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EXPERIMENTAL WORKSHOP ON
"HIGH TEMPERATURE SUPERCONDUCTORS"
(30 March - 14 April 1989)

PHENOMENOLOGY AND THEORY OF SUPERCONDUCTIVITY
(Lectures I & II)

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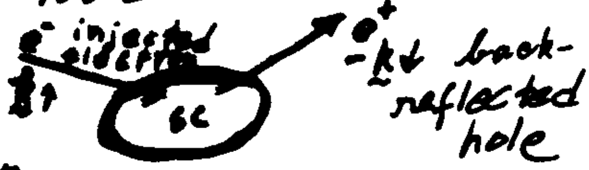
INTRODUCTION

* High-T_c Superconductivity (HTSC): A surprise in Experimental and Theoretical Solid State Physics and Solid St. chemistry. Highly chemical SC: Prototype $La_{2-x}(Ba,Sr)_x CuO_4$, $YBa_2Cu_3O_{7-\delta}$ and other Bi and Tl based compounds. A Golden triangle of Ionicity, Covalency and metallicity $\Rightarrow$ possibility of Chemical Tuning for the first time. This, together with obvious technological potential of cheap flux $\Rightarrow$ HTSC heat wave globally.

* Theoretical Understanding: Single most important Question $\rightarrow$ ARE THEY DIFFERENT? Debatable. General Consensus: phonon mediated pairing will not do; T_c just too high ($> 40K$); Also $^{16}O \rightleftarrows {}^{18}O$ isotope effect absent, or much smaller than expected. This per se does not imply failure of BCS PAIRING, the essential idea underlying BCS is not in doubt $\leftrightarrow$

- Flux Quantization : $\Phi = n\Phi_0$, $\Phi_0 = \frac{hc}{2|e|}$
- AC Josephson effect $h\nu = 2|e|V$
- Andreev reflection (electron-hole transmutation by pair potential $V\langle c_{k\uparrow} c_{-k\downarrow}\rangle$)



In Question is Nature of and Mechanism for PAIRING:

Momentum Space ($k\uparrow, -k\downarrow$) pairing of Cooper ⇒ Resonant, loose pairs with binding energy $E_b \ll E_F$ of size $\xi_0 \sim 10^{-4}$ cm $\gg k_F^{-1} \sim 10^{-8}$ cm $\sim 10^6$ pairs overlap. This pairwise occupation of time-reversed states ⇔ condensate superconducting. only small fraction E_b/E_F of electrons effectively condense.

OR

Realspace Pairing: compact pairs of size $\xi_0 \sim$ 10-20 Å ~ carrier spacing; binding energy $E_b \sim E_F$, supercond. resulting from Bosonic condensation of pairs Pre-existing above T_c. All carriers effectively condense.

Electronic Mechanism of Pairing:

- Exchange of charge degrees of freedom e.g. Valence fluctuation $Cu^{2+}Cu^{3+} \rightleftharpoons Cu^{3+}Cu^{2+}$; charge transfer fluctuation $Cu^{2+} \rightleftharpoons Cu^{+}L$ (Energy scale ~ charge transfer energy)
- Exchange of Spin degrees of freedom (Energy scale ~ $k_B T_N$, magnetic)
- PAIRING inherent in strongly correlated (Repulsive) electron system near half-band Filling. supercond. as derived from an Insulating state - oddelectron insulator (Mott-Hubbard type insulator) carriers generated by doping + deviation from ½-filling ⇒ a Fermi-Puddle ($n \sim 10^{21}$ cm^{-3}) rather than a Fermi Sea ($n \sim 10^{23}$ cm^{-3}) of usual metallic superconductors. Non-Fermi liquid behavior?
- PAIRING of WHAT: Hole-like objects (one hole per Ba^{2+}, Sr^{2+} replacing La^{3+}). Their statistics in question (holons?). Electron-like objects too reported.

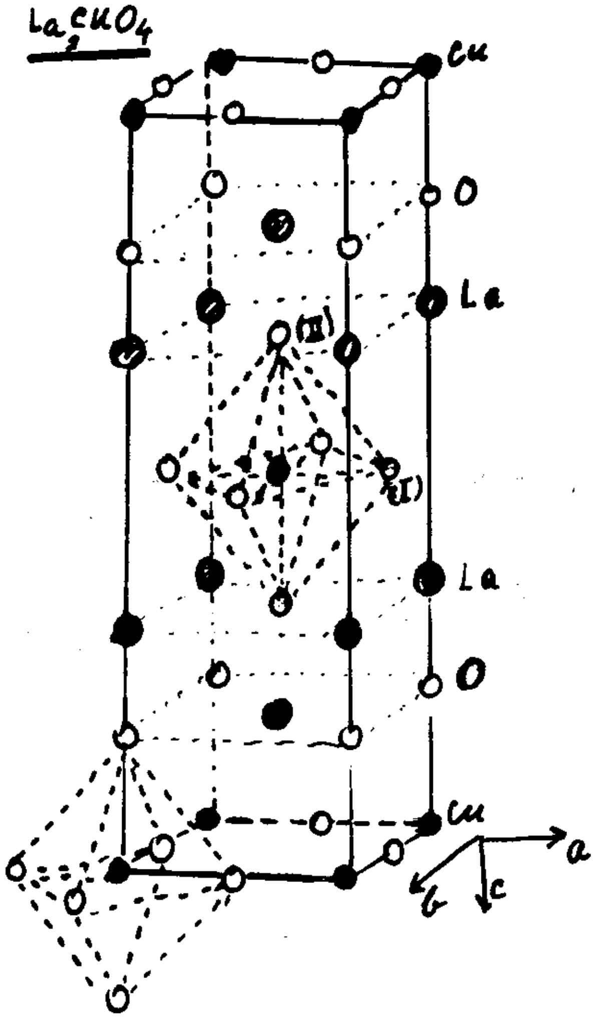
- HTSC has striking differences but also remarkable similarities with LTSC. From experimental viewpoint, the Ginzburg-Landau phenomenology will continue to provide a meaningful description of phenomenon. Also, the Pairing Theory of BCS should continue to provide a reference frame in the absence of a possibly different microscopic theory.

- In the following, we will have a quick look at the phenomenon of SC in general, leading to the idea that SC is a pure thermodynamic phase and then treat the associated II-order phase transition a-la Ginzburg-Landau Order parameter theory – the most successful phenomenology known. Particular emphasis placed on the fluctuations that manifest as precursor phenomena in HTSC because of smallness of coherence length ξ.

- But first, for orientation and perspective, we have a quick overview of HTSC.

HIGH TEMPERATURE SUPERCONDUCTIVITY

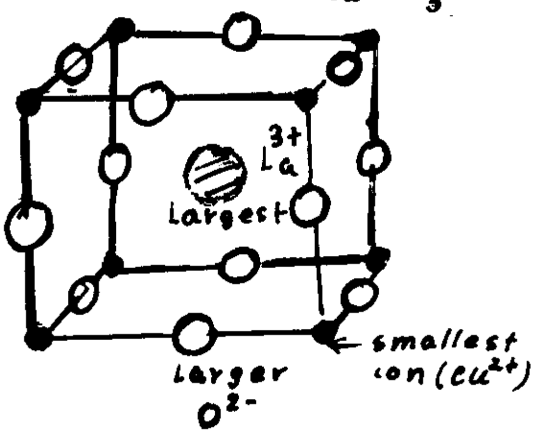
<u>Prototype</u>: $La_{2-\delta} Ba_{\delta} CuO_4$, $\delta \sim 0.15$, $T_c \sim 35\,K$
(Ceramic transition metal oxide)
La_2CuO_4 : parent compound. <u>AF INSULATOR</u>
Tetragonal <u>Layered</u> Perovskite (K_2NiF_4) structure



$LaCuO_4 \equiv LaCuO_3$ (Perovskite) + LaO (Rocksalt) stacked along c-axis

<u>But</u> $La_{2-\delta} Ba_{\delta} NiO_4$ is <u>Not</u> sc (?)

