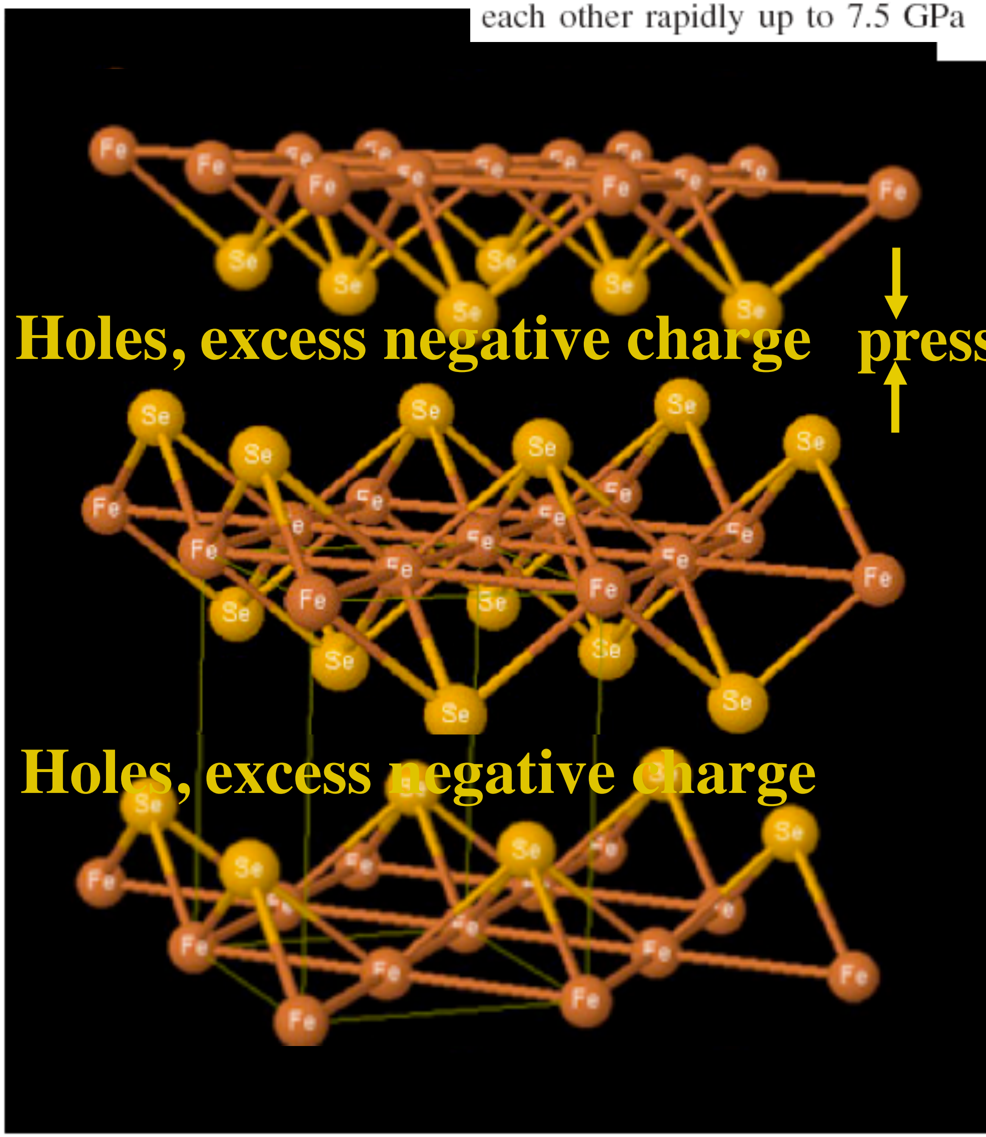
Kumar et al, J.Phys.Chem. B114, 12597 (2010)



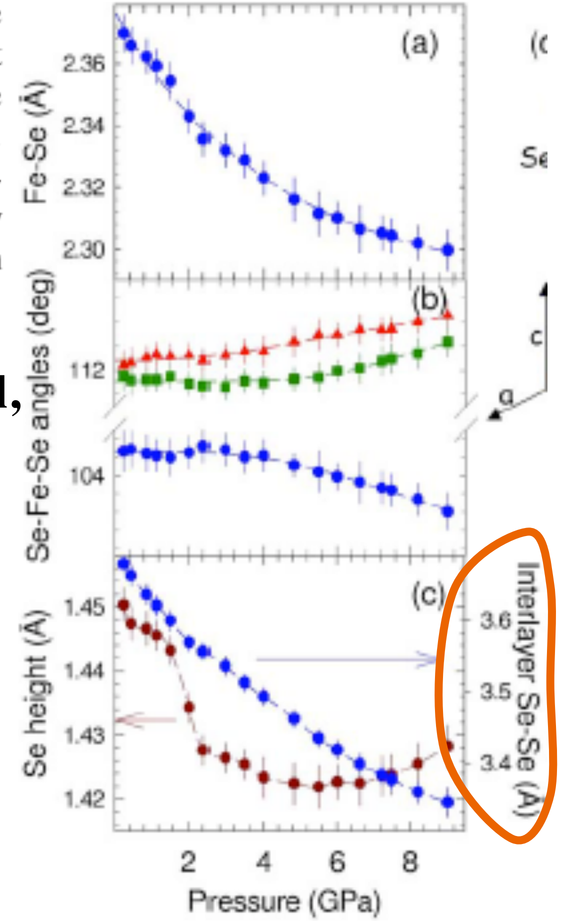
FeSe:

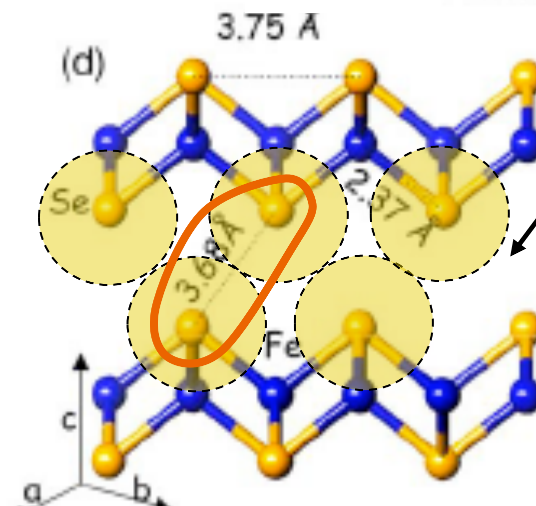
T_c=8K ⟶ 37K
pressure

The Fe-Se bonds contract smoothly with an overall decrease of 2.9% at 9.0 GPa. Similarly the intralayer Se-Se distances decrease monotonically with a somewhat larger contraction of 3.8%. However, the pressure response of the interlayer Se-Se contacts is much steeper with a 9.1% decrease reflecting the very large interlayer compressibility—the SeFeSe slabs approach each other rapidly up to 7.5 GPa



Margadonna et al, PRB80, 064506 (2009)





Pauling radius of $Se^{=}$

FeSe under pressure:

Kumar et al, 2010

Ambient pressure

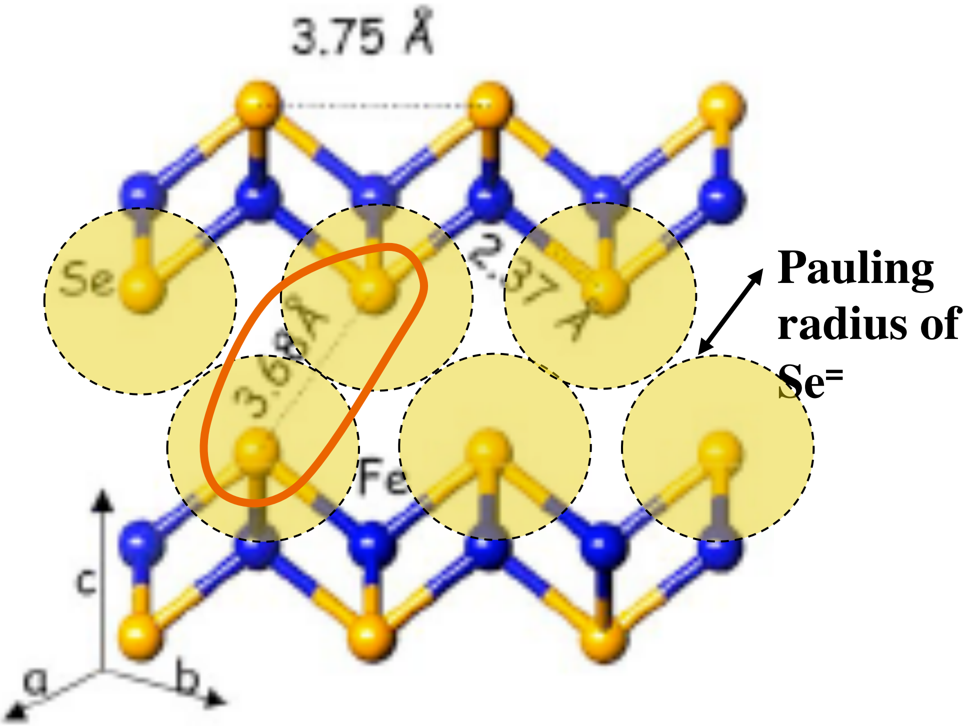
Fe–Fe (Å)	2.6647(3)
Fe–Se (Å)	2.3999(7)
Se1–Se1 (Å)	3.7684(9)
Se1–Se2 (Å)	3.6871(7)

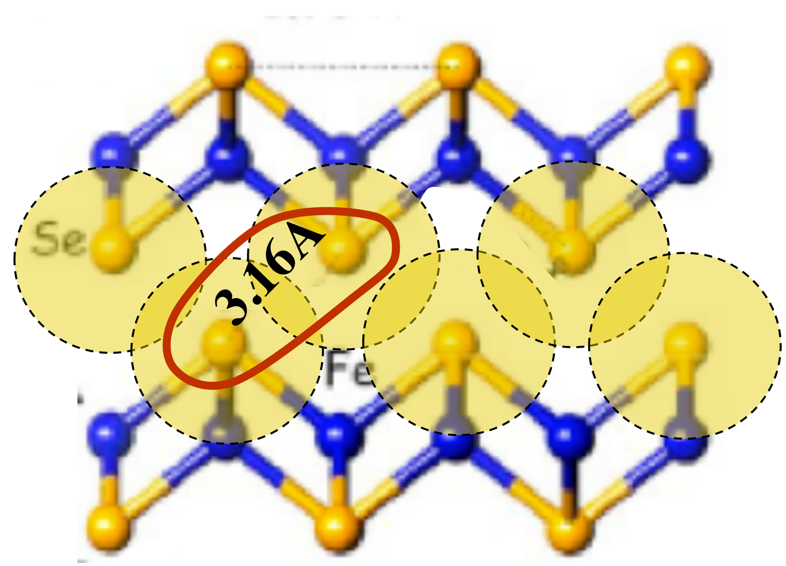
T_c = 8K

P= 8.5 GPa

Fe–Fe (Å)	2.5712(5)
Fe–Se (Å)	2.4412(8)
Se1–Se1 (Å)	3.6362(9)
Se1–Se2 (Å)	3.1688(4)

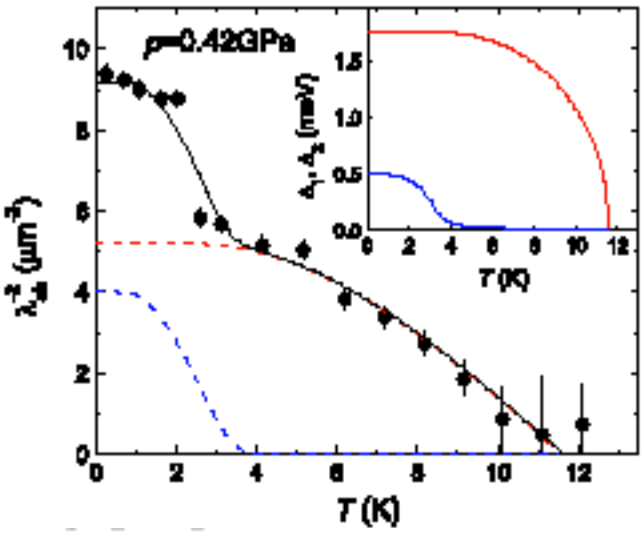
T_c = 37K





Two gaps in FeSe:

Khasanov et al, PRL 104, 087004 (2010)
(muon spin rotation)



superconductivity is driven by holes conducting through closely packed $Se^{=}$ anion network

the main effect on $T_c(p)$ and $\lambda_{ab}^{-2}(T, p) \propto \rho_s(T, p)$ arises from the energy band(s) where the large superconducting gap, Δ_1, develops.

Our results imply, therefore, that the transition temperature in $FeSe_{1-x}$ is entirely determined by the intra-band interaction within the band(s) where the dominant gap is opened.

- Large size of As^{3-},Se^{2-} relative to Fe^{2+} leads to tetrahedral structures with anion contact (edge shared tetrahedra). David J. Singh

Superconductivity in SnO: A Nonmagnetic Analog to Fe-Based Superconductors?

