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

3:06 PM–3:42 PM

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/~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 electrodynamical 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:

Elements

Common features:

MgB$_2$

Differences:

Pnictides

Common features:

Cuprates

Common features:
The continuum of superconductivity in materials

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

Elements

Common features:

Differences:

MgB$_2$

Common features: BaKBiO? Sr$_2$RuO$_4$? Borocarbides? Cobaltates?

Pnictides

Common features: Heavy fermion compounds? Organic superconductors?

Differences:

Cuprates

Differences:
The continuum of superconductivity in materials.

**Common Features:**
- MgB$_2$
- Pnictides
- Cuprates

**Differences:**
- Heavy fermion compounds
- Cobaltates
- Borocarbides
- Sr$_2$RuO$_4$
- BaKBiO?
- Organic superconductors

There is NO BCS-non-BCS divide!

The continuum of superconductivity in materials.
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...
BaBi$_{1-x}$Pb$_x$O$_3$ ($T_c=13K$) versus Ba$_{1-x}$K$_x$BiO$_3$ ($T_c=29K$):

"As the $T_c$ 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."
HOLE SUPERCONDUCTIVITY

J.E. HIRSCH

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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

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.

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.
**Hall effect:** $R_H =$ Hall coefficient

Lorentz force:

\[
\vec{F} = q \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right)
\]

- **Electron carriers**
  - \( R_H < 0 \)
  - Electrons

- **Hole carriers**
  - \( R_H > 0 \)
  - Holes

1948

On the other hand, we have found an empirical rule that indicates a correlation between superconductivity and lattice structure; namely, that 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.

<table>
<thead>
<tr>
<th>Lattice type</th>
<th>Superconductive elements</th>
<th>Non-superconductive elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body-centred cubic</td>
<td>V, Ta, βZr</td>
<td>Li, Na, K, Rb, C</td>
</tr>
<tr>
<td>Face-centred cubic</td>
<td>Al, βLa, βTl, Th, Pb(?)</td>
<td>1.008 Ca, Sr</td>
</tr>
<tr>
<td>Close packed hexagonal</td>
<td>Zn</td>
<td>Cu ≤0.75</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>Au, Ag, Cu ≥0.78</td>
</tr>
<tr>
<td></td>
<td>αTl</td>
<td></td>
</tr>
<tr>
<td></td>
<td>αLa</td>
<td></td>
</tr>
</tbody>
</table>

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

Orange: superconductors;
White: non-superconductors
Brown: magnetic

Lanthanides (rare earths):
- Orange: Transition element superconductors
- Light orange: Transition element superconductors (only under pressure)
- White: Extrapolated
- Light grey: Rare earths and transuranic elements
- Brown: Magnetic transition elements
- White: Not superconducting
Correlations between normal-state properties and superconductivity

Heat capacity

Debye temperature

Hall coefficient
Fermi surfaces in Nb$_3$Sn 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$_3$Si


A.A. Manuel, S. Samoilov, R. Sachot, P. Descouts, M. Peter
High $T_c$ cuprates

Hall coefficient

**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.
Holes and electrons

Torrance et al PRL 61, 1127 (1988)

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

Matthias rules

Moruzzi, Janak & Williams

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

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.
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, 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$^-$).
Anomalous Transport Properties in Superconducting Nd$_{1.85}$Ce$_{0.15}$CuO$_{4\pm\delta}$


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$_x$CuO$_{4\pm\delta}$ epitaxial thin films and crystals by both increasing and decreasing $\delta$ 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$_x$CuO$_{4\pm\delta}$.