Perovskite $LaCuO_3$



● La^{3+} $a = 3.78\,Å$
● Cu^{2+} $b = a$
○ O^{2-} $c = 13.25\,Å$

Doping by <u>divalent</u> alkaline earth Ba^{2+} replacing <u>trivalent</u> rare-earth La^{3+} creates <u>mobile</u> carriers – 'holes'

INTRODUCTION to HTSC

- $La_{2-\delta}(Ba, Sr)_{\delta} CuO_{4-y}$ (214), $T_c \sim 40K$ ($\delta \sim 0.15$, $y \sim 0$)
- $YBa_2Cu_3O_{7-\delta}$ (123), $T_c \sim 90K$ ($\delta \sim 0$)

. . . .

- $\left\{ \begin{array}{l} Tl_2 Ca - Ba_2 Cu_3 - O_y \\ Bi_2 Ca \; Sr_2 Cu_2 O_y \end{array} \right.$ $T_c \sim 80 - 125K$

$H_{c_1} \gtrsim 10\ Oe$

$H_{c_2} \gtrsim 100T$

compare: $T_c(Hg) \gtrsim 4K$

$T_c(Nb_3Ge) \simeq 23.2K$

$He \sim 4.2K$

$LN_2 \sim 77K$

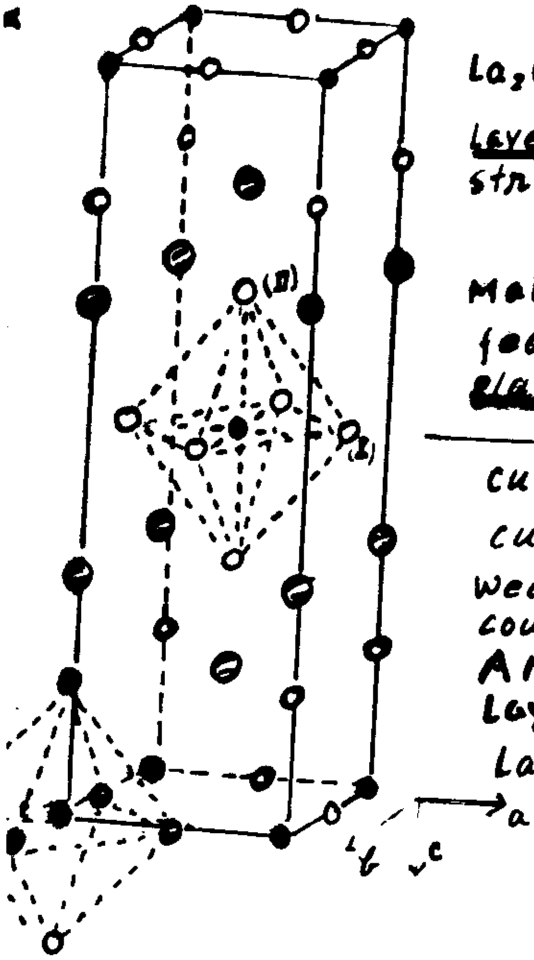
$H_c \sim 10^2\ Oe$

$H_{c_2} \sim 10T$

- 'Chemical' SUPERCONDUCTORS
ceramic oxides, stoichiometry important.

Band Metals
Intermetallics

Also $\left\{ \begin{array}{l} BaPb_{1-x}Bi_xO_3, \ T_c \sim 12K, \ x \sim 0.25 \\ K_{1-x}Ba_xBiO_3, \ T_c \sim 30K, \ x \simeq 0.6 \end{array} \right.$



La_2CuO_4: Tetragonal
Layered Perovskite
structure (K_2NiF_4)

Main Electronic
feature: square
planar CuO_2 layers

Cu-O(I) : 1.9 Å

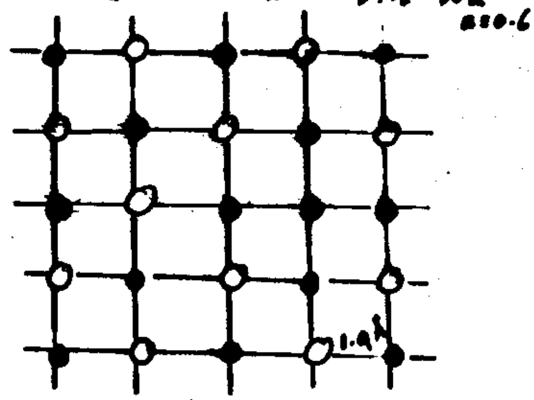
Cu-O(II) : 2.4 Å

Weak inter-layer
coupling

ANISOTROPIC

Layered (low dimensional)

La_2CuO_4 undoped - Insulator
Conductivity gap 2-3 eV.



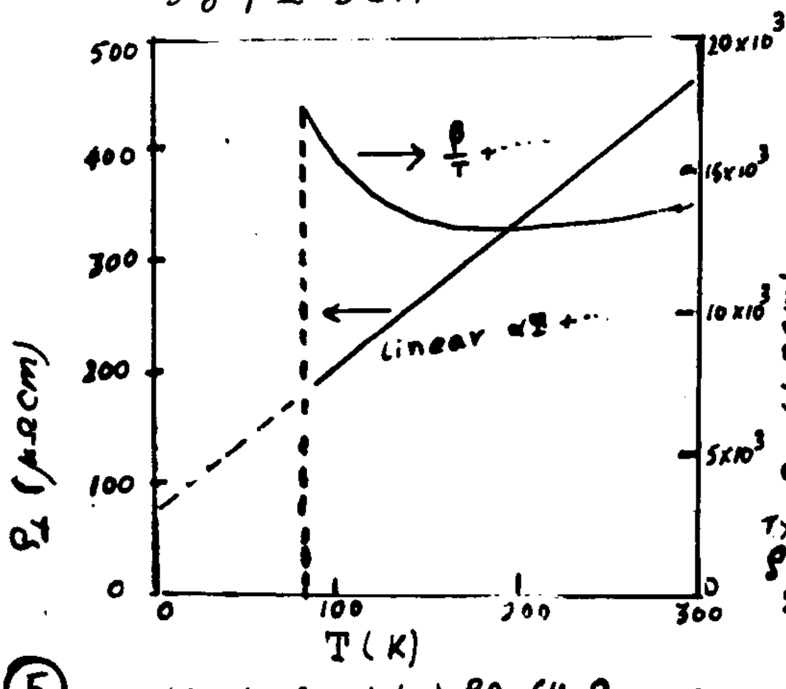
CuO_2 Planes
⊥ c-axis separated
by ~6 Å

● La^{3+} $a = 3.78$ Å

● Cu^{2+} $b = a$

○ O^{2-} $c = 13.25$ Å

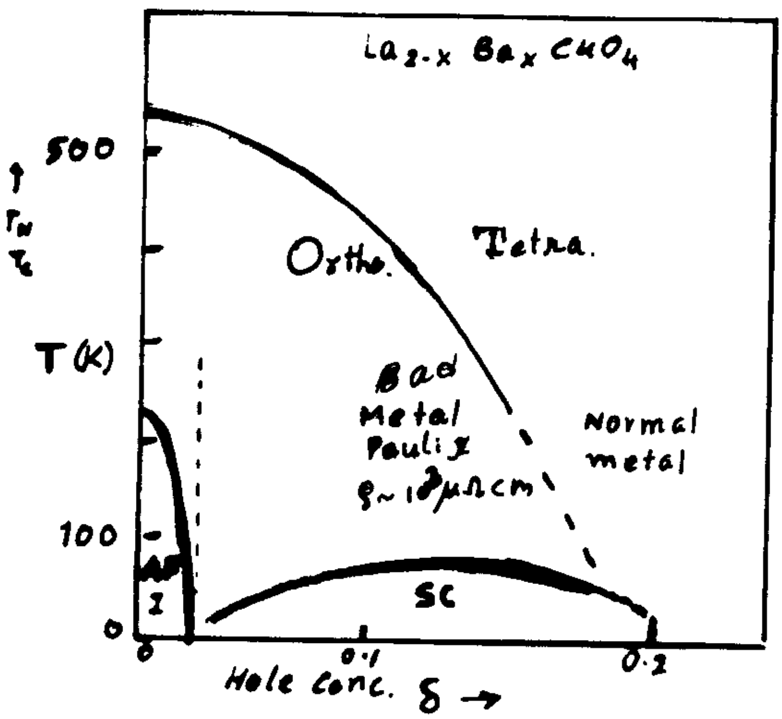
$Cu^{2+} = 3d^9$: half-filled
band should be a
band metal. But
actually an AF ($S=\frac{1}{2}$)
insulator (pure)
same for $YBa_2Cu_3O_{7-\delta}$.