M. K. Forthaus,[1] K. Sengupta,[1,*] O. Heyer,[1] N. E. Christensen,[2] A. Svane,[2] K. Syassen,[3] D. I. Khomskii,[1] T. Lorenz,[1] and M. M. Abd-Elmeguid[1]

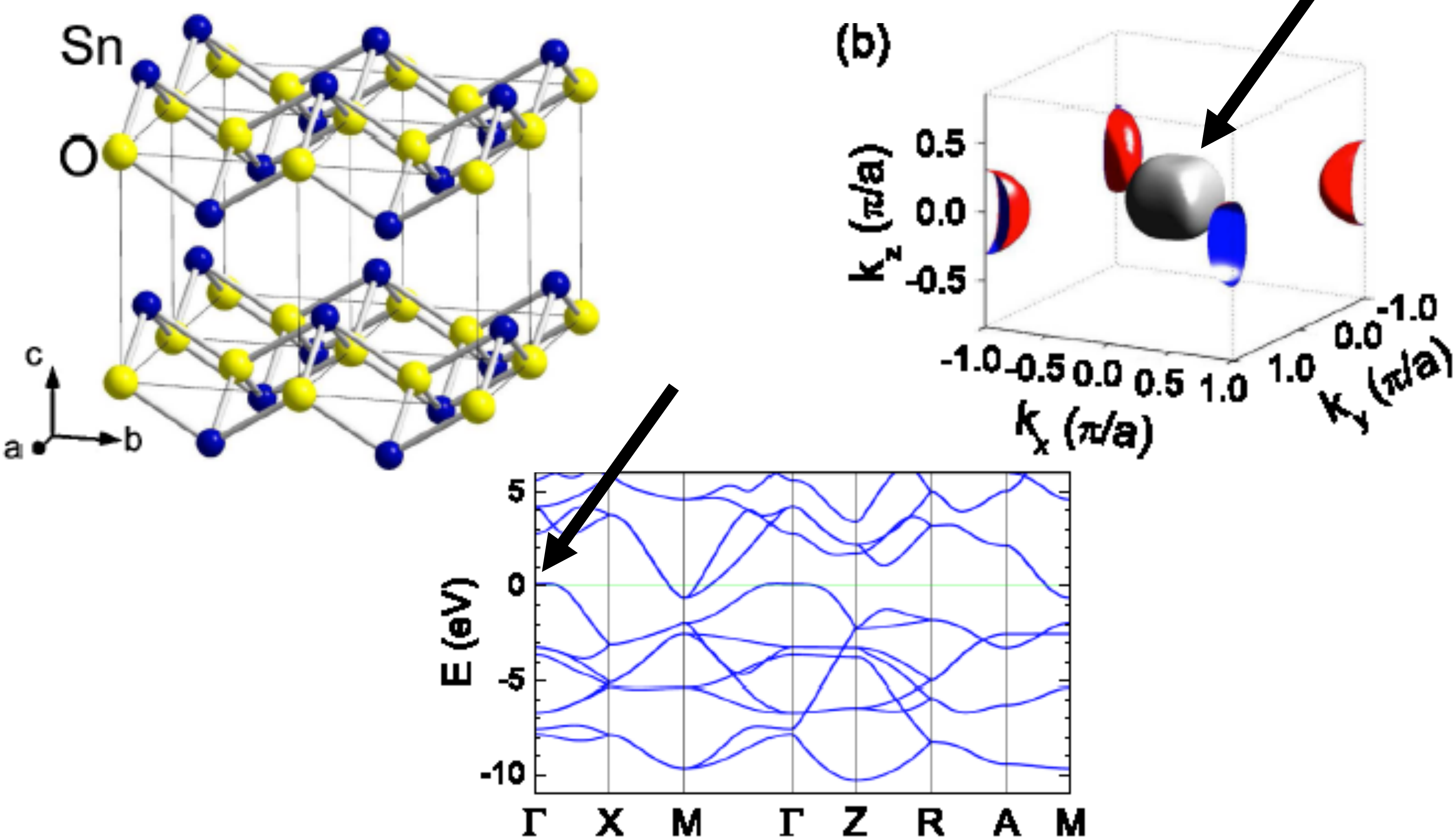


FIG. 4 (color online). The band structure of SnO at 7 GPa. The

Hole-doped semiconductors

BOND-CHARGE REPULSION AND HOLE SUPERCONDUCTIVITY :

Physcia C 158 (1989) 326–336

A valid model should also be capable of explaining why some materials do not become superconducting. For example, why don't p-doped Si and Ge become superconductors?

Superconductivity in diamond

Nature **428**, 542-545 (1 April 2004) |

incorporated into diamond[3]; as boron acts as a charge acceptor, the resulting diamond is effectively hole-doped. Here we report the discovery of superconductivity in boron-doped diamond synthesized at high pressure (nearly 100,000 atmospheres) and temperature (2,500–2,800 K). Electrical resistivity, magnetic sus-

Vol 444 | 23 November 2006 | **doi:10.1038/nature05340**

Superconductivity in doped cubic silicon

remained largely underdeveloped. Here we report that superconductivity can be induced when boron is locally introduced into silicon at concentrations above its equilibrium solubility. For suf-

Phys. Rev. Lett. 102, 217003 (2009) [4 pages]

Superconducting State in a Gallium-Doped Germanium Layer at Low Temperatures

In order to obtain superconductivity in group-IV semiconductors, heavy *p*-type doping well above the metal-insulator transition is required. Otherwise the charge-

Superconductivity in simple and early transition metals under high pressure

Superconductivity in compressed lithium at 20 K (2002)

Katsuya Shimizu[1,2], Hiroto Ishikawa[1], Daigoroh Takao[1], Takehiko Yagi[3] & Kiichi Amaya[1,2]

Superconductivity at 20 K in yttrium metal at pressures exceeding 1 Mbar (2006)

J.J. Hamlin[a], V.G. Tissen[b] and J.S. Schilling[a],

Pressure-induced superconductivity in Sc to 74 GPa (2007)

J. J. Hamlin and J. S. Schilling

Superconductivity of Ca Exceeding 25 K at Megabar Pressures (2006)

Takahiro Yabuuchi, Takahiro Matsuoka, Yuki Nakamoto and Katsuya Shimizu

Why non-superconducting metallic elements become superconducting under high pressure

J.J. Hamlin, JEH (2009)

Table 1
Non-superconducting simple and early transition metal elements that become superconducting under pressure. Maximum T_c and corresponding pressure P is given, as well as the Hall coefficient R_H at ambient pressure. The Hall coefficient at high pressure $R_H(P)$ has not yet been measured.

Element	T_c (K)	P (GPa)	R_H (10^{-11} m^3/C)	R_H (P)
Li	20	48	−150	>0 predicted
Cs	1.3	12	−71	>0 predicted
Ca	25	161	−18	>0 predicted
Sc	19.6	106	−3	>0 predicted
Y	19.5	115	−10	>0 predicted

Lattice distortion creates holes

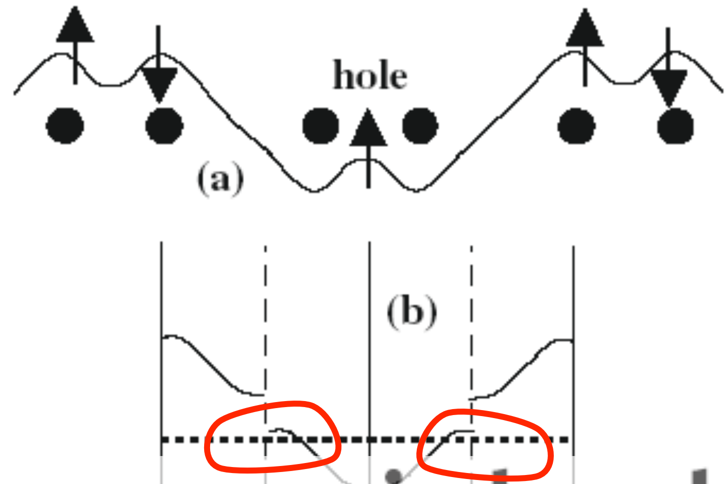


Fig. 2. When the lattice distorts, the band that was nearly half full becomes nearly full. The top part of the figure shows schematically the wavefunction in real space for a state at the Fermi energy. There is approximately one electron per site. The wavefunction changes sign between unit cells. The bottom part of the figure shows the band in k-space in the extended zone scheme and the dotted line indicates the position of the Fermi energy.

Fig. 1. (a) At ambient pressure, the structure is simple and the first Brillouin zone is approximately half full. (b) Under pressure, the lattice deforms, new Bragg planes appear and the first Brillouin zone becomes almost full.

Direct observation of a pressure-induced metal-to-semiconductor transition in lithium

Takahiro Matsuoka[1] & Katsuya Shimizu[1]

Simple metals at high pressures: the Fermi sphere – Brillouin zone interaction model

V F Degtyareva

Physics – Uspekhi 49 (4) 369 – 388 (2006)

When metals are in a compressed state, the band contribution of valence electrons grows, and the crucial factor in reducing the energy of the crystal structure is the emergence of faces of the Brillouin zone near the Fermi level.

* Elements
* Transition metal alloys
* A 15' s, other compounds
* Hole-doped high Tc cuprates

1) Observe that among known superconducting materials there are pervasive correlations even among very different classes.

2) Infer empirical rules from these observed correlations.

> *Hole carriers are necessary for superconductivity at any T*
>
> *Negatively charged structures give high Tc* (1989)

3) See whether or not newly found superconductors (found after these empirical rules were formulated) conform to the same rules.

* Electron-doped high Tc cuprates
* Magnesium diboride
* Fe-As compounds, FeSe
* Hole-doped semiconductors
* Elements under high pressure

✓

4) Understand the essential physics that gives rise to these empirical rules.
   Build simplified models containing this physics.
5) Calculate from these models measurable properties, predict / compare with expt.
6) Bonus: discover that this essential physics explains other long known experimental facts (not used in getting to this physics).

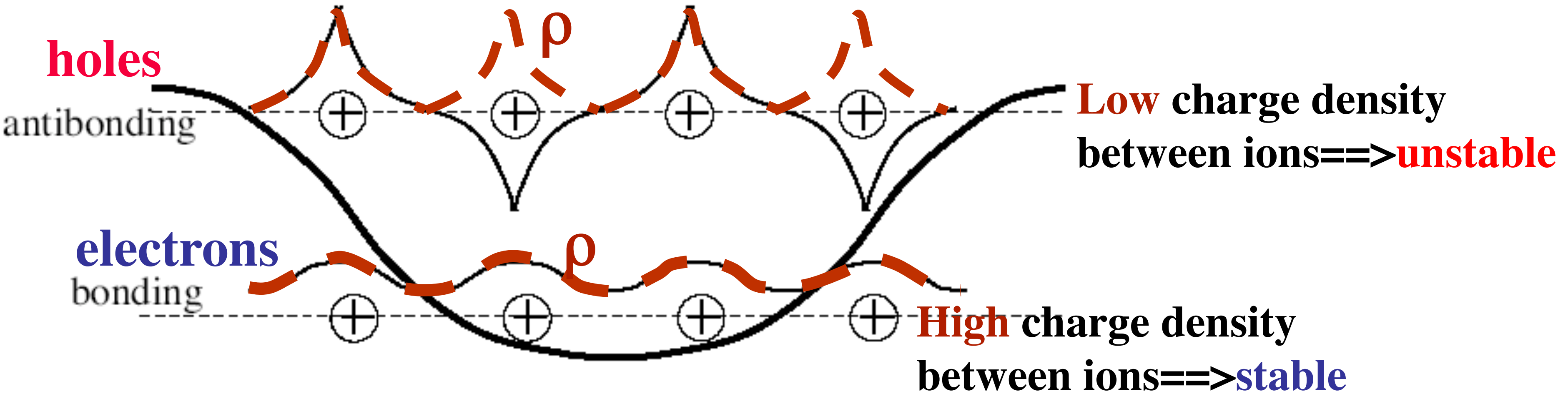
CRITERIA FOR SUPERCONDUCTING TRANSITION TEMPERATURES

B. T. MATTHIAS *Physica* **69** (1973) 54–56

Synopsis

Crystallographic instabilities seem to be a necessary condition for high superconducting transition temperatures in multicomponent phases.

From now on, I shall look for systems that should exist, but won't – unless one can persuade them.