PHYSICAL REVIEW B 76, 024506 (2007)

Hole superconductivity in the electron-doped superconductor Pr$_{2-x}$Ce$_x$CuO$_4$

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

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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$_x$CuO$_4$ as a function of doping and temperature. The resistivity $\rho_{xx}$ at temperatures $100 \, \text{K} < T < 300 \, \text{K}$ 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 $\rho_{xy}$, or the Hall angle $\theta_H$, 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)


undoped
doped

MgB$_2$ ($T_c$=39K): a smoking gun

Wrong sizes

Negatively charged ions: B$^-$

Conduction by holes

Armstrong et al, '79

Akimitsu et al, 2001

$a=3.086\text{Å}$
$c=3.524\text{Å}$
MgB$_2$

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  

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

FeAs compounds: $T_{c}^{\text{max}} = 56$K

Iron-Based Layered Superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05-0.12$) 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:
  \[ \text{Fe}^{2+}\text{As}^{3-} = \Theta \]

* Hole carriers?

**Superconductivity at 25 K in hole-doped \((\text{La}_{1-x}\text{Sr}_x)\text{OFFeAs}\)**

Hai-Hu Wen (a), Gang Mu, Lei Fang, Huan Yang and Xi Yi (c)

Electron-doped arsenides

Electron-doped cuprates

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


Fig. 1. Schematic depiction of how holes are created by electron doping. The electron added to $\text{Cu}^{2+}$ repels an electron from $\text{O}^{2-}$ to the neighboring $\text{Cu}^{2+}$, leaving behind a hole in oxygen ($\text{O}^{-}$).
Importance of Fermi surface topology for high temperature superconductivity in electron-doped iron arsenic superconductors


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:

$T_c = 8K \rightarrow T_c = 37K \rightarrow T_c = 0$

Pressure: ambient $\rightarrow \sim 9GPa \rightarrow > 10GPa$

FeSe: $T_c=8\text{K}$ pressure $37\text{K}$

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)
FeSe under pressure:

**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)

\[ T_c = 8\, \text{K} \]

**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)

\[ T_c = 37\, \text{K} \]

Pauling radius of Se:

- 3.75 Å
- 3.16 Å
Two gaps in FeSe: superconductivity is driven by holes conducting through closely packed \( \text{Se}^= \) 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, \( \Delta_1 \), 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-Elmeguid¹

**FIG. 4 (color online).** The band structure of SnO at 7 GPa. The
Hole-doped semiconductors

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

incorporated into diamond³; 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-

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-

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

Katsuya Shimizu\textsuperscript{1,2}, Hiroto Ishikawa\textsuperscript{1}, Daigoroh Takao\textsuperscript{1}, Takehiko Yagi\textsuperscript{3} & Kiichi Amaya\textsuperscript{1,2}

Superconductivity at 20 K in yttrium metal at pressures exceeding 1 Mbar

J.J. Hamlin\textsuperscript{a}, V.G. Tissen\textsuperscript{b} and J.S. Schilling\textsuperscript{a}

Pressure-induced superconductivity in Sc to 74 GPa

J. J. Hamlin and J. S. Schilling

Superconductivity of Ca Exceeding 25 K at Megabar Pressures

Takahiro Yabuuchi, Takahiro Matsuoka, Yuki Nakamoto and Katsuya Shimizu
Why non-superconducting metallic elements become superconducting under high pressure

J.J. Hamlin, JEH (2009)

Lattice distortion creates holes

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.

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_c$ (K)</th>
<th>$P$ (GPa)</th>
<th>$R_H$ ($10^{-11}$ m$^3$/C)</th>
<th>$R_H$ (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>20</td>
<td>48</td>
<td>-150</td>
<td>&gt;0 predicted</td>
</tr>
<tr>
<td>Cs</td>
<td>1.3</td>
<td>12</td>
<td>-71</td>
<td>&gt;0 predicted</td>
</tr>
<tr>
<td>Ca</td>
<td>25</td>
<td>161</td>
<td>-18</td>
<td>&gt;0 predicted</td>
</tr>
<tr>
<td>Sc</td>
<td>19.6</td>
<td>106</td>
<td>-3</td>
<td>&gt;0 predicted</td>
</tr>
<tr>
<td>Y</td>
<td>19.5</td>
<td>115</td>
<td>-10</td>
<td>&gt;0 predicted</td>
</tr>
</tbody>
</table>

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

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.
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).
High charge density between ions ==> stable

Low charge density between ions ==> unstable

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

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

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.
Why *holes* are not like *electrons*

\[ \varphi(r) = ce^{-Zr} \]
Why *holes* are not like *electrons*

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

Single holes have trouble moving.