Typically
ρ (metals)
$\lesssim 10\ \mu\frac{\Omega}{cm}$

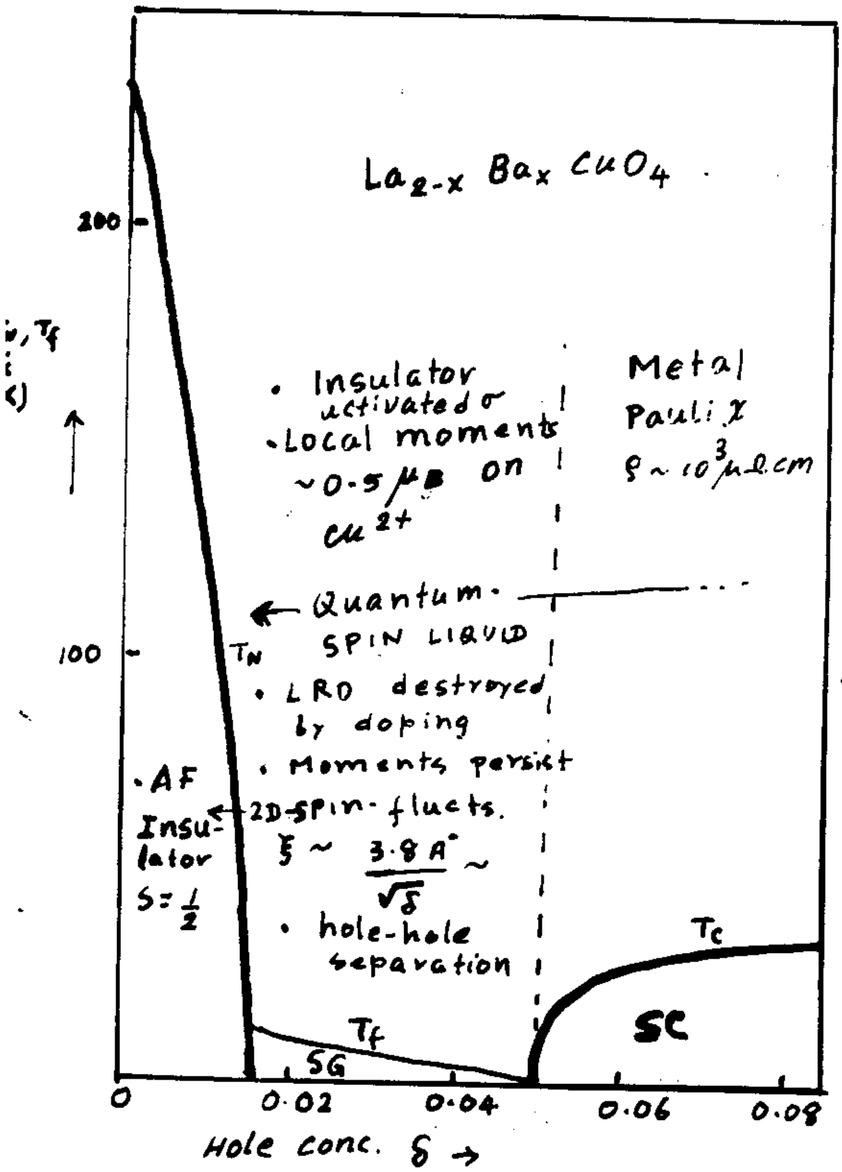
⑤ single Crystal $YBa_2Cu_3O_{7-\delta}$ $\delta \sim 0$

* PHASE DIAGRAM



NEUTRON scattering

- Pure La_2CuO_4 : AF ($T_N \sim 200$.
- $T > T_N$ Cu^{2+}: $S = \frac{1}{2}$, $0.5\mu_B$ Primarily 2D spin-spin correlation $\xi \sim 200$,
- A $T = T_N$ 3D ordering sets
- T/O transition $\sim 550K$
- Both T_N, T (T/O) $\downarrow$ with $\delta \uparrow$
- AF order lost for $\delta > 0.03$ << percolation threshold.
-



- spin-spin corr. length $\xi \downarrow$ to $\sim 10 A^\circ$ as $\delta \uparrow \sim 3\%$ for $T > T_N$
- spins fluctuate rapidly $\tau_{SF} \sim 10^{-14}$ s for $T > T_N$ (totally dynamic $S(q, \omega)$)

AF $\rightarrow$ SPINGLASS $\rightarrow$ SC
insul. insul.
as $\delta \uparrow$

Thus unlike $S \geq 1$ system (e.g. La_2NiO_4, La_2MnO_4) we have truly 2D-Quantum spin Liquid and AF ordering is driven by the third dimensionality

SUMMARY

HTSC: Some observations

* Geometrically - Low (2) dimensional layers
  Weak interlayer coupling
* CRITICALLY - Precursor effects, large fluctuation regime.
* Chemically - Transition Metal Oxide, Mixed chemical valence $Cu^{2+}O^{2-} \rightleftharpoons Cu^{1+}O^{2-}$ (formally)
  Sensitive to doping and O stoichiometry
* Electronically - Highly correlated electrons (large repulsion)
  odd-electron Insulator, doping $\delta \rightarrow$ hole (n_h) type carriers. where are the holes?
  $n_h \propto \delta$ initially. NO Fermi surface? Pauli-like χ.
* Magnetically - $S = \frac{1}{2}$ AF with strong 2D correlations (~200 Å)
  $0.5 \mu_B$ moments on copper. $T_N \downarrow$ rapidly with δ (3%).
  but moments survive → spin Glass → SC.
* Electrically - bad metal $\rho \sim 10^3 \mu\Omega cm$, $d\rho/dT \sim 2 \mu\Omega cm/K$. highly Anisotropic. Linear T dependence for $T_c < T \lesssim 1000K$.
* Isotope Effect - $O^{16} \rightleftharpoons O^{18}$ small effect (214) but none (123)

* Gap Ratio (Tunneling) $\frac{2\Delta}{k_B T_c} \sim 4.5$ (BCS 3.53)

* sp. heat Jump - $\Delta C_p / \gamma T_c \sim 1.2$ (BCS 1.43)
  Also linear sp. heat at low temp.!

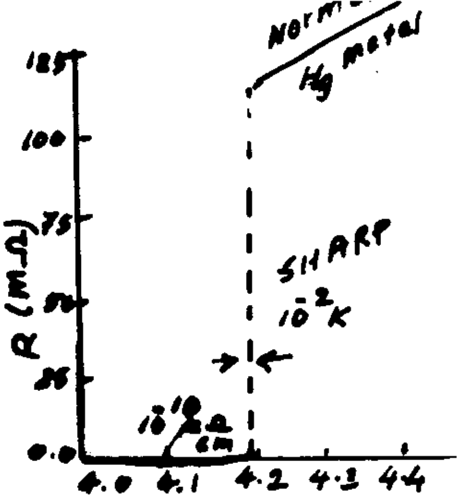
* $T_c \propto \delta$ (for $\delta < 0.2$). optimal doping $\delta \sim 0.15$.

* $\lambda_L \sim 10^3 A^\circ$ (conventional ~ $10^2 A^\circ$) Anisotropic
  obeys BCS temp dependence accurately

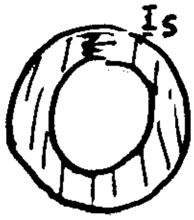
* $\xi \sim 5 A^\circ - 30 Å$ (conventional ~ 10^{-4} cm) Anisotropic

* PAIRING - Strongly indicated
* Type II SC, $H_{c_2} \sim 10^2 T$, $H_{c_1} \lesssim 10^{-2} T$, $\kappa \sim 10^2$

- **DEFINING PROPERTY**
  Perfect conductor
  - Zero dc Resistivity : $\rho_{dc} = 0,\ T \leq T_c$
    $E = \dot{B} = 0 \Rightarrow$ PERSISTENT Current
  - Phonons, defects still there but do not degrade supercurrent
  - Even radiative damping seems absent! $\Rightarrow$ PERSISTENT CURRENT:



RESISTIVE TRANSITION
(Non-equilibrium property).