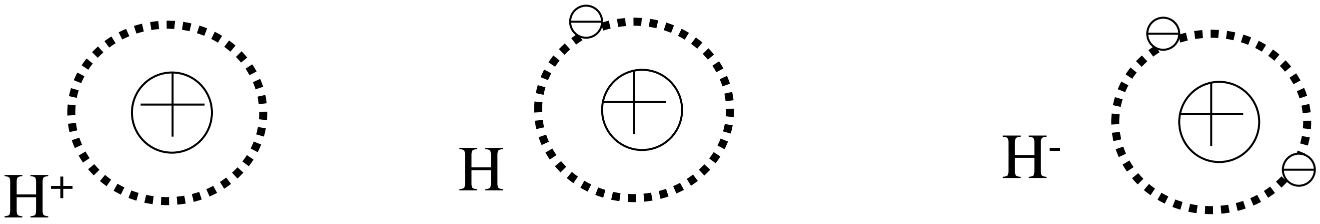


Electronic energy band

Lattice instabilities result from the presence of too many <u>antibonding electrons</u> ==> almost filled bands ==> hole carriers

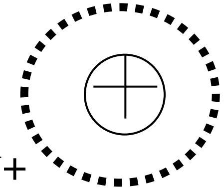
(Antibonding electrons are always at the top of the band)

Why holes are not like electrons

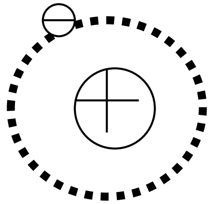


$$\varphi(r) = ce^{-Zr}$$

Why holes are not like electrons

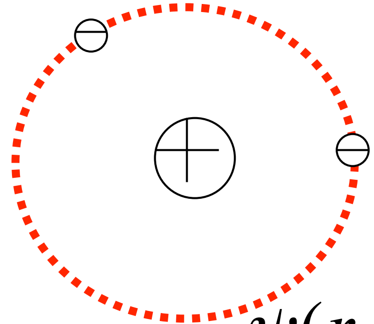


H^+



H

$$\varphi(r) = ce^{-Zr}$$

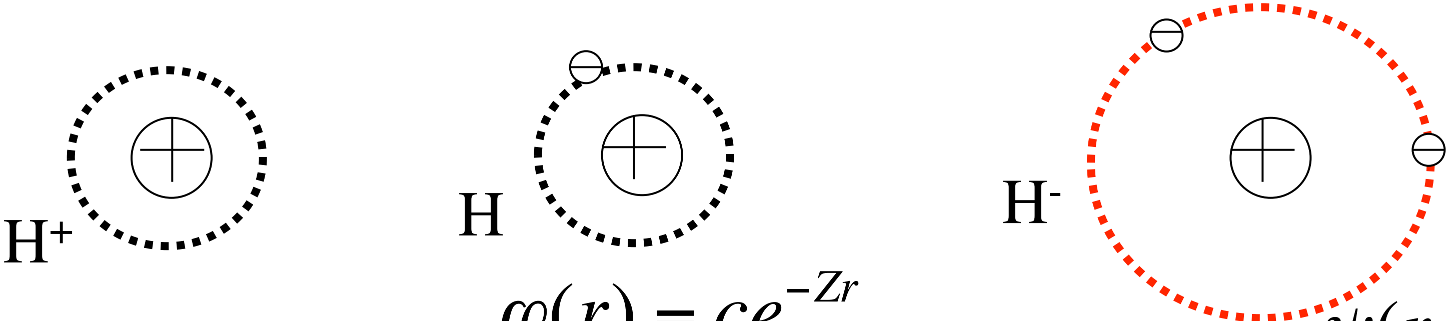


H^-

$$\overline{\varphi}(r) = ce^{-\overline{Z}r}$$

$$\psi(r_1, r_2) = \overline{\varphi}(r_1)\overline{\varphi}(r_2)$$

Why holes are not like electrons

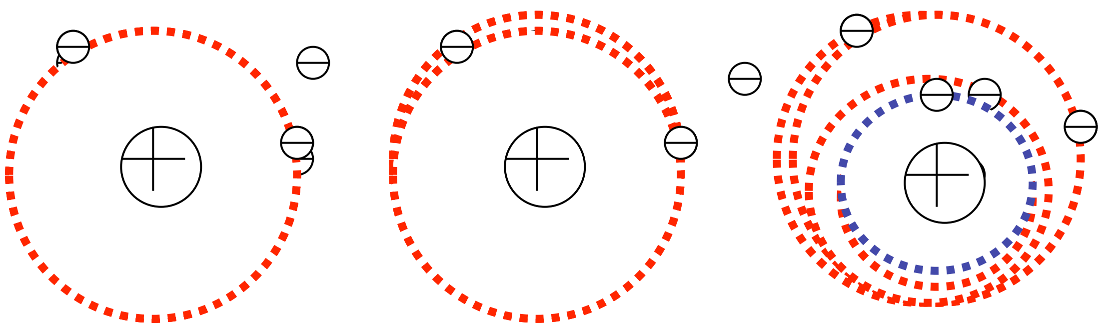


$$\varphi(r) = ce^{-Zr}$$

$$\bar{\varphi}(r) = ce^{-\bar{Z}r}$$

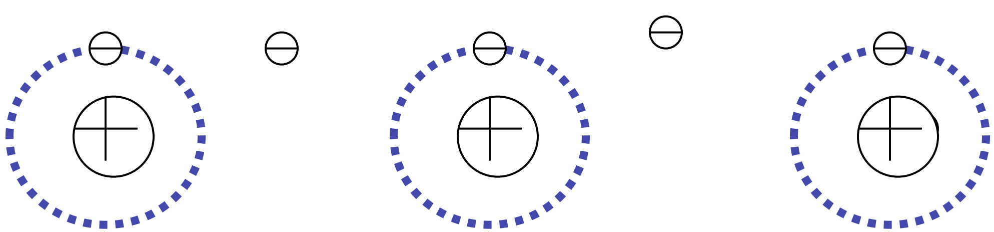
$$\psi(r_1, r_2) = \bar{\varphi}(r_1)\bar{\varphi}(r_2)$$

Single holes have trouble moving



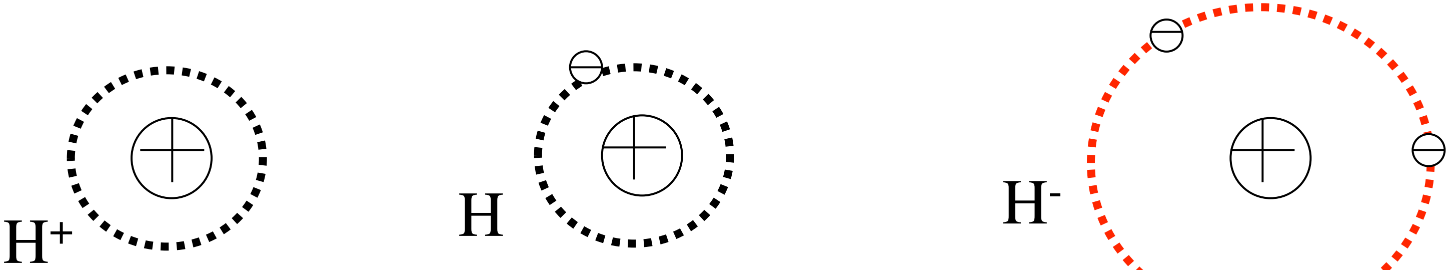
single hole

Single electrons don't



single electron

Why holes are not like electrons

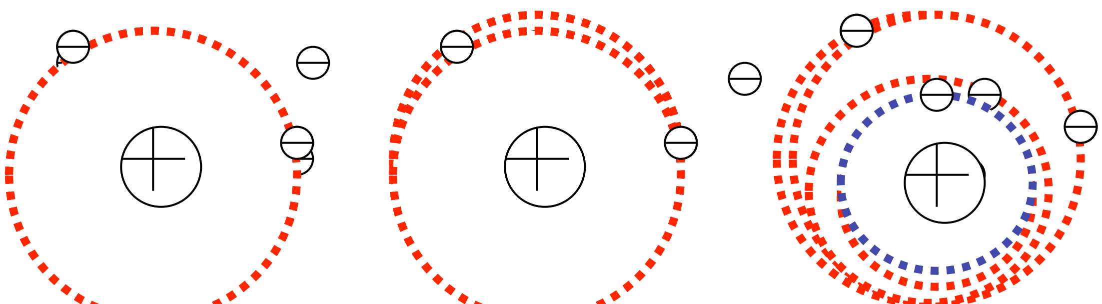


$$\varphi(r) = ce^{-Zr}$$

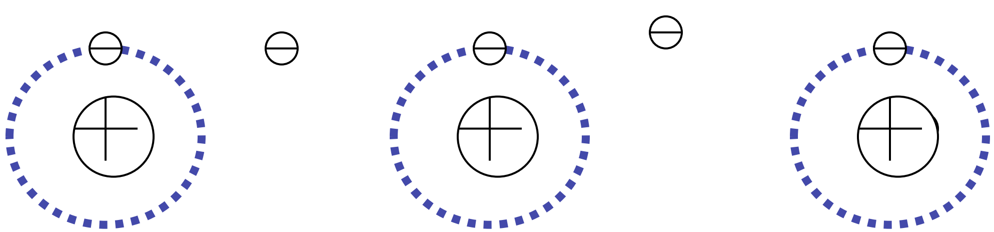
$$\bar{\varphi}(r) = ce^{-\bar{Z}r}$$

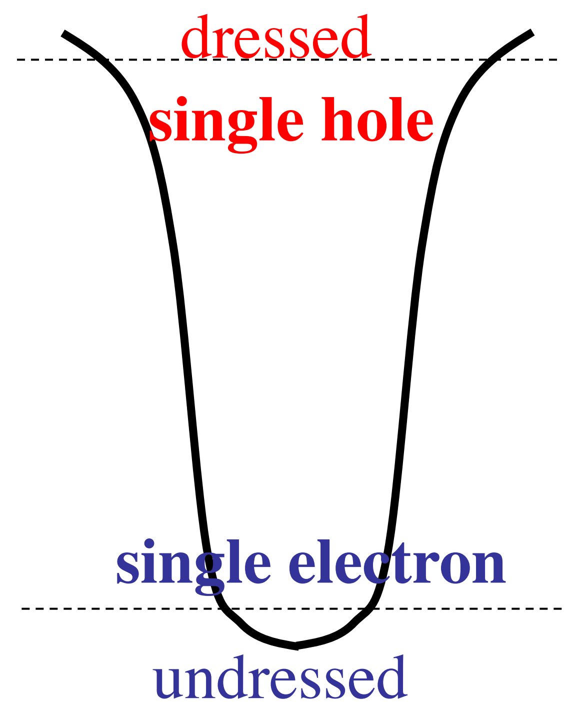
$$\psi(r_1, r_2) = \bar{\varphi}(r_1)\bar{\varphi}(r_2)$$