Single electrons don't.

\[ \psi(r_1, r_2) = \overline{\varphi}(r_1)\overline{\varphi}(r_2) \]
Why **holes** are not like **electrons**

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

\[ \psi(r_1, r_2) = \varphi(r_1)\varphi(r_2) \]

Single holes have trouble moving

Single electrons don't

**single hole**

**single electron**
Why **holes** are not like **electrons**

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

\[
\psi(r_1, r_2) = \varphi(r_1)\varphi(r_2)
\]

Single holes have trouble moving

Single electrons don't
Electron-hole asymmetry in electronic energy bands

\[ A(k,\omega) z_h = 2 \]

\[ z_h < 1 \]

\[ z_e = 1 \]

\( z_h \) is small for negative ions

holes

electrons

dressed holes

undressed electrons

hole pairing

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

\[ A(k, \omega) \]
Optical sum rule violation in cuprates:

$$\Delta W = \int_{0}^{\omega_m} [\sigma_1^\ell(\omega) - \sigma_1^s(\omega)] d\omega$$

Van der Marel et al
(Science 295, 2239 (2002))

Santander et al
(cond-mat/0111539 (2001))

Prediction (Phys. C 199, 305, 1992)

Kinetic energy lowering $\sim 1 \text{meV}$
Dynamic Hubbard models  

(PRL 87, 206402 (2001))

1) Hubbard model + auxiliary boson degree of freedom

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

(spectral function for hole creation)

(i) Harmonic oscillator:

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

(or anharmonicity)

(ii) Spin 1/2 degree of freedom

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

(dressed hole)

(spectral function for electron creation)

(undressed electron)
2) Electronic dynamic Hubbard model

2 electronic levels per site

\[ H_i = U n_i^{\uparrow} n_i^{\downarrow} + U' n_i'^{\uparrow} n_i'^{\downarrow} + V n_i n_i' + \epsilon n_i - t \sum_{\sigma} (c_i^{\sigma \dagger} c_i'^{\sigma \dagger} + h.c) \]

If \( U' + 2\epsilon < U \), 2 electrons will occupy the higher single particle orbital

\[ H = - \sum_{ij\sigma} \left[ t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + t_{ij}' (c_{i\sigma}^{\dagger} c_{j\sigma} + h.c) + t_{ij}'' c_{i\sigma}^{\dagger} c_{j\sigma} \right] + \sum_i H_i \]

dressed hole

undressed electron
Low energy effective Hamiltonian:
Hubbard model with correlated hopping

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

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

With hole operators:

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

\[
t_h = t_2, \quad \Delta t = t_1 - t_2 \]

\[
t(n_h) = t_h + n_h \Delta t
\]
Pairing through kinetic energy lowering

Electrons

$t_0$  $t_1$  $t_2$

$\Delta t = t_1 - t_2$

Drives pairing of holes

Holes

$t_0$  $t_1$  $t_2$

$\epsilon_{\text{kin}} = -zt_2$

$\epsilon_{\text{kin}} = -zt_1$
Electron-electron interaction terms that break electron-hole symmetry:

The only term that breaks electron-hole symmetry is related to kinetic energy. It is attractive for holes, repulsive for electrons and gives lowering of kinetic energy when holes pair.

\[ \mathcal{H} = -t_0 \sum_{\langle ij \rangle} (c_{i\sigma}^+ c_{j\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\langle ij \rangle} n_i n_j + \Delta t \sum_{\langle ij \rangle} (c_{i\sigma}^+ c_{j\sigma} + h.c.)(n_{i,-\sigma} + n_{j,-\sigma}) + J \sum_{\langle ij \rangle} c_{i\sigma}^+ c_{j\sigma} c_{j\sigma}^+ c_{i\sigma}^\dagger + J' \sum_{\langle ij \rangle} (c_{i\uparrow}^+ c_{j\uparrow} c_{i\downarrow}^+ c_{j\downarrow} + h.c.) \]