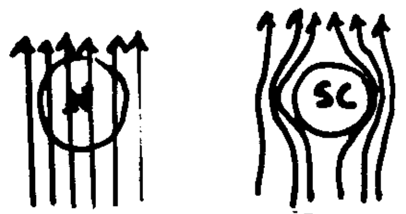


L = geometric Inductance
R = Resistence
$\tau = L/R$ Inductive decay time of persistent current I_s

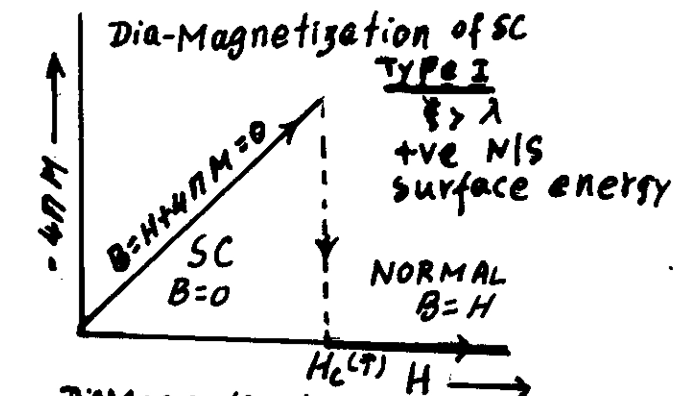
$\tau > 10^7 s, \quad \rho(T<T_c) \leq 10^{-23} \Omega cm$

$\rho_{good\ metal} \sim 10^{-9} \Omega$ cm.

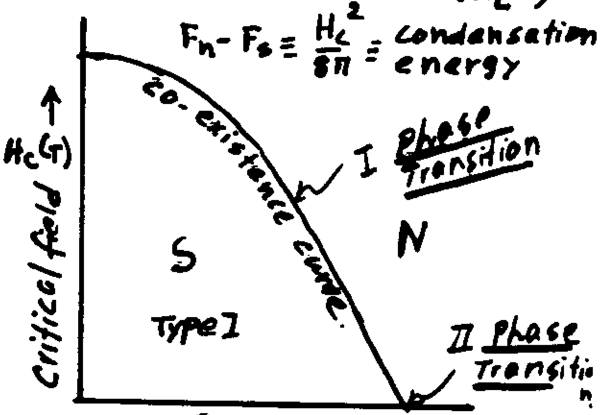
- **DECIDING PROPERTY** $\Rightarrow$ Flux Expulsion (MEISSNER effect)
  Perfect Diamagnetism
  $B = H + 4\pi M = 0 \quad \therefore \chi = \frac{M}{H} = -\frac{1}{4\pi}$
  More than mere shielding ($\dot{B} = 0$)
  Normal metallic $\chi_{dia} \sim -10^{-5}$
  $\Rightarrow$ Single Thermodynamic Equilibrium Phase:

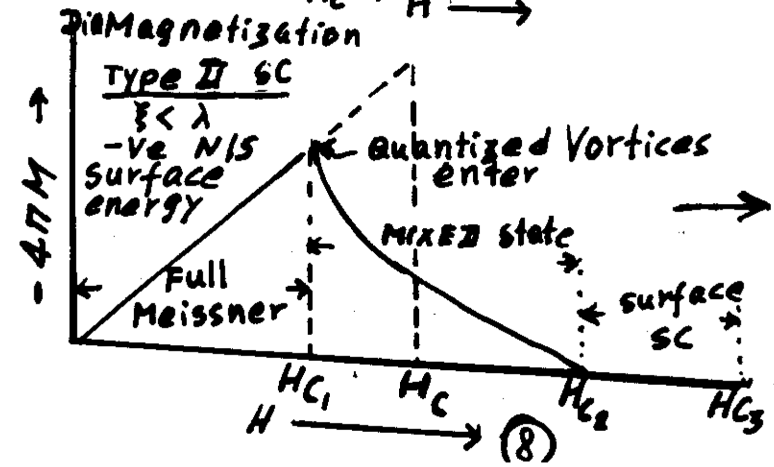


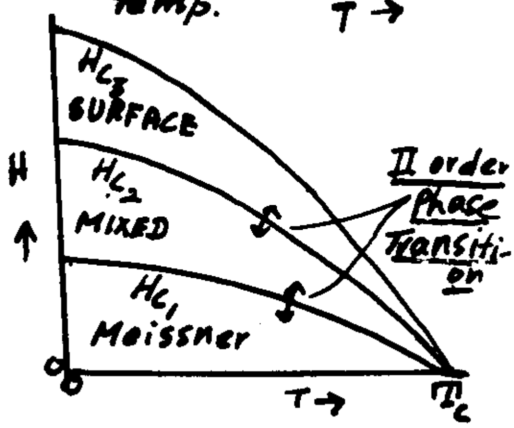
$T > T_c$ $\quad$ $T < T_c$, $H < H_c(T)$

- 

$F_n - F_s = \frac{H_c^2}{8\pi}$ = condensation energy







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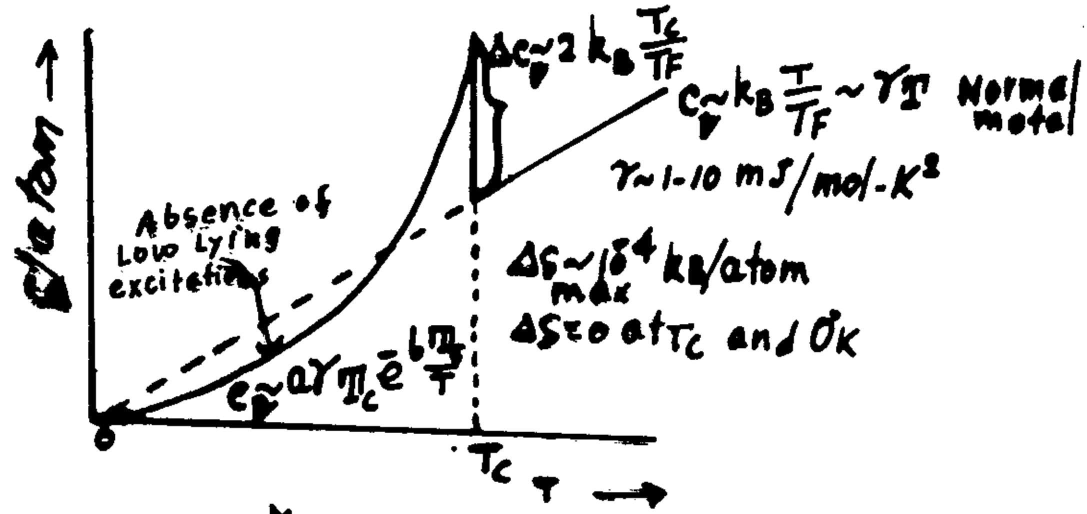
Thermodynamic Nature of SC Phase and II order N/S transition is explicitly demonstrated by sp. heat singularity at T_c (DISCONTINUITY ΔC_v):



⇓

- GINZBURG-LANDAU PHENOMENOLOGICAL DESCRIPTIONS

Treats SC transition as any other II order phase transition a la Landau, e.g. Ferromagnetic transition, λ-transition of ^4He, etc.

- Complex Order Parameter (Two-component):

$$\Psi(\underset{\sim}{r}) = \sqrt{n^*}\, e^{i\theta} \quad ; \quad n^* \begin{cases} = 0, & T > T_c \\ \neq 0, & T < T_c \end{cases}$$

in analogy with magnets (XY-model) where Magnetization $\langle \underset{\sim}{S} \rangle \equiv \underset{\sim}{M} \equiv (M_x, M_y)$ is the order parameter, non-zero in the low-temp. ordered phase.