Single holes have trouble moving

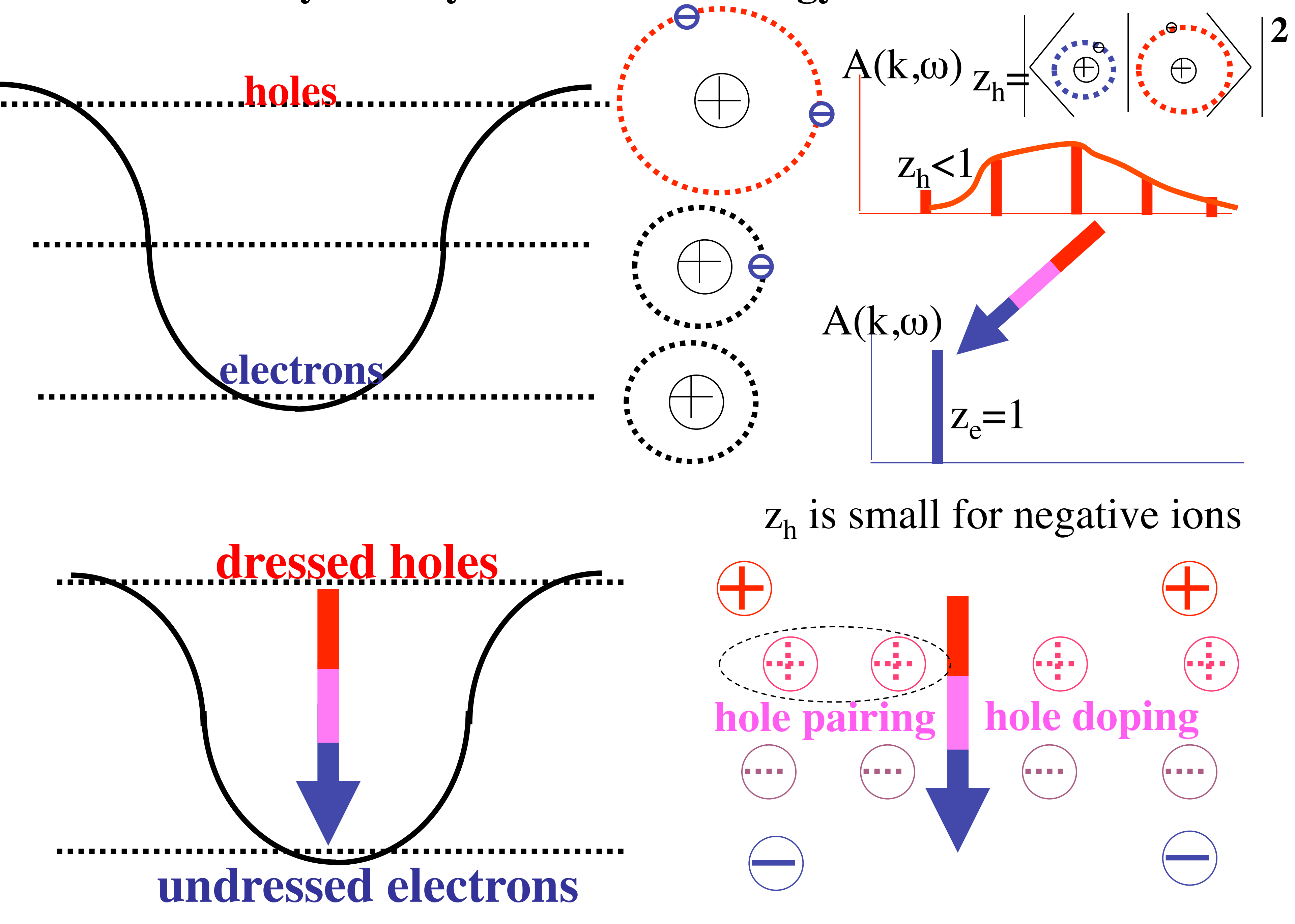


Single electrons don't

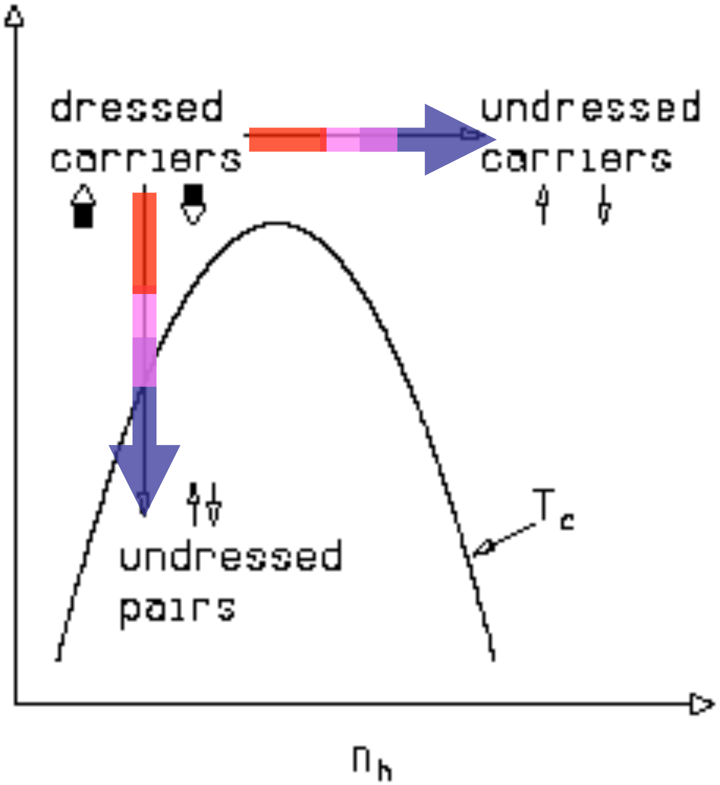


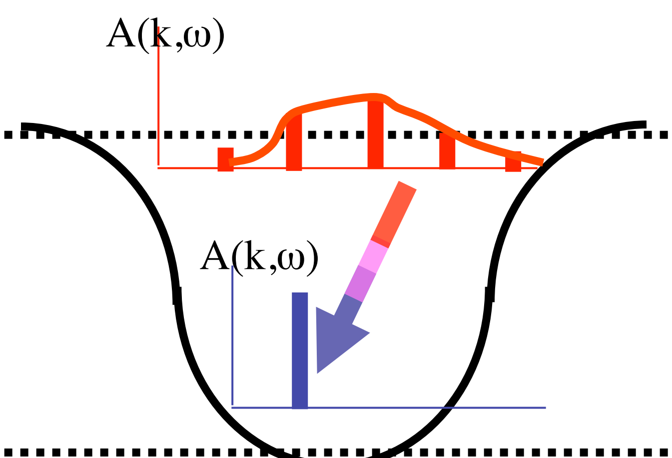


Electron-hole asymmetry in electronic energy bands

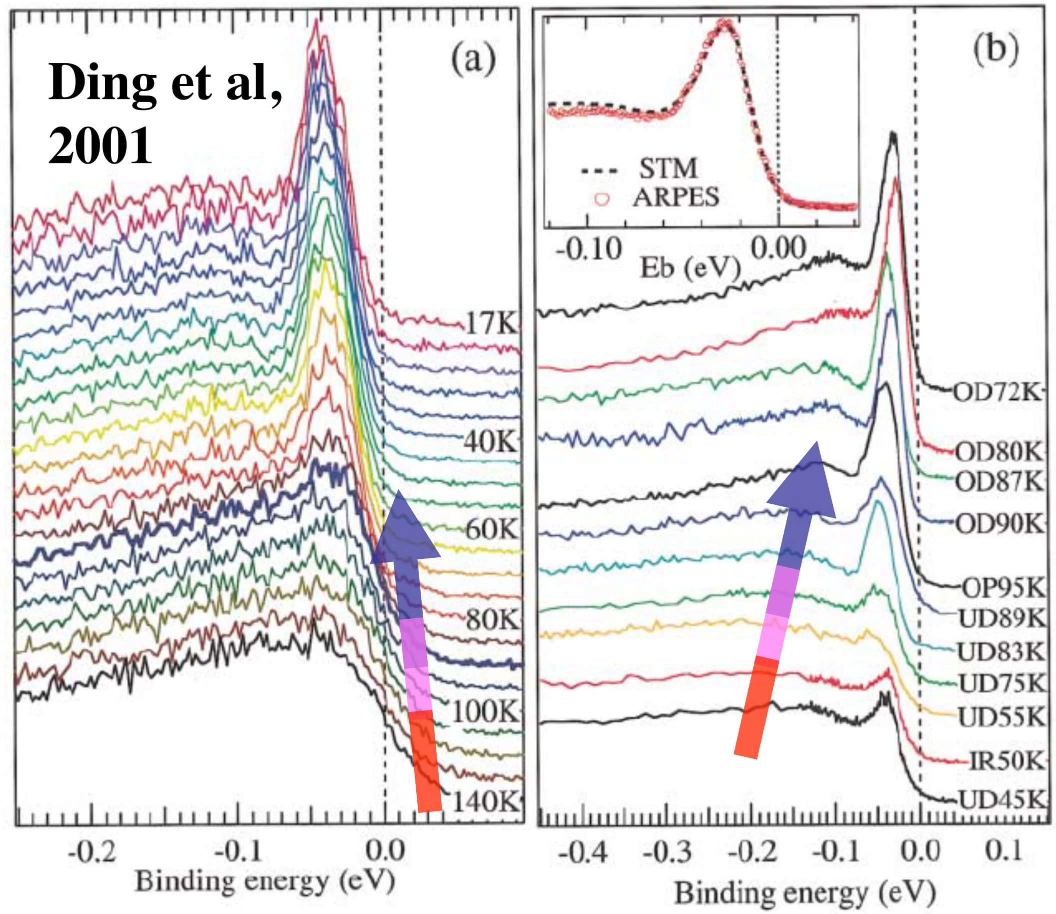


- Superconductivity causes 'undressing'
- Hole doping in the normal state causes 'undressing'





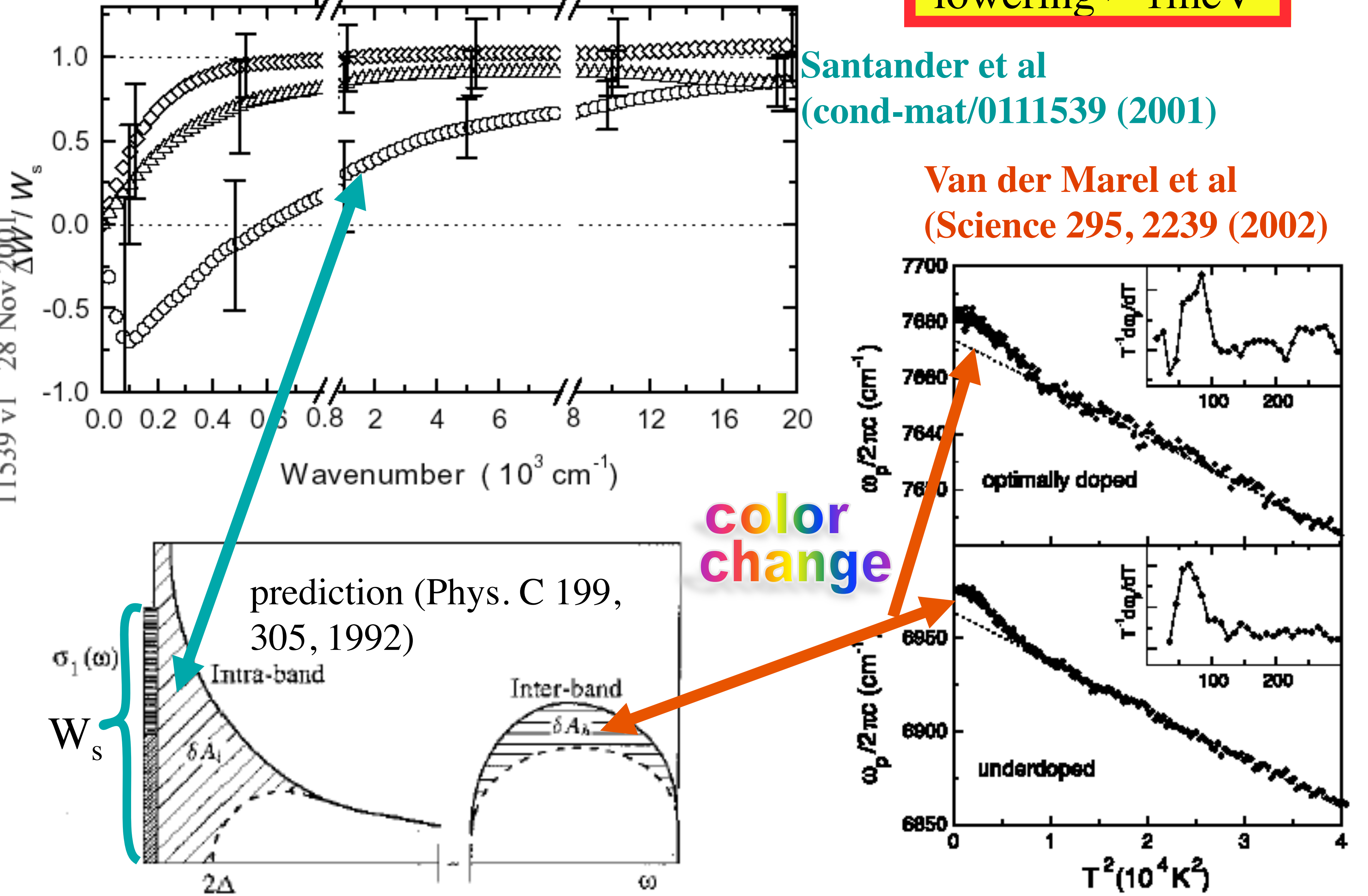
Photoemission



Optical sum rule violation in cuprates:

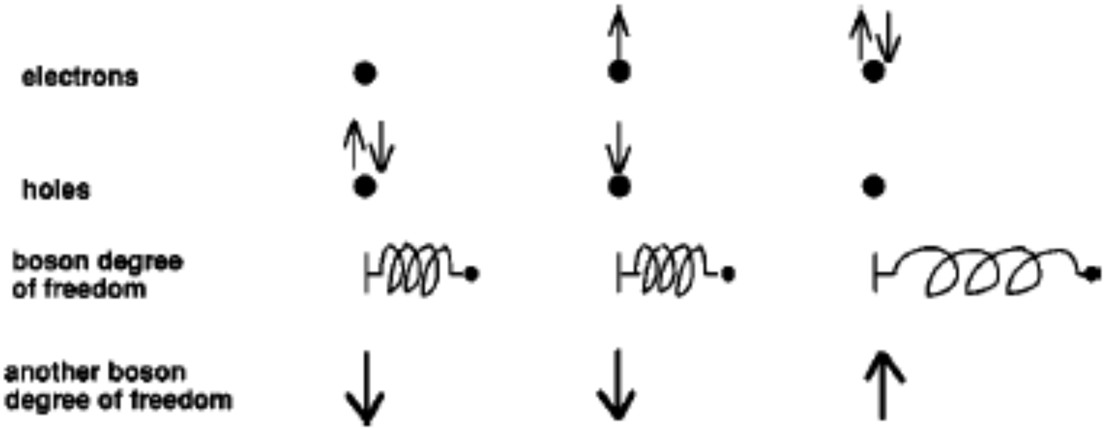
$$\Delta W = \int_0^{\omega_m} [\sigma_1^n(\omega) - \sigma_1^s(\omega)] d\omega$$

kinetic energy lowering ~ 1meV

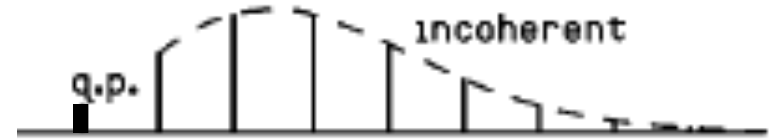


Dynamic Hubbard models (PRL 87, 206402 (2001))

1) Hubbard model + auxiliary boson degree of freedom



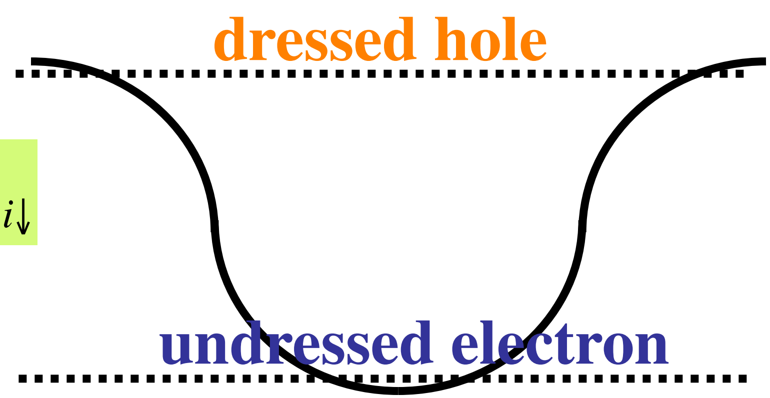
spectral function for hole creation



spectral function for electron creation

(i) Harmonic oscillator:

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2}Kq_i^2 + (U + \alpha q_i) n_{i\uparrow} n_{i\downarrow}$$ (or anharmonicity)



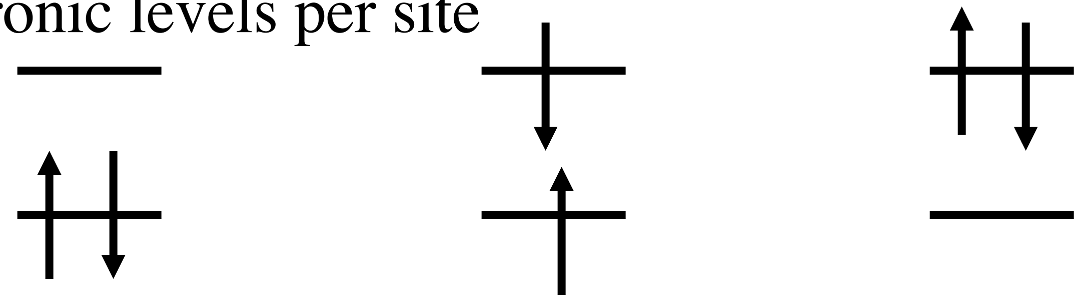
(ii) Spin 1/2 degree of freedom

$$H_i = \omega_0 \sigma_x^i + g\omega_0 \sigma_z^i + [U - 2g\omega_0 \sigma_z^i] n_{i\uparrow} n_{i\downarrow}$$

$$H = -\sum_{ij} t_{ij} c_{i\sigma}^{+} c_{j\sigma} + \sum_i H_i$$

2) Electronic dynamic Hubbard model

2 electronic levels per site

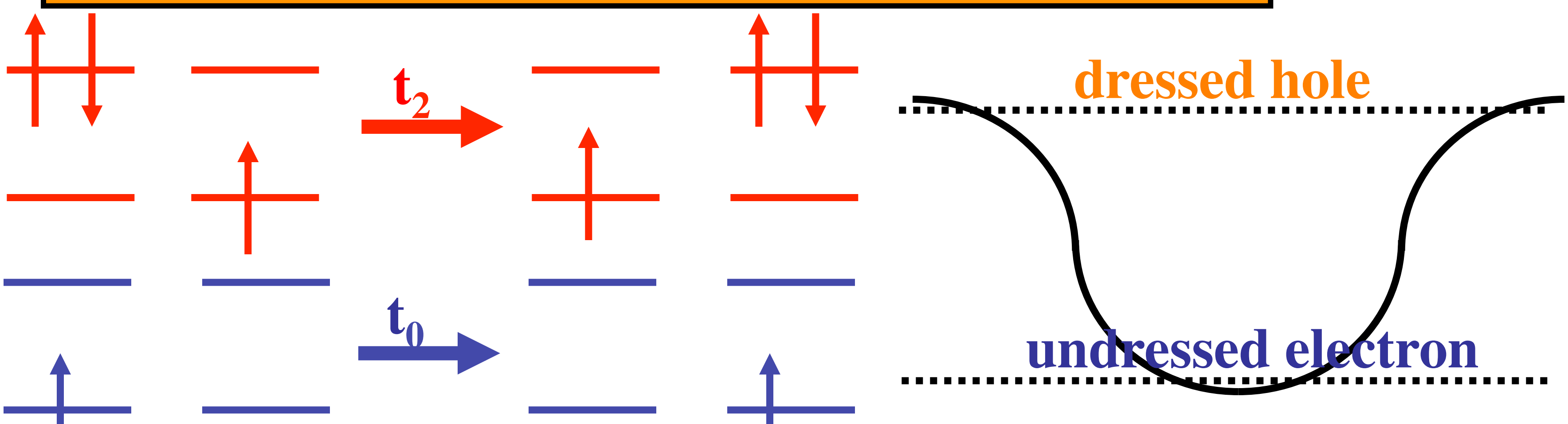


E=U E=V+ε E=U'+2ε

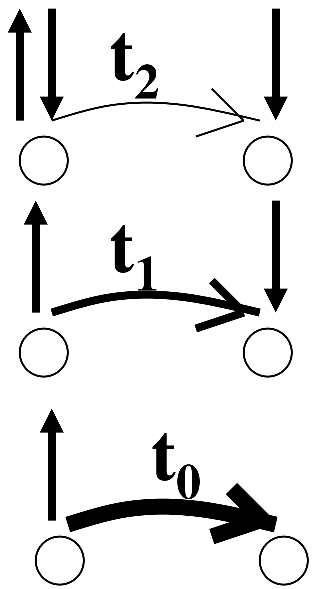
If U'+2ε<U, 2 electrons will occupy the higher single particle orbital

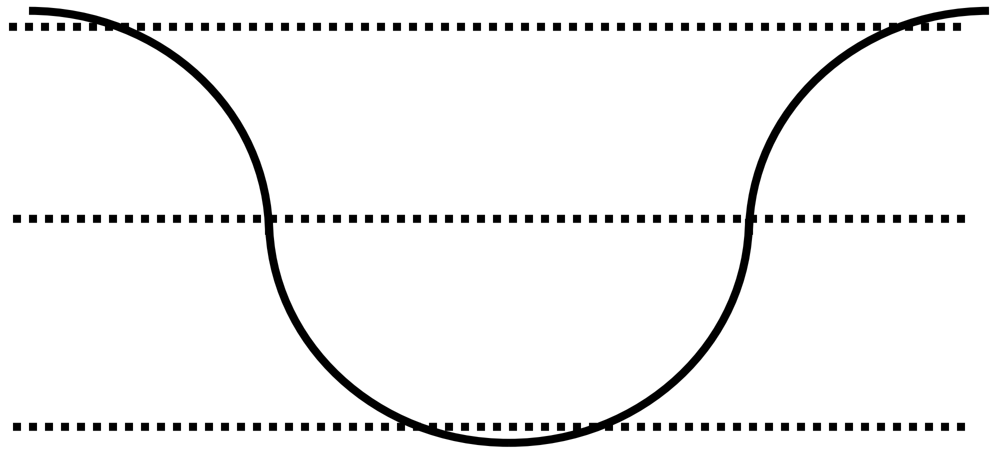
$$H_i = U n_{i\uparrow} n_{i\downarrow} + U' n'_{i\uparrow} n'_{i\downarrow} + V n_i n'_i + \varepsilon n'_i - t' \sum_{\sigma} (c^{+}_{i\sigma} c'_{i\sigma} + hc)$$

$$H = -\sum_{ij\sigma} [t_{ij} c^{+}_{i\sigma} c_{j\sigma} + t'_{ij} (c^{+}_{i\sigma} c'_{j\sigma} + hc) + t''_{ij} c^{+}_{i\sigma} c_{j\sigma}] + \sum_i H_i$$



Low energy effective Hamiltonian: Hubbard model with correlated hopping





$t_2 = tS^2$,

$t_1 = tS$,

$t_0 = t$,

$t_0 > t_1 > t_2$

$$H_{eff} = -\sum_{ij\sigma} t_{ij}^{\sigma} [\tilde{c}_{i\sigma}^{+} \tilde{c}_{j\sigma} + h.c.] + U \sum_{i} \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}$$

$$t_{ij}^{\sigma} = t_0 (1 - \tilde{n}_{i,-\sigma})(1 - \tilde{n}_{j,-\sigma}) + t_1 (\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma} - 2\tilde{n}_{i,-\sigma} \tilde{n}_{j,-\sigma}) + t_2 \tilde{n}_{i,-\sigma} \tilde{n}_{j,-\sigma}$$

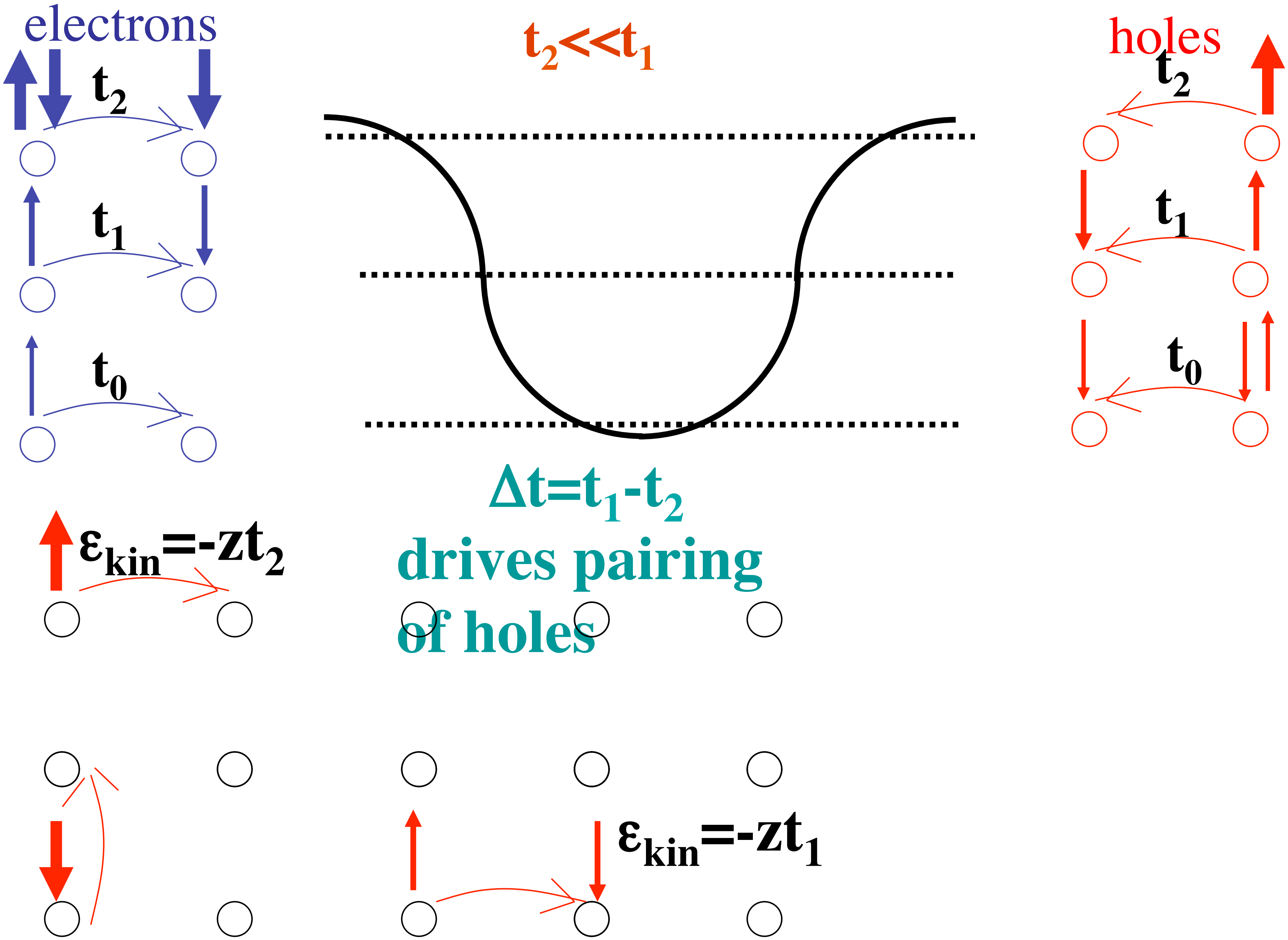
With hole operators: *correlated hopping*

$$H_{eff} \cong -\sum_{ij\sigma} [t_h + \Delta t (\tilde{n}_{i,-\sigma} + \tilde{n}_{j,-\sigma})][\tilde{c}_{i\sigma}^{+} \tilde{c}_{j\sigma} + h.c.] + U \sum_{i} \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}$$

$t_h = t_2, \quad \Delta t = t_1 - t_2$

$t(n_h) = t_h + n_h \Delta t$

Pairing through kinetic energy lowering



* Electron-hole asymmetry is key to superconductivity==>

==> superconductivity is kinetic energy driven

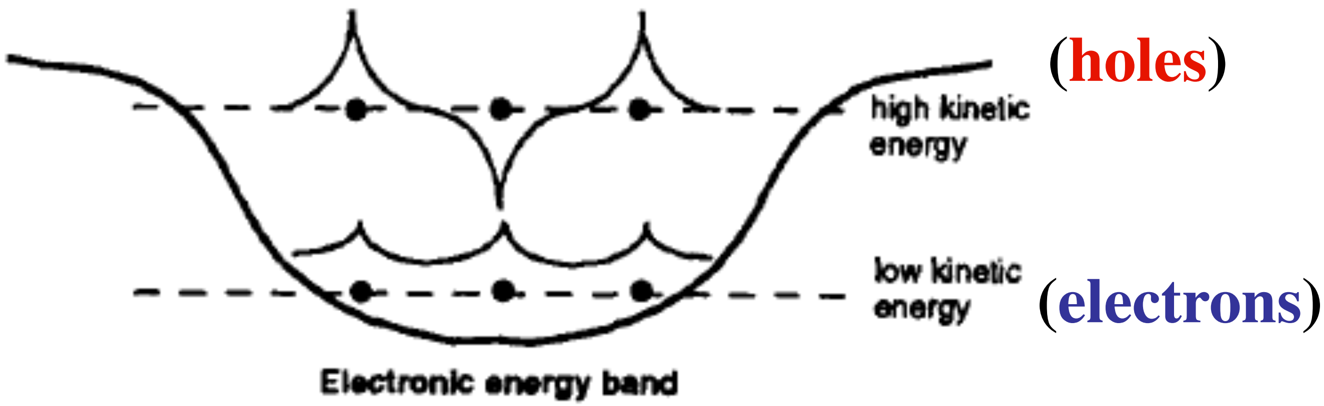


Fig. 4: Electronic energy states in a solid (schematic). The states near the top of the band (hole states) have higher kinetic energy than those at the bottom.