* Electron-hole asymmetry is key to superconductivity

\[ \implies \text{superconductivity is kinetic energy driven} \]
Electron-hole asymmetry is key to superconductivity

Superconductivity is kinetic energy driven

Electronic orbits expand in the transition to superconductivity

Negative charge is 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 $\implies$ negative charge expulsion
Superconductivity is **kinetic energy driven** $\Rightarrow$ **negative charge expulsion**

**Atom**

high kinetic energy

**kinetic energy lowering**

**Superconductor**

normal state: lowest **potential energy**

kinetic energy energy

charge separation

**kinetic energy lowering**

potential energy
How negative charge expulsion explains the Meissner effect

Electrons flow away from the interior of the superconductor towards the surface and towards the normal regions carrying the field lines with them.
Electrons flow away from the interior of the superconductor towards the surface and towards the normal regions carrying the field lines with them.
New London-like equations for superconductors (JEH, PRB69, 214515(2004))

1) \[ J = -\frac{ne^2}{mc} A = -\frac{c}{4\pi\lambda^2_L} A \quad ; \quad \frac{1}{\lambda^2_L} \equiv \frac{4\pi ne^2}{mc^2} \]

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

\[ \nabla \cdot J = -\frac{c}{4\pi\lambda^2_L} \nabla \cdot A \quad , \quad \text{continuity equation:} \quad \nabla \cdot J + \frac{\partial \rho}{\partial t} = 0 \quad \implies \]

\[ \frac{\partial \rho}{\partial t} = -\frac{1}{4\pi\lambda^2_L} \frac{\partial \phi}{\partial t} \quad \text{integrate in time, 1 integration constant } \rho_0 \ldots \]

\[ \rho(r,t) - \rho_0 = -\frac{1}{4\pi\lambda^2_L} [\phi(r,t) - \phi_0(r)] \]

\[ \phi_0(r) = \int d^3r' \frac{\rho_0}{|r - r'|} \]
Electrodynamics

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

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

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

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

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

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

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:

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

\[ \nabla^2 \phi(r) = -4\pi \rho(r) \quad \nabla^2 \phi_0(r) = -4\pi \rho_0 \]

\[ \nabla^2 \rho(r) = \rho_0 \]

outside supercond.

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

Solution for sphere of radius \( R \):

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

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

No electric field outside sphere
How much charge is expelled?

<table>
<thead>
<tr>
<th>element</th>
<th>$T_c$(K)</th>
<th>$H_c$(G)</th>
<th>$\lambda_L$(A)</th>
<th>Extra electrons</th>
<th>$E_m$ (Volts/cm)</th>
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<tbody>
<tr>
<td>Al</td>
<td>1.14</td>
<td>105</td>
<td>500</td>
<td>1/17 mill</td>
<td>31,500</td>
</tr>
<tr>
<td>Sn</td>
<td>3.72</td>
<td>309</td>
<td>510</td>
<td>1/3.7 mill</td>
<td>92,700</td>
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<tr>
<td>Hg</td>
<td>4.15</td>
<td>412</td>
<td>410</td>
<td>1/2.5 mill</td>
<td>123,600</td>
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<tr>
<td>Pb</td>
<td>7.19</td>
<td>803</td>
<td>390</td>
<td>1/1 mill</td>
<td>240,900</td>
</tr>
<tr>
<td>Nb</td>
<td>9.50</td>
<td>1980</td>
<td>400</td>
<td>1/1.3 mill</td>
<td>308,400</td>
</tr>
</tbody>
</table>
Sample size dependence of expelled charge \( (Q) \) and E-field

\[
\rho_- < 0 = \text{charge density near surface}
\]

\[
\rho_0 > 0 = \text{charge density in interior}
\]

\[
Q \sim \rho_0 R^3 \sim -\rho_- R^2 \lambda_L
\]

Electrostatic energy cost:

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

\[\Rightarrow \rho_- \text{ independent of } R, \quad \rho_0 \sim 1/R\]