- Appearance of $\underset{\sim}{M} \neq 0$ at $T < T_c$ amounts to spontaneous symmetry breaking (that is the Hamiltonian was Rotationally Invariant in spin-space, but the state $\underset{\sim}{M} \neq 0$ selects a definite direction (which could be any direction of course). Arbitrarily small external magnetic field will 'solicit' a direction of the macroscopic magnetization.

- The $\Psi(x)$ Order parameter, however, has the nature of quantum mech. wave function: $|\Psi(x)|^2 = n^*$ is the density of supercurrent carriers (pairs) of charge e^* and mass m^*. This combination of Quantum and Thermodynamic aspects makes $\Psi(x)$ different from all other Order parameters.
- Here the Spontaneous symm. broken is the Global Gauge Symmetry – the basic quantum Hamiltonian is invariant for arbitrary global multiplicative phase-factors (the Ray-freedom of quantum mechanics) but $\Psi \neq 0$ in SC state $\Rightarrow$ a definite phase ϕ for the whole sample:
- Ψ is gauge covariant:
- Ψ is single-valued
- Ψ couples to magnetic fields through Vector potential $\underset{\sim}{A}$ in gauge invariant fashion : $B = \nabla \times A$

} Whole electrodynamics of Superconductors follows

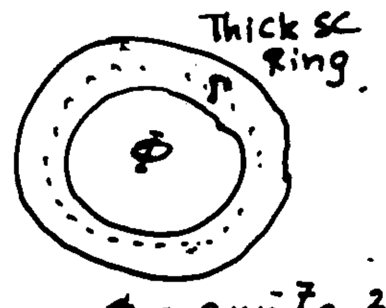
Thus:

$$j_s(x) = \frac{-ie^*\hbar}{2m^*}\left(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\right) - \frac{e^*}{m^*c}\Psi^*\Psi\underset{\sim}{A}$$

$$A \to A + \nabla\chi \Rightarrow \Psi \to \Psi e^{\frac{ie^*}{\hbar c}\chi}$$

Enclosed flux ϕ modifies $\Psi \to$

$\Psi e^{\frac{ie^*}{\hbar c}\oint_\Gamma A\cdot dl}$. But $\oint_\Gamma A\cdot dl = \Phi$



$\therefore$ single-valuedness $\Rightarrow \phi = n\left(\frac{hc}{e^*}\right) = n\Phi_0$

Flux quantization.

$\Phi_0 = 2\times10^{-7}\,\mathrm{G\,cm^2}$

← In General fluxoid quantization

* Rigidity of SC WAVEFUNCTION Ψ_s $\Rightarrow$ LONDON Electrodynamics

MEISSNER- OCHSENFELD EFFECT

($\nabla \cdot A = 0$ London Gauge $A \cdot n = 0$ surface)
Body simply connected

$$\underset{\sim}{j}_s(\underset{\sim}{r}) = \left(\frac{-i e^* \hbar}{2 m^*}\right) \int \cdots \int \sum_i \left(\Psi_s^* \nabla_i \Psi_s - c.c.\right) \delta(\underset{\sim}{r} - \underset{\sim}{r}_i) \cdots d\underset{\sim}{r}_i \cdots - \int \frac{e^{*2}}{m^* c} \sum_i \underset{\sim}{A}(\underset{\sim}{r}_i) \cdot \Psi_s^*(\underset{\sim}{r}_i) \Psi_s(\underset{\sim}{r}_i)\, d\underset{\sim}{r}_i \cdots$$

paramag. (Metals...) distortion of Ψ_s. BUT Rigidity makes it 0

Diamag. (Atoms ...)

(Normal state the two nearly cancel, leaving small Landau diamagnetic $\chi \sim 10^{-5}$)

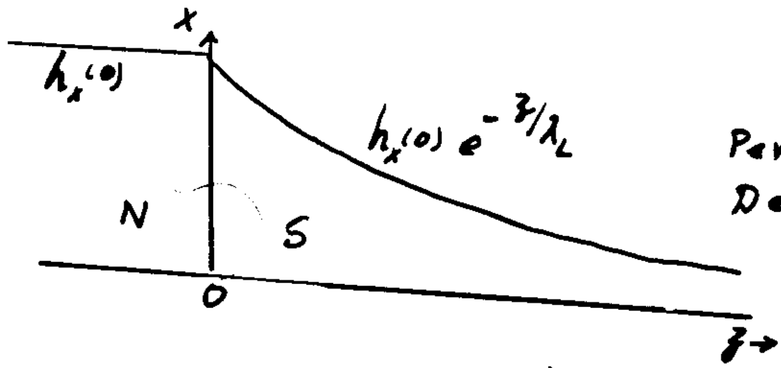
$\therefore$

$$\underset{\sim}{j}_s(r) = \left(\frac{-n_s^* e^{*2}}{m c}\right) \underset{\sim}{A}(\underset{\sim}{r}) \quad \ldots \quad \text{Local relation}$$

$$\underset{\sim}{\nabla} \times \underset{\sim}{h}(\underset{\sim}{r}) = \left(\frac{4\pi}{c}\right) \underset{\sim}{j}_s(\underset{\sim}{r}) \quad \text{and} \quad \underset{\sim}{h}(\underset{\sim}{r}) = \underset{\sim}{\nabla} \times \underset{\sim}{A}$$

$\therefore$

$$\boxed{\nabla^2 \underset{\sim}{h} = \frac{1}{\lambda_L^2} \underset{\sim}{h}, \quad \lambda_L = \frac{c}{\omega_s}, \quad \omega_s^2 = \left(\frac{4\pi n_s^* e^{*2}}{m^*}\right)}$$



Penetration Depth

Note: $e^* = 2e$
$m^* = 2m$ leaves λ_L unchanged
$n_s^* = n_s/2$ pairs

Temp. dependence $\lambda(T)$ comes from n_s^* (Density of superconducting electrons).

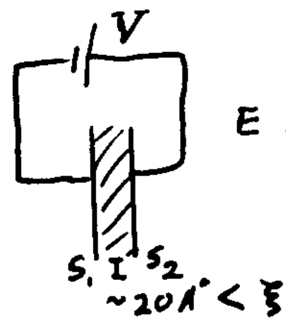
- JUST AS SPIN-ROTATION GLOBAL SYMMETRY FOR F-MAGNET ⇒ conservation of magnetization (order parameter), ~~the~~ global gauge symm. of SC ⇒ conservation of particle number N^*. Thus, ~~the~~ global

- Phase θ and number N^* are conjugate in the same macroscopic sense ~~as~~ Entropy and Temp, volume and pressure etc.:

- $$\hbar \frac{d\theta}{dt} = \left(\frac{\partial E}{\partial N^*}\right) \equiv \mu \quad \text{chemical potential}$$
  $$\hbar \frac{dN^*}{dt} = -\left(\frac{\partial E}{\partial \theta}\right) \qquad E \equiv \langle H \rangle$$
  analogue of $\frac{dx}{dt} = \frac{\partial H}{\partial p}$, $\frac{dp}{dt} = -\frac{\partial H}{\partial x}$ Hamiltons equation

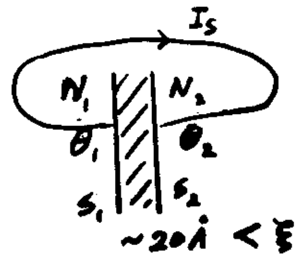
- ⇒ all macroscopic coherence phenomena in Josephson tunnel junctions, weak supercond. & granular metels.