Electron-electron interaction terms that break electron-hole symmetry

$$\mathcal{H} = -t_0 \sum_{\langle ij \rangle} (c^+_{i\sigma} c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j$$

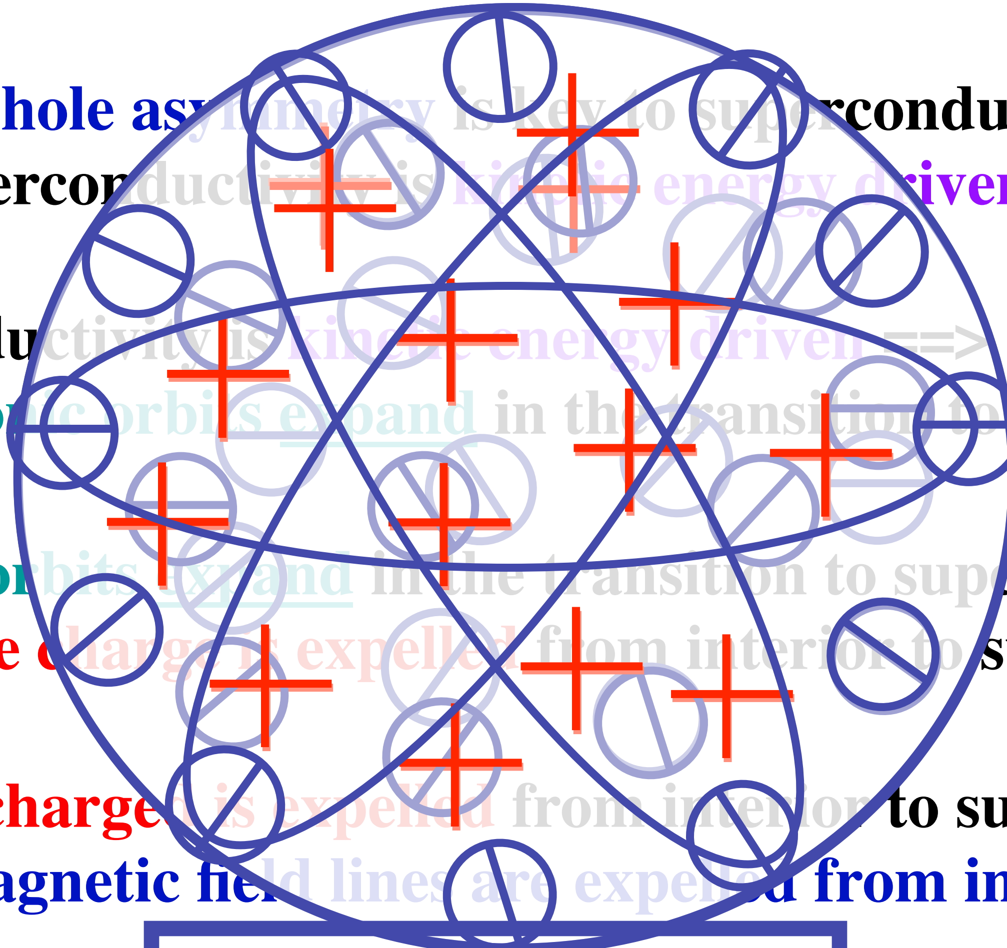
$$+ \Delta t \sum_{\langle ij \rangle} (c^+_{i\sigma} c_{j\sigma} + h.c.)(n_{i,-\sigma} + n_{j,-\sigma}) + J \sum_{\langle ij \rangle} c^+_{i\sigma} c_{j\sigma} c^+_{j\sigma'} c_{i\sigma'} + J' \sum_{\langle ij \rangle} (c^+_{i\uparrow} c_{j\uparrow} c^+_{i\downarrow} c_{j\downarrow} + h.c.)$$

only term that breaks electron-hole symmetry is related to kinetic energy

is attractive for holes, repulsive for electrons

gives lowering of kinetic energy when holes pair

Essential physics of `hole superconductivity'



* **Electron-hole asymmetry is key to superconductivity==>**
==> superconductivity is kinetic energy driven

* **Superconductivity is kinetic energy driven ==>**
==> electronic orbits expand in the transition to superconductivity

* **Electronic orbits expand in the transition to superconductivity ==>**
==>negative charge is expelled from interior to surface

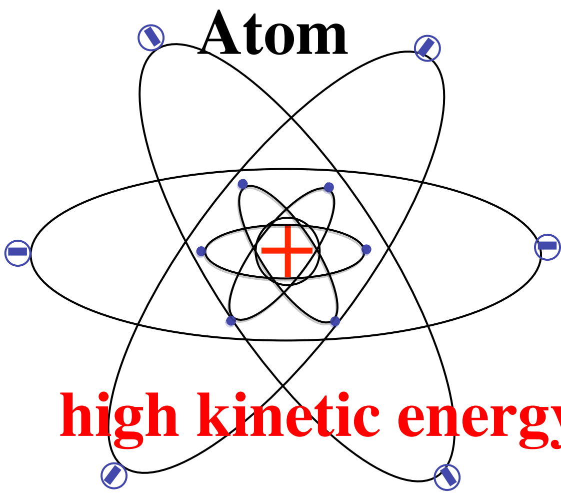
* **Negative charge is expelled from interior to surface==>**
==> any magnetic field lines are expelled from interior to surface!

= Meissner effect

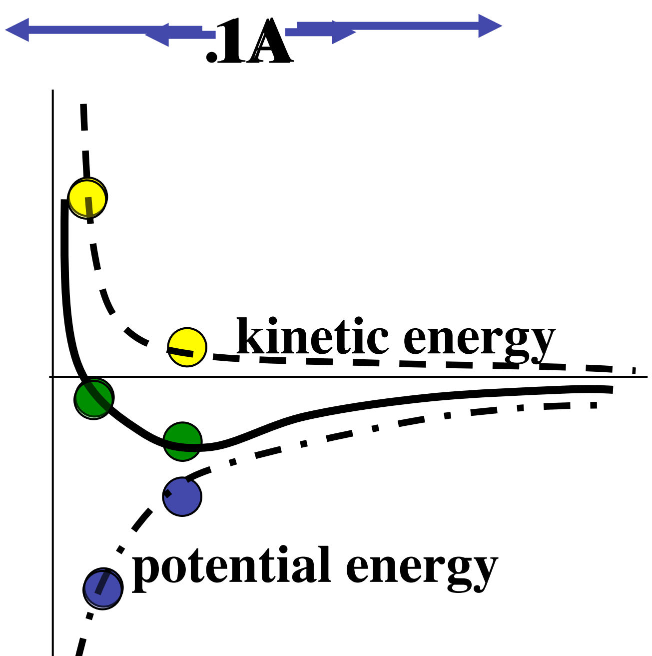
Negative charge is expelled because there is too much of it: band almost full (holes), + negatively charged structures

- **Superconductivity is kinetic energy driven ==> negative charge expulsion**

•Superconductivity is kinetic energy driven ==> negative charge expulsion

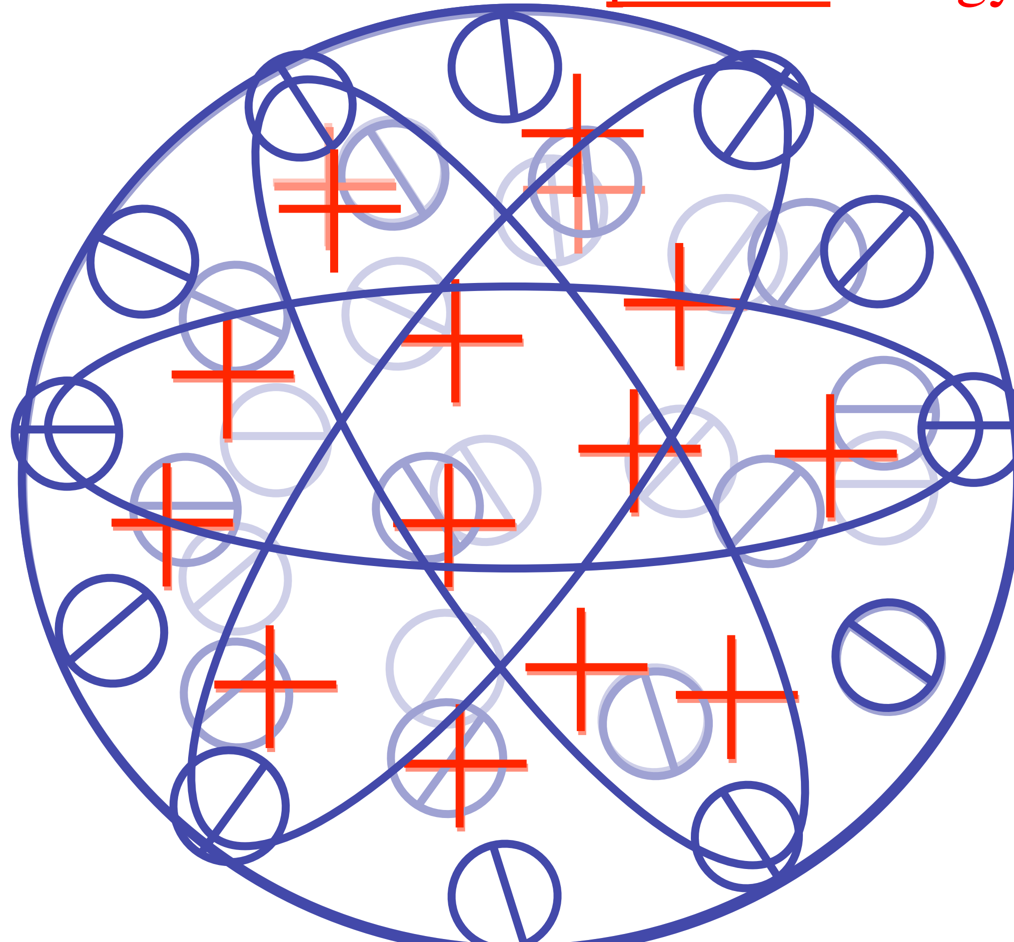


kinetic energy lowering



Superconductor

normal state: lowest potential energy



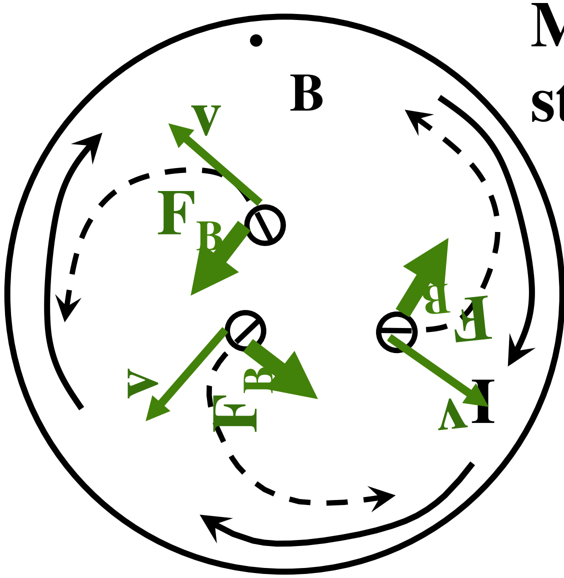
charge separation

kinetic energy lowering

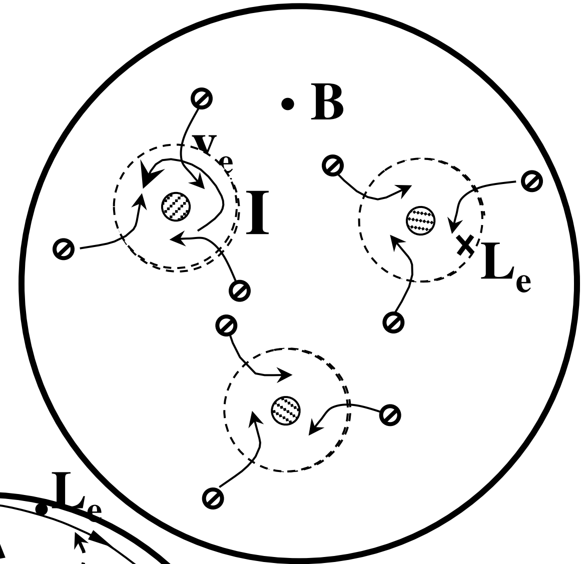
1cm

How negative charge expulsion explains the Meissner effect

Meissner state

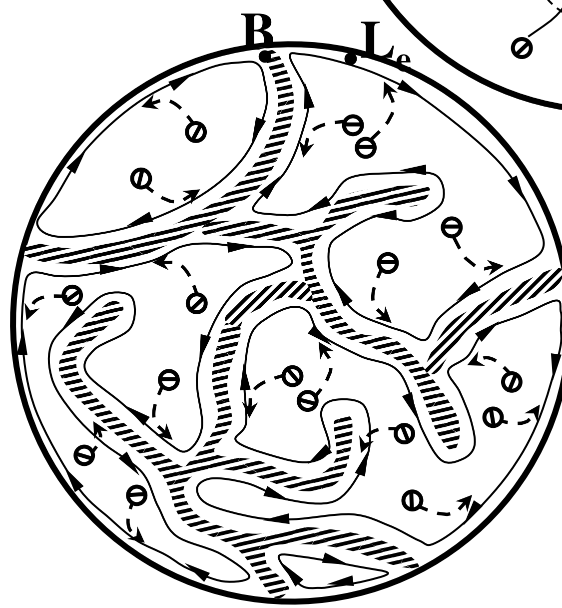


Vortex state



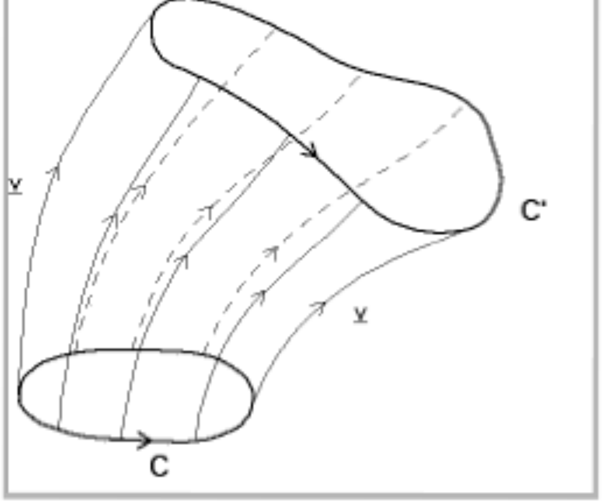
$$\vec{F}_B = \frac{e}{c}\vec{v} \times \vec{B}$$