Electric field vs. \( r \):

\[
E_m = -4\pi\lambda_L \rho_-
\]

independent of \( R \)

\[
E_m = H_{c1}
\]

(Gauss=300V/cm)

(200 Gauss=60,000V/cm)
**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

\[
J_{\text{charge}} = \frac{n}{2} (v_{\uparrow} + v_{\downarrow}) = 0 \quad \text{no charge current} \implies \text{no B-field}
\]

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

**Spin current without charge current**

Flows within a London penetration depth of the surface

Speed of spin current carriers: 
$\sim 100,000$ cm/s

Number of spin current carriers: 
= superfluid density
There is a spontaneous spin current in the ground state of superconductors, flowing within $\lambda_L$ of the surface (JH, EPL81, 67003 (2008)).

$$\vec{v}_{\sigma 0} = -\frac{\hbar}{4m_e\lambda_L} \vec{\sigma} \times \hat{n} \quad \text{no external fields applied}$$

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

# 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

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

\[ J_{\sigma_0} = (\vec{J}_{\sigma_0}, ic\rho_{\sigma_0}) \]

\[ J_\sigma(\vec{r}, t) - J_{\sigma_0} = -\frac{c}{8\pi\lambda^2} (A_\sigma(\vec{r}, t) - A_{\sigma_0}(\vec{r})) \]

\[ \tilde{J}_\sigma(\vec{r}, t) - \tilde{J}_{\sigma_0} = -\frac{c}{8\pi\lambda^2} (\lambda L \bar{\sigma} \times \vec{E}(\vec{r}, t) + \vec{A}(\vec{r}, t)) \]

\[ \rho_\sigma(\vec{r}, t) - \rho_{\sigma_0} = \frac{1}{8\pi\lambda_L} \bar{\sigma} \cdot \vec{B}(\vec{r}, t) - \frac{1}{8\pi\lambda^2} (\phi(\vec{r}, t) - \phi_0(\vec{r})) \]

\[ A_\sigma(\vec{r}, t) = (A_\sigma(\vec{r}, t), i\phi_\sigma(\vec{r}, t)) \]

\[ A_{\sigma_0}(\vec{r}) = (\vec{A}_{\sigma_0}(\vec{r}), i\phi_{\sigma_0}(\vec{r})) \]

\[ \tilde{A}_\sigma(\vec{r}, t) = \lambda L \bar{\sigma} \times \vec{E}(\vec{r}, t) + \vec{A}(\vec{r}, t) \]

\[ \tilde{A}_{\sigma_0}(\vec{r}) = \lambda L \bar{\sigma} \times \vec{E}_0(\vec{r}) \]

\[ \phi_\sigma(\vec{r}, t) = -\lambda L \bar{\sigma} \cdot \vec{B}(\vec{r}, t) + \phi(\vec{r}, t) \]

\[ \phi_{\sigma_0}(\vec{r}) = \phi_0(\vec{r}) \]

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

\[ J_\sigma(\vec{r}, t) = \frac{e\nu_s}{2} \vec{v}_\sigma(\vec{r}, t), ic\rho_\sigma(\vec{r}, t) \]

\[ J_{\sigma_0} = \left( \frac{e\nu_s}{2} \vec{v}_{\sigma_0}, ic\rho_{\sigma_0} \right) \]

\[ \square^2 (A_\sigma - A_{\sigma_0}) = \frac{1}{\lambda^2} (A_\sigma - A_{\sigma_0}) \]

\[ \square^2 (J_\sigma - J_{\sigma_0}) = \frac{1}{\lambda^2} (J_\sigma - J_{\sigma_0}) \]

\[ \square^2 = \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \]
Hole carriers are necessary for superconductivity at any $T$.

Negatively charged structures give high $T_c$.

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 $\rightarrow$ Lattice instabilities

Charge expulsion from interior to the surface $\rightarrow$ Meissner effect explained

Zero-point spin current near the surface of superconductors

Electric field in the interior and around superconductors