1. AC Josephson effect



$E \equiv e^* V (N_1 - N_2)$

$$\hbar \frac{d}{dt}(\theta_1 - \theta_2) = e^* V$$
$$\therefore \theta_1 - \theta_2 = \left(\frac{e^* V}{\hbar}\right) + \text{const}$$
$$\therefore I_s = I_J \sin\left(\frac{e^* V}{\hbar}\right)$$

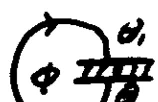


2. DC Josephson effect
   E is periodic function of $\theta_1 - \theta_2$, $E \equiv K \cos(\theta_1 - \theta_2)$

$$\therefore I_s = e^* \frac{dN_1}{dt} \equiv -e^* \frac{dN_2}{dt} = -\frac{e^*}{\hbar} K \frac{d}{d\theta_1} \cos(\theta_1 - \theta_2) \equiv I_J \sin(\theta_1 - \theta_2)$$

↑ critical current

3. Flux periodic current :



$$\theta_1 - \theta_2 = 2\pi \frac{\Phi}{\Phi_0} \qquad \therefore I_s = I_J \sin(2\pi \Phi/\Phi_0)$$

⇒ BASIS of SQUID and Weak-Link devices.

(12) Weak Superconductivity (polycrystalline HTSC)

Dynamical effect Associated With Phase θ (An example):

Dephasing by charging of SC grains

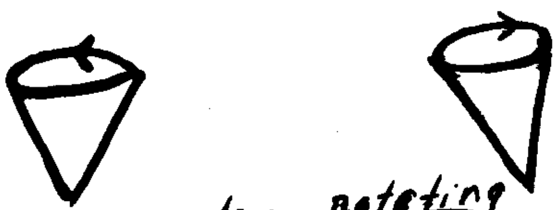
- $\theta_1(t)$ SC Grain I $\qquad$ $\theta_2(t)$ SC Grain II

Q can be due to normal electron (quasi-particle) tunneling

For $R \sim 100$ Å $\Delta\mu \sim 0.1$ eV

$\Delta\mu_1 = -\frac{Q e^*}{4\pi\epsilon_0 R_1}$ $\qquad$ $\Delta\mu_2 = +\frac{Q e^*}{4\pi\epsilon_0 R_2}$

- $\Psi_1 \rightarrow \Psi_1 e^{i\frac{\Delta\mu_1 t}{\hbar}}$ $\qquad$ $\Psi_2 \rightarrow \Psi_2 e^{i\frac{\Delta\mu_2 t}{\hbar}}$



counter rotating phases

- Thus normal (charging current) between small grains can destroy phase coherence

  Important for granular superconductors and Weak superconductors (HTSC with granular structure on sub-micron scale).

- This effect is fundamental to SC of highly localized (fermion) systems $\leftrightarrow$ associated with phase fluctuation number fluctuation.

  Phase coherence requires compressibility of the electron system. Fixing N, (i.e. $\Delta N = 0$ due to incompressibility due to large charging energy, say) makes $\Delta\theta \to \infty$ destroying phase coherence).

GINZBURG-LANDAU PHENOMENOLOGY: FLUCTUATIONS

PRECURSOR EFFECTS

- Ψ- Order Parameter
- Mean-Field Approximation (MFA)
- Fluctuations, Size of Critical Region
  Low dimensions, Layered structures, clean or Dirty limit

- Questions: • Why G-L so Good for Low-T_c SC in MFA
  • Why fluctuations so important for high-T_c SC
  • → observable effects
  → fluctuations as probe.

- Introduce complex scalar (two-component) Order Parameter (local)

$$\Psi(\underset{\sim}{r}) = |\Psi(\underset{\sim}{r})| e^{i\phi}$$

$\langle \Psi \rangle = 0$, $T > T_c$ Normal (disordered) phase

$\neq 0$, $T < T_c$ Super. (ordered) phase

- Construct Helmholtz free-energy functional $F[\Psi] \equiv F_n + \int f_s(\Psi(\underset{\sim}{r}))\, d\underset{\sim}{r}$ that gives statistical weight for any configuration of $\Psi(\underset{\sim}{r})$: e.g.,

$$\langle \Psi(\underset{\sim}{r}) \rangle = \frac{\int e^{-\beta F[\Psi]}\, \Psi(\underset{\sim}{r})\, \mathcal{D}[\Psi(\underset{\sim}{r})]}{\underbrace{Z \equiv \int e^{-\beta F[\Psi(\underset{\sim}{r})]}\, \mathcal{D}[\Psi(\underset{\sim}{r})]}_{\text{Partition function}}}, \quad \beta = \frac{1}{k_B T}.$$

- Note: Functional because $\Psi(\underset{\sim}{r})$ at each point $\underset{\sim}{r}$ can fluctuate as an independent variable ∴ F is a function of infinitely many variables (function of function). $\mathcal{D}[\Psi(\underset{\sim}{r})]$: symbol for the infinite integrations.

- Functional form $F[\Psi(x)]$ determined by General Consideration of

1. Symmetry of underlying Hamiltonian = symm. of high temp. phase $T > T_c$: Both external symm. (translation, rotation) and internal symm. (gauge symm.)

2. Reality : F must be real

3. Analyticity at $\Psi = 0$. Thus for $T \simeq T_c$, when $\Psi(x)$ is small and slow varying F can be Taylor expanded in Ψ and $\nabla\Psi$ with coeff. parametrically dependent on $T - T_c$. Also true for type II sc near H_{c2}, in the dirty limit

- $f_s \equiv$ free energy/volume

$$= \underbrace{a(T)\,|\Psi|^2}_{\text{free}} + \underbrace{\frac{b(T)}{2}|\Psi|^4}_{\text{self-interaction}} + \underbrace{C'|\nabla\Psi|^2}_{\substack{\text{torsional}\\ \text{energy for}\\ \text{cubic symm.}\\ \equiv \text{kinetic}\\ \text{energy}}} + \dots$$

- Introduce magnetic field $\underset{\sim}{h} = \underset{\sim}{\nabla} \times \underset{\sim}{A}$ in gauge-invariant way: i.e. treat Ψ as a wavefunction

$$-i\hbar\nabla \rightarrow -i\hbar\nabla - \frac{e^*}{c}A$$

and add field energy density $= h^2/8\pi$:

$$f_s(h) = a(T)|\Psi|^2 + \frac{b(T)}{2}|\Psi|^4 + C\left|\left(-i\hbar\nabla - \frac{e^*}{c}A\right)\Psi\right|^2 + \frac{h^2}{8\pi}$$

e^* is charge of the basic superfluid carrier (cooper pairs) $= +2e$, $-|e|$ electron charge. If Ψ is normalized $|\Psi| = \sqrt{n_s^*}$, $n_s^* = n_s/2$, then $C = \frac{\hbar^2}{2m^*}$ with $m^* = 2m$.

Note: $e^* = 2e$ is fundamental (for pairing)
$m^* = 2m$, result of normalization
$n^* = n_s/2$, n_s = superfluid density.
<u>Supercond. is the only case where</u>
<u>C is known from first principles.</u>

- F is the correct thermodynamical potential if field (microscopic field $\underset{\sim}{h}$) is produced by permanent magnet ($B = \overline{\underset{\sim}{h}}$, coarse grained). In practice, one controls current in field-coils) and the control field is $\underset{\sim}{H}$ the thermodynamic field. Then, then must use Gibbs potential

$$G = F - \frac{1}{4\pi}\int \underset{\sim}{B}\cdot\underset{\sim}{H}\, d\underset{\sim}{r} \quad \text{(Legendre' Transformation)}$$

- Mean-field GL equations obtained by minimizing G with respect to Ψ & $\underset{\sim}{A}$:

- $a\Psi + b|\Psi|^2\Psi + \frac{1}{2m^*}\left(-i\hbar - \frac{e^*}{c}\right)^2\Psi = 0 \Rightarrow \xi(T) = \left(\frac{\hbar^2}{2m^* a(T)}\right)^{1/2}$

  non-linear <u>Sch. eq. gives spatial</u> Variation of Ψ $\quad n_s^* = -\frac{a(T)}{b(T)}$

- $j = \frac{-ie^*\hbar}{2m^*}\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right) - \frac{e^{*2}}{m^* c}\Psi^*\Psi\underset{\sim}{A} \Rightarrow \lambda(T) = \left(\frac{m^* c^2}{4\pi n_s^* e^{*}}\right.$

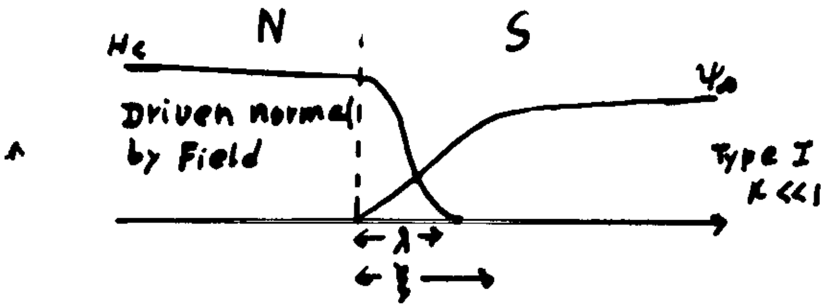
  along with $\underset{\sim}{\nabla}\times\underset{\sim}{h} = \frac{4\pi \underset{\sim}{j}}{c}$, $\underset{\sim}{h} = \nabla\times A$ determines magnetic field.