Intermediate state



Electrons flow away from the interior of the superconductor towards the surface and towards the normal regions carrying the field lines with them

MHD theory



3) MHD equations, flux freezing

Alfven's theorem (1943): " In a perfectly conducting fluid, magnetic field lines move with the fluid: field lines are "frozen" into the plasma."
--> A motion along magnetic field lines does not change the field, motions transverse to the field carry the field with them.

Integrate induction equation $\frac{\partial \mathbf{B}}{\partial t} = \nabla \times (\mathbf{v} \times \mathbf{B})$. with Gauss' theorem $\int_V \nabla \cdot \mathbf{A} \, dV = \int_S \mathbf{A} \cdot d\mathbf{S}$,

(**S** is a closed surface enclosing volume **V**) and with Stokes' theorem $\int_S \nabla \times \mathbf{A} \cdot d\mathbf{S} = \int_C \mathbf{A} \cdot d\mathbf{l}$,

(**C** is a closed curve around the open surface **S**; $d\mathbf{S} = \hat{\mathbf{n}} \, dS$ with the outward unit normal $\hat{\mathbf{n}}$)

(i) Since for all time $\nabla \cdot \mathbf{B} = 0$ ==> $0 = \int_V \nabla \cdot \mathbf{B} \, dV = \int_S \mathbf{B} \cdot d\mathbf{S}$, $\forall t$, (closed surface **S**)

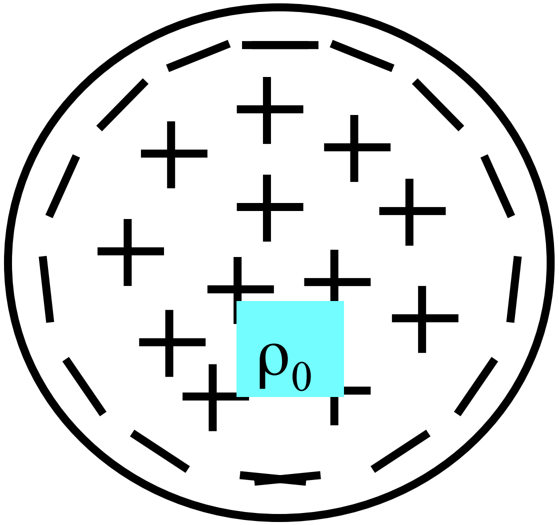
Electrons flow away from the interior of the superconductor towards the surface and towards the normal regions carrying the field lines with them

curve **C**, around an open surface **S**1:

C changes in response to plasma motions.

fendt/Lehre/Lecture_OUT/lect_jets4.pdf

New London-like equations for superconductors (JEH, PRB69, 214515(2004))



1) $J = -\frac{ne^2}{mc} A = -\frac{c}{4\pi\lambda_L^2} A \quad ; \quad \frac{1}{\lambda_L^2} \equiv \frac{4\pi n e^2}{mc^2}$

2) $\nabla \cdot A + \frac{1}{c}\frac{\partial \phi}{\partial t} = 0 \quad ; \quad$ (Lorenz gauge)

$\nabla \cdot J = -\frac{c}{4\pi\lambda_L^2} \nabla \cdot A$, continuity equation: $\nabla \cdot J + \frac{\partial \rho}{\partial t} = 0$ ==>

$$\frac{\partial \rho}{\partial t} = -\frac{1}{4\pi\lambda_L^2}\frac{\partial \phi}{\partial t}$$

integrate in time, 1 integration constant ρ_0 , ...

==> $\rho(r,t) - \rho_0 = -\frac{1}{4\pi\lambda_L^2}[\phi(r,t) - \phi_0(r)]$ | $\phi_0(r) = \int d^3r' \frac{\rho_0}{|r - r'|}$

Electrodynamics

$$\nabla^2 B = \frac{1}{\lambda_L^2} B + \frac{1}{c^2} \frac{\partial^2 B}{\partial t^2} \qquad \nabla^2 J = \frac{1}{\lambda_L^2} J + \frac{1}{c^2} \frac{\partial^2 J}{\partial t^2}$$

$$\nabla^2 (E - E_0) = \frac{1}{\lambda_L^2} (E - E_0) + \frac{1}{c^2} \frac{\partial^2 (E - E_0)}{\partial t^2}$$

$$\nabla^2 (\rho - \rho_0) = \frac{1}{\lambda_L^2} (\rho - \rho_0) + \frac{1}{c^2} \frac{\partial^2 (\rho - \rho_0)}{\partial t^2}$$

Relativistic form: $\Box^2 \equiv \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}$

$$\Box^2 (A - A_0) = \frac{1}{\lambda_L^2} (A - A_0)$$

or equivalently

$$J - J_0 = -\frac{c}{4\pi\lambda_L^2} (A - A_0)$$

$$A = (\vec{A}(\vec{r},t), i\phi(\vec{r},t))$$
$$A_0 = (0, i\phi_0(\vec{r}))$$
$$J = (\vec{J}(\vec{r},t), ic\rho(\vec{r},t))$$
$$J_0 = (0, ic\rho_0)$$

Electrostatics:

$$\nabla^2(\phi(r)-\phi_0(r))=\frac{1}{\lambda_L^2}(\phi(r)-\phi_0(r))$$

$$\nabla^2(\rho(r)-\rho_0)=\frac{1}{\lambda_L^2}(\rho(r)-\rho_0)$$

$$\nabla^2\phi(r)=-4\pi\rho(r)$$

$$\nabla^2\phi_0(r)=-4\pi\rho_0$$

$$\nabla^2(\vec{E}-\vec{E}_0)=\frac{1}{\lambda_L^2}(\vec{E}-\vec{E}_0)$$

$$\nabla^2\phi(r)=0$$

outside supercond.

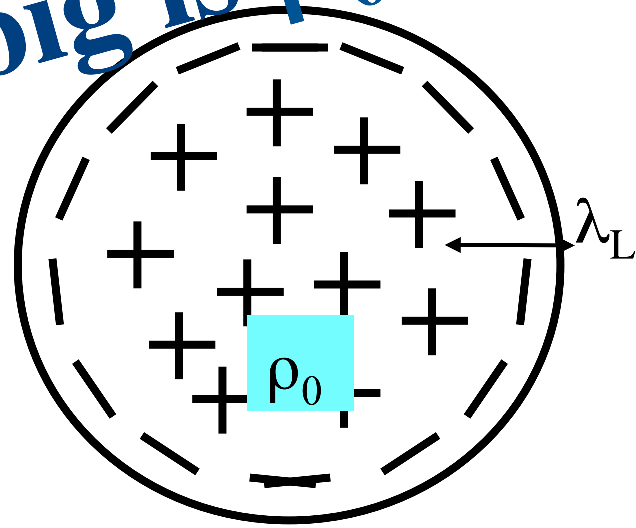
+assume ϕ(r) and its normal derivative are continuous at surface

how big is ρ_0?

Solution for sphere of radius R:

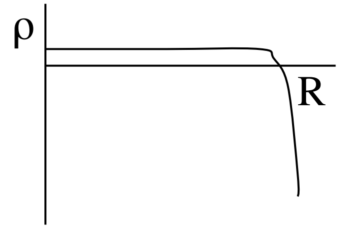
$$\rho(\mathrm{r})=\rho_0\left(1-\frac{R^3}{3\lambda_L^2}\frac{\sinh(r/\lambda_L)}{R/\lambda_L\cosh(R/\lambda_L)-\sinh(R/\lambda_L)}\right)$$

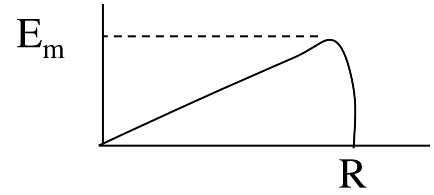
$$\vec{E}(\mathrm{r})=\frac{4}{3}\pi\rho_0\left[1-\frac{R^3}{r^3}\frac{r/\lambda_L\cosh(r/\lambda_L)-\sinh(r/\lambda_L)}{R/\lambda_L\cosh(R/\lambda_L)-\sinh(R/\lambda_L)}\right]\vec{r}$$

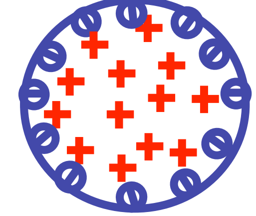


No electric field outside sphere

How much charge is expelled?







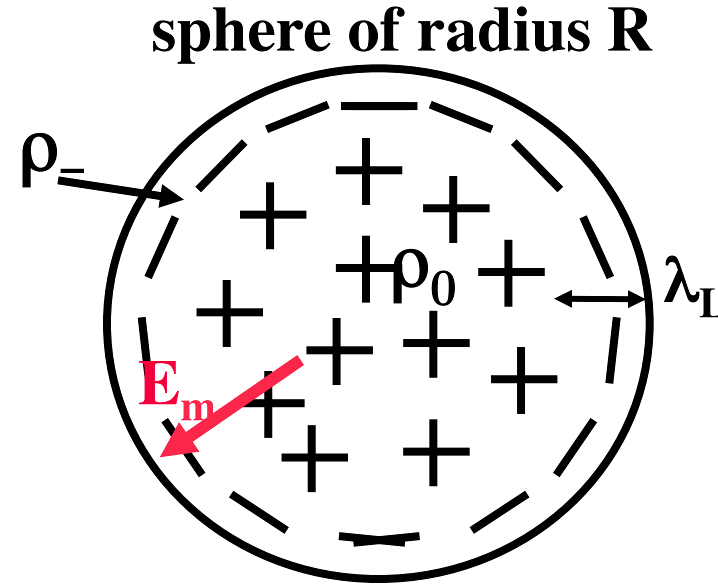
element	T_c(K)	H_c(G)	λ_L(A)	Extra electrons	E_m (Volts/cm)
Al	1.14	105	500	1/17 mill	31,500
Sn	3.72	309	510	1/3.7 mill	92,700
Hg	4.15	412	410	1/2.5 mill	123,600
Pb	7.19	803	390	1/1 mill	240,900
Nb	9.50	1980	400	1/1.3 mill	308,400

Sample size dependence of expelled charge (Q) and E-field

$\rho_- < 0$ = charge density near surface

$\rho_0 > 0$ = charge density in interior

$Q \sim \rho_0 R^3 \sim -\rho_- R^2 \lambda_L$



Electrostatic energy cost:

$U_E \sim Q^2/R \sim (\rho_- R^2 \lambda_L)^2/R \sim (\rho_-)^2 R^3 \sim (\rho_0)^2 R^5 \sim \text{Volume} \sim R^3$

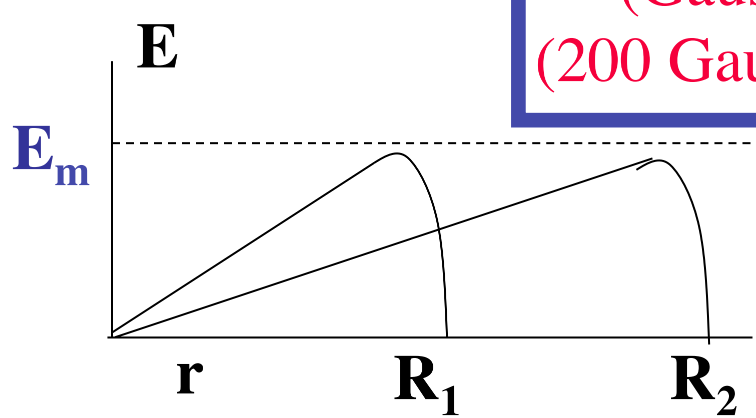
$\Longrightarrow$ ρ_- independent of R, $\rho_0 \sim 1/R$