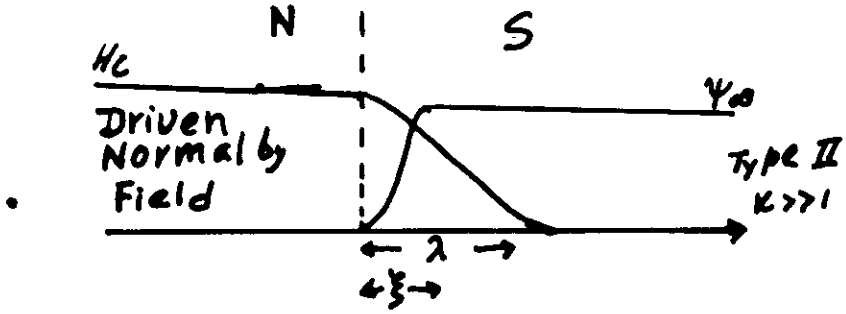
- Boundary conditions: No SC current across boundary.

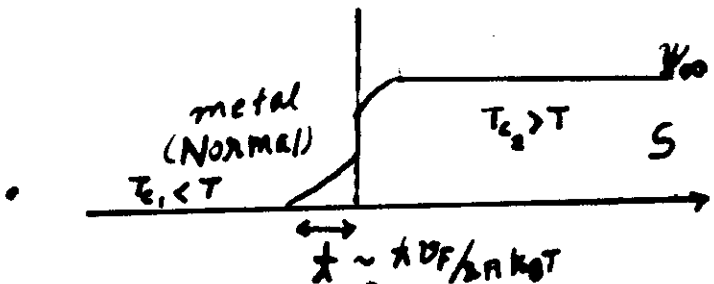
$n\cdot\left(-i\hbar\nabla - \frac{e^*}{c}\underset{\sim}{A}\right)\Psi = 0$ . . . . . for SC|Insulator

$n\cdot\left(-i\hbar\nabla - \frac{e^*}{c}A\right)\Psi = i\lambda\Psi$, $\underset{\sim}{j}\cdot n = 0$ . . . SC|metal

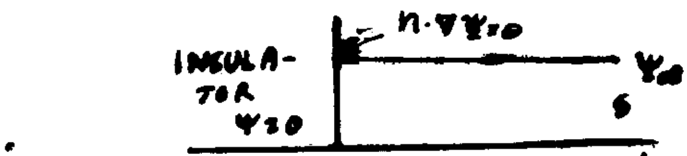
$1/\lambda$ = extrapolation length $\sim \hbar v_F / 2\pi k_B T$ (Proximity effect)







Proximity effect



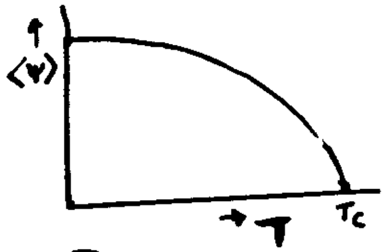
This allow us in small colloidal particles and thin films, size << ξ.

The 'free energy' density

- $f_s = a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*}|\nabla\Psi|^2$

Assume no spatial variation first

- Variationally gives :



$$\Psi_0 \equiv \langle\Psi\rangle = \left(-\frac{a}{b}\right)^{1/2} \begin{array}{l} = 0 \text{ for } T > T_c \\ \neq 0 \quad " \quad T < T_c \end{array}$$

- order-parameter

$$\therefore \; a(T) = a'(T_c)(T - T_c) \equiv a' \cdot T_c \cdot \tau$$

$$\tau = \left|\frac{T - T_c}{T_c}\right|$$

- spatial variation of Ψ:

$$-\xi^2(T)\nabla^2\chi - \chi + \chi^3 = 0, \text{ with } \chi = \frac{\Psi}{\langle\Psi\rangle}$$

- Coherence length

$$\xi(T) = \left(\frac{\hbar^2}{2m^*|a|}\right)^{1/2} = \xi(0)\,\tau^{-1/2}$$

- Condensation density

$$-f_s(\Psi_0) = +\frac{|a|^2}{2b} \equiv \frac{H_c^2}{8\pi} \quad \therefore$$

$H_c \equiv$ Thermo. Critical field $= H_c(0)\cdot\tau$

- $\delta C_v(T) \equiv$ sp. heat discont. $= \frac{a'^2 T_c}{b(T_c)}$

Also,

- $\lambda(T) = \left(\frac{m^* c^2}{4\pi e^{*2}} \cdot \frac{b}{a}\right)^{1/2} = \lambda(0)\,\tau^{-1/2}$

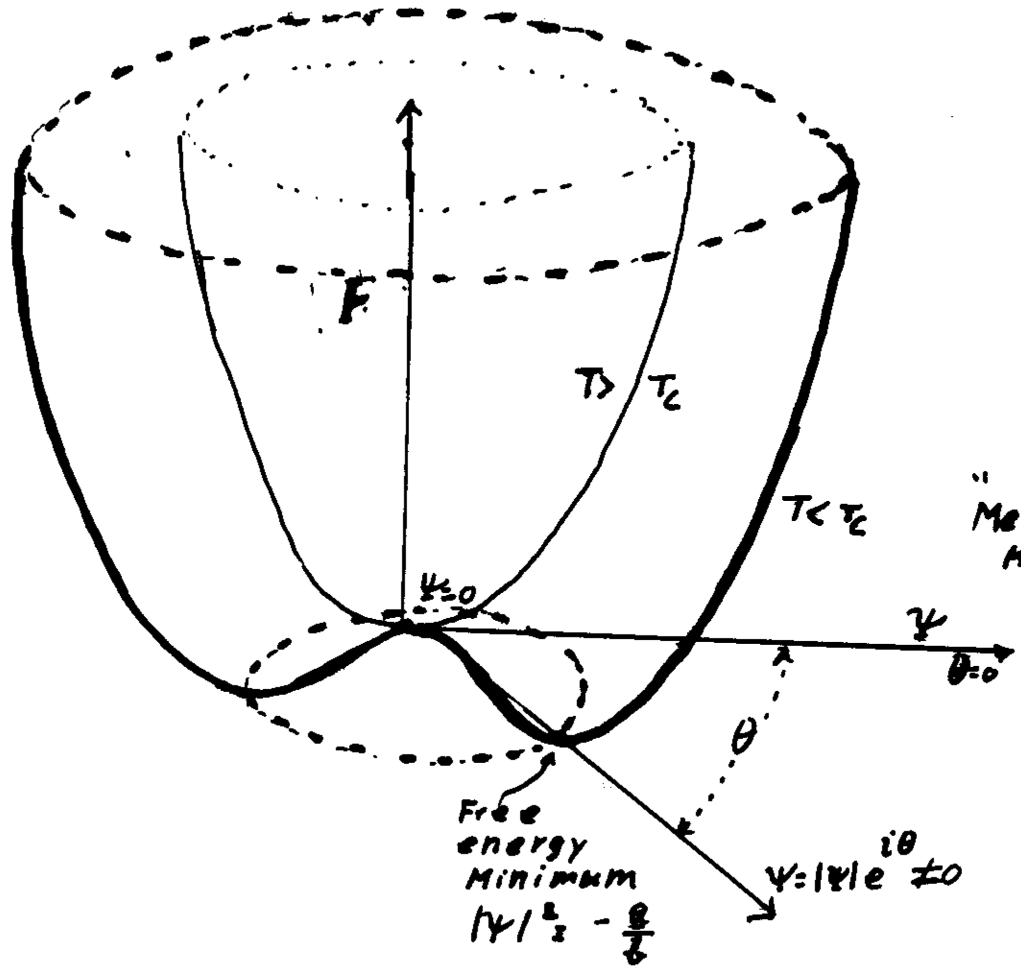
- $\kappa \equiv \frac{\lambda(T)}{\xi(T)} \equiv$ Ginzburg-Landau parameter

$$= \left(\frac{m^* c}{\hbar e^*}\right)\left(\frac{b}{2\pi}\right)^{1/2} \text{ temp. independent.}$$