$E_m = H_{c1}$
(Gauss=300V/cm)
(200 Gauss=60,000V/cm)

Electric field vs. r:

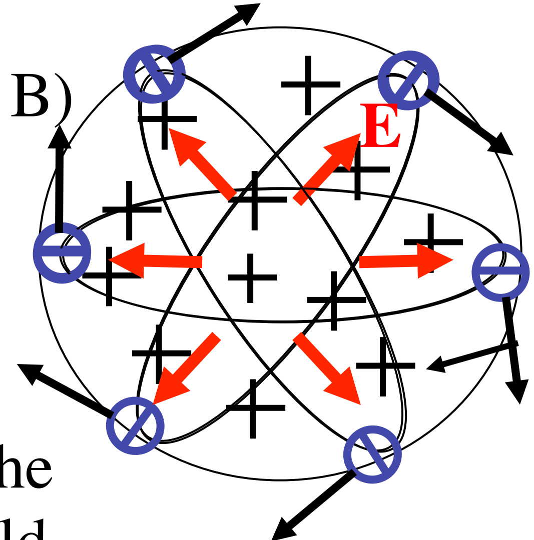
$$E_m = -4\pi\lambda_L\rho_-$$

independent of R



Spin currents: Spin Meissner effect

Internal electric field (in the absence of applied B) pointing out $(\hat{n})$

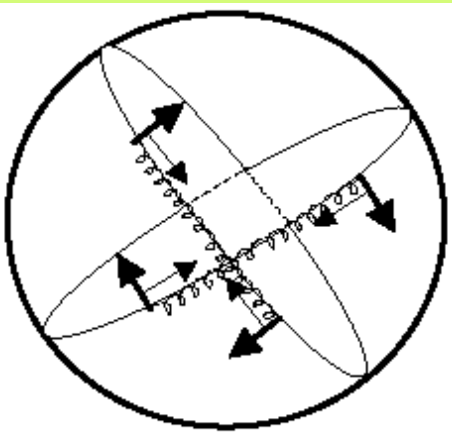


- $c^{+}_{k\uparrow}c^{+}_{-k\downarrow}$ carries a spin current
- $< c^{+}_{k\uparrow}c^{+}_{-k\downarrow} > \neq < c^{+}_{-k\uparrow}c^{+}_{k\downarrow} >$ necessarily in the presence of internal E-field

$$J_{charge} = \frac{n}{2}(v_{\uparrow} + v_{\downarrow}) = 0$$

no charge current ==> no B-field

$$J_{spin} = \frac{n}{2}(v_{\uparrow} - v_{\downarrow}) \neq 0$$



Spin current without charge current

Flows within a London penetration depth of the surface

Speed of spin current carriers: ~ 100,000 cm/s

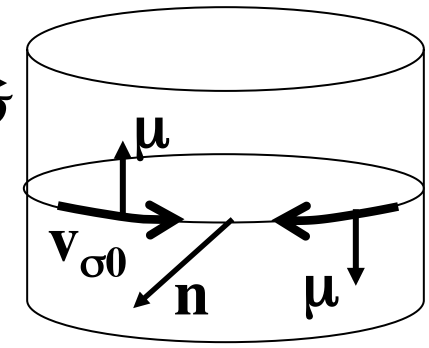
Number of spin current carriers: =superfluid density

There is a spontaneous spin current in the ground state of superconductors, flowing within λ_L of the surface **(JH, EPL81, 67003 (2008))**

$$\vec{v}_{\sigma 0} = -\frac{\hbar}{4m_e\lambda_L}\vec{\sigma}\times\hat{n}$$

no external fields applied

$$\vec{\mu} = \frac{e\hbar}{2m_e c}\vec{\sigma}$$

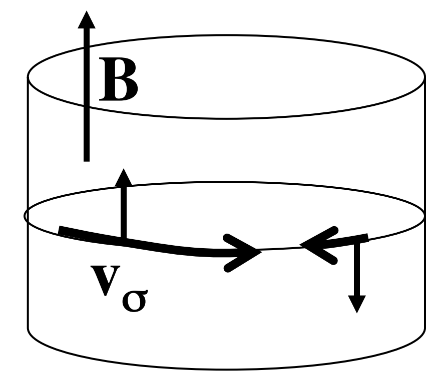


For λ_L=400A, $v_{\sigma 0}$=72,395cm/s

# of carriers in the spin current: n_s

When a magnetic field is applied:

$$\vec{v}_{\sigma} = \vec{v}_{\sigma 0} - \frac{e}{m_e c}\lambda_L\vec{B}\times\hat{n}$$



The slowed-down spin component stops when

$$B = \frac{m_e c}{e\lambda_L}v_{\sigma 0} = \frac{\hbar c}{4e\lambda_L^2} = \frac{\phi_0}{4\pi\lambda_L^2} \sim H_{c1}!$$

Electronic orbits have radius $2\lambda_L$ (to explain Meissner effect)

Angular momentum: $L = m_e v_{\sigma 0}(2\lambda_L)$ ==> $L = \hbar/2$

Spin current electrodynamics

$$J_\sigma(\vec{r},t) = (\vec{J}_\sigma(\vec{r},t), ic\rho_\sigma(\vec{r},t))$$

$$J_\sigma(\vec{r},t) = (\frac{en_s}{2}\vec{v}_\sigma(\vec{r},t), ic\rho_\sigma(\vec{r},t))$$

$$J_{\sigma 0} = (\vec{J}_{\sigma 0}, ic\rho_{\sigma 0})$$

$$J_\sigma(\vec{r},t) - J_{\sigma 0} = -\frac{c}{8\pi\lambda_L^2}(A_\sigma(\vec{r},t) - A_{\sigma 0}(\vec{r}))$$

$$J_{\sigma 0} = (\frac{en_s}{2}\vec{v}_{\sigma 0}, ic\rho_{\sigma 0})$$

$$\vec{J}_\sigma(\vec{r},t) - \vec{J}_{\sigma 0} = -\frac{c}{8\pi\lambda_L^2}(\lambda_L\vec{\sigma}\times\vec{E}(\vec{r},t) + \vec{A}(\vec{r},t))$$

$$\rho_\sigma(\vec{r},t) - \rho_{\sigma 0} = \frac{1}{8\pi\lambda_L}\vec{\sigma}\cdot\vec{B}(\vec{r},t) - \frac{1}{8\pi\lambda_L^2}(\phi(\vec{r},t) - \phi_0(\vec{r}))$$

$$A_\sigma(\vec{r},t) = (\vec{A}_\sigma(\vec{r},t), i\phi_\sigma(\vec{r},t))$$

$$J_\sigma(\vec{r},t) = \rho_\sigma(\vec{r},t)c(-\vec{\sigma}\times\hat{r}, i)$$

$$A_{\sigma 0}(\vec{r}) = (\vec{A}_{\sigma 0}(\vec{r}), i\phi_{\sigma 0}(\vec{r}))$$

$$J_{\sigma 0} = \frac{\rho_0 c}{2}(-\vec{\sigma}\times\hat{r}, i)$$

$$\vec{A}_\sigma(\vec{r},t) = \lambda_L\vec{\sigma}\times\vec{E}(\vec{r},t) + \vec{A}(\vec{r},t)$$

$$\square^2(A_\sigma - A_{\sigma 0}) = \frac{1}{\lambda_L^2}(A_\sigma - A_{\sigma 0})$$

$$\vec{A}_{\sigma 0}(\vec{r}) = \lambda_L\vec{\sigma}\times\vec{E}_0(\vec{r})$$

$$\phi_\sigma(\vec{r},t) = -\lambda_L\vec{\sigma}\cdot B(\vec{r},t) + \phi(\vec{r},t)$$

$$\square^2(J_\sigma - J_{\sigma 0}) = \frac{1}{\lambda_L^2}(J_\sigma - J_{\sigma 0}).$$

$$\phi_{\sigma 0}(\vec{r}) = \phi_0(\vec{r})$$

$$(A_\sigma)_\alpha = \frac{i\lambda_L}{2}\epsilon_{\alpha\beta\gamma\delta}\sigma_\beta F_{\gamma\delta} + A_\alpha$$

$$\square^2 = \nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}$$

Rules of the game:

Hole carriers are necessary for superconductivity at any T

Negatively charged structures give high Tc

Negatively charged anions

Direct overlap between anion orbitals

Structures as three-dimensional as possible compatible with above

Problem is:

Negatively charged anions strongly repel each other

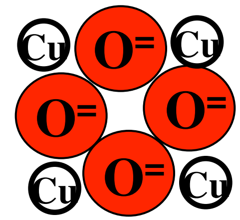
Antibonding electrons drive lattices unstable

The three (so far) ways to reach high T_c:

= three ways to pack big negative ions very close together, and have holes conducting through them:

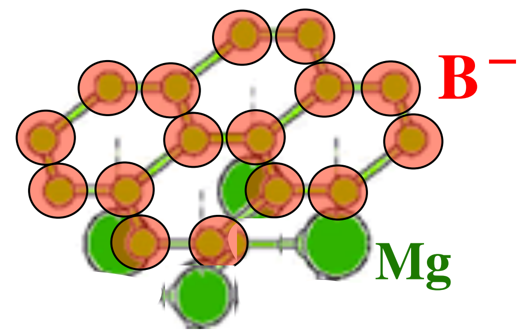
1) Coplanar cation-anion

(cuprates)



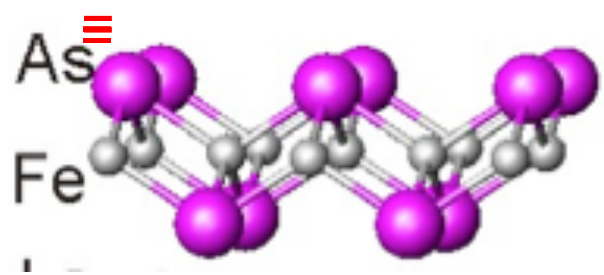
2) Planes of anions only

(MgB_2)



3) Cation-anion tetrahedra

(FeAs, FeSe, …)



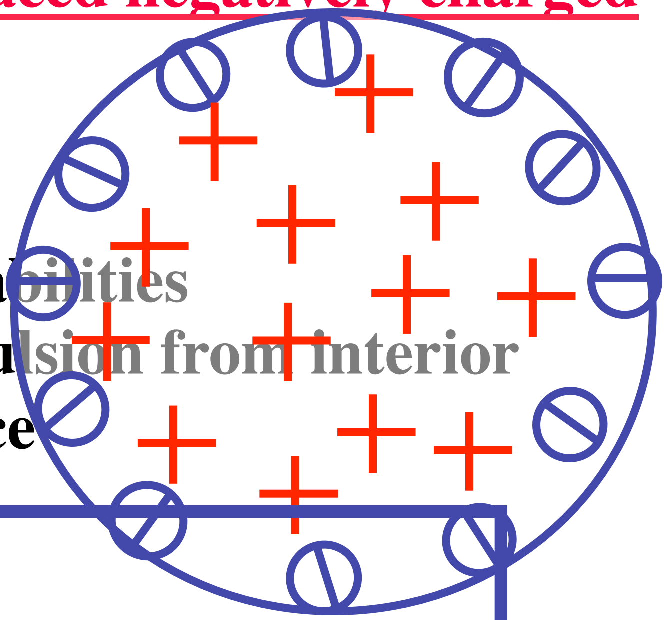
Cations should be small

Summary:

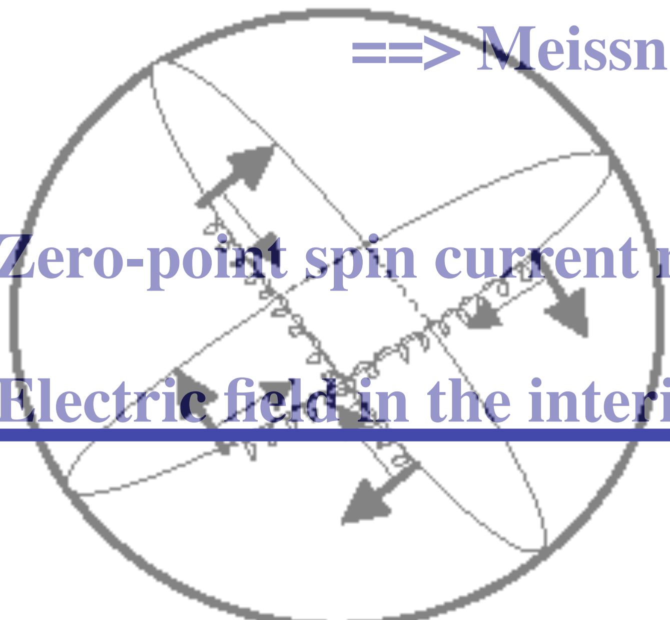
Superconductivity is caused by pairing of hole carriers

High T_c: holes conducting through closely spaced negatively charged anions

Atoms from right side of the periodic table



Antibonding electrons + a lot of negative charge ⟶ **Lattice instabilities**
Charge expulsion from interior to the surface



==> Meissner effect explained

Zero-point spin current near the surface of superconductors

Electric field in the interior and around superconductors