- $H_{c_2} = \sqrt{2}\kappa H_c = \frac{\Phi_0}{2\pi\xi^2(T)}, \; \Phi_0 = \frac{hc}{2|e|}$

- $H_{c_1} = \frac{1}{\sqrt{2}\kappa} H_c = \frac{\Phi_0}{8\pi\lambda^2(T)}$

SPONTANEOUSLY BROKEN GLOBAL GAUGE (θ) symmetry (SSB)



$f_s = a|\Psi|^2 + \frac{b}{2}|\Psi|^4 + \frac{\hbar^2}{2m^*}|\nabla\Psi|^2$, symm. with respect to global θ.

f_s minimum independent of θ (global)

A global choice of θ $\rightarrow$ spontaneously broken symm.

FLUCTUATIONS OF ORDER-PARAMETER

- $f = a(T)|\Psi|^2 + \frac{b}{2}|\Psi|^4 + c|\nabla\Psi|^2$, $c = \frac{\hbar^2}{2m^*}$

  Now $a(T) \to 0$ as $T \to T_c$.

- $\therefore$ Free-energy cost for fluctuations in Ψ become smaller as $T \to T_c$, and fluctuations grow.

  At $T \lesssim T_c$

- $\langle\Psi\rangle \equiv \Psi_0 = \left(-\frac{a(T)}{b(T)}\right)^{1/2}$

  $\delta\Psi \equiv \Psi - \Psi_0 \equiv$ fluctuation, $\langle\delta\Psi\rangle \equiv 0$

- Must Calculate $\langle|\delta\Psi|^2\rangle$

- $\frac{\langle|\delta\Psi|^2\rangle}{\langle\Psi\rangle^2} \geq 1$ implies break-down of MFA.

- The temperature region associated $\tau^G \equiv \left|\frac{T-T_c}{T_c}\right| \lessdot 1$: Ginzburg Criterion is the critical region where precursor effects of super-cond. fluctuations will be observed. Even for $T \gtrsim T_c$, the system anticipates SC order $\Rightarrow$

- Fluctuation enhanced excess cond.
- " " diamagnetism
- " enhanced (suppressed) thermoelectric power
- " 'critical exponent' modifications etc.

- These effects are highly dependent on
  Dimensionality d (More for Low d & Layered structures)
  Coherence length ξ (more for smaller ξ)
  $\therefore$ pronounced in dirty (amorphous) thin films. WHAT ABOUT High-T_c materials?

- Fourier components :

$$\Psi(\underset{\sim}{r}) = \sum_{\underset{\sim}{k}} \Psi(k) e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}, \quad \Psi(k) = \frac{1}{\Omega}\int_{\Omega} \Psi(\underset{\sim}{r}) e^{+ik\cdot r} dr$$

$$\langle |\Psi(r)|^2 \rangle = \sum_{K,K'} \langle \Psi^*(k)\Psi(k') e^{i(k-k')\cdot r} \rangle \equiv \sum_{K} \langle |\Psi(k)|^2 \rangle$$

- To evaluate $\langle \cdots \rangle$, must write the excess free-energy also in the Fourier space:

$$F - F_0 = \Omega \sum_K (2|a| + ck^2)\, \Psi^*(K)\Psi(K) +$$

+ quartic terms giving mode coupling among fourier components
In MFA this is neglected
($\equiv$ Gaussian approximation)

- Thus different fourier components are decoupled $\Rightarrow$ simple averaging with gaussian weight:

$$\langle \Psi^*(K)\Psi(k) \rangle = \frac{\iint \Psi^*(k)\Psi(k)\, e^{-\beta\sum_K (2|a| + ck^2)\Psi^*(k)\Psi(k)} \prod_k d\Psi^*(k)\, d\Psi(k)}{Z \equiv \text{Normalization}}$$

$$= \frac{1}{\Omega}\left(\frac{k_B T_c / C}{k^2 + \xi^{-2}(T)}\right)$$

$\beta = \frac{1}{k_B T}$, $\xi^2 = \frac{2|a|}{C}$ (21) , $T \gtrsim T_c$

- ∴ Mean-squared fluctuations

$$\langle|\Psi|^2\rangle = \sum_K \langle \Psi^*(K)\Psi(K)\rangle = \sum_K \frac{1}{\Omega}\,\frac{k_B T_c / C}{k^2+\xi^{-2}(T)}$$ } Dimensionality dependent. Also geometry, e.g. films, layered etc.

- Now, k-summation must be cut-off $k \lesssim \xi^{-1}$ (this means only wave-lengths > coherence length contribute. shorter wave lengths absorbed already in the definition of macroscopic (coarse-grained) order parameter Ψ. The latter makes $a(T)$, $b(T)$ etc. temp. dependent).

- $$\langle|\Psi|^2\rangle = \left(\frac{1}{2\pi^2}\right)\left(1-\frac{\pi}{4}\right)\left(\frac{k_B T_c}{C_\cdot}\right)\frac{1}{\xi(T)}$$

The Condition

- $$\frac{\langle|\Psi|^2\rangle}{|\langle\Psi\rangle|^2} \gtrsim 1$$ gives the size of critical region

$$\tau^G \equiv \left|\frac{T-T_c}{T_c}\right|^G = \underbrace{\left(1-\frac{\pi}{4}\right)^2\left(\frac{1}{\xi\pi}\right)^4}_{\approx 10^{-4}\text{-}10^{-3}}\left(\frac{k_B}{\delta C_v\,\xi^3(0)}\right)^2$$

in terms of Sp. heat discont. and zero-temp. coherence length.

- $$= \left(1-\frac{\pi}{4}\right)^2\frac{(3\pi)^2}{2^4}\left(\frac{\left(\frac{k_B T_c}{\varepsilon_F}\right)}{\left(\frac{\delta C_v}{\gamma T_c}\right)\left(\frac{k_B T_c}{E_g}\right)}\right)^2$$

In terms of <u>Critical ratios</u> (experimental)

$E_g = 2\Delta$ = gap, $\xi(0) = \frac{\hbar v_F}{\pi\Delta}$.

v_F = Fermi speed, ε_F = fermi energy

γ = coeff. of linear sp. heat.

- BCS (conventional) Low-T_c SC

It is easy to see that the critical region shrinks beyond experimental resolution and MFA holds right up to T_c practically.
For BCS, clean SC: $\xi_0 = \xi(0) = \hbar v_F / \pi\Delta$

$$\tau_G^{clean} \approx \left(\frac{1}{k_F^2 \xi_0^2}\right) \approx \left(\frac{\Delta}{E_F}\right)^4 \sim 10^{-14} - 10^{-16} \quad \cdots \text{clean limit} \; (k_F \ell_e \gg 1)$$

$\therefore$ Coherence length $\xi_0 \sim 1\mu m$ is too large

- For the dirty limit, $k_F \ell \sim 1$, $\xi^2(0) \to \xi_0 \ell \ll \xi_0^2$

$$\tau^G_{dirty} \approx 10^{-2} \left(\frac{\Delta}{E_F}\right)\left(\frac{1}{k_F \ell}\right)^3$$

$$\sim 10^{-11} \quad , \text{for } k_F \ell_e = 10$$

- For $\ell_e k_F < 1$, we are in the localization (weak) regime and $\tau^G_{loc} \sim 1$, $\therefore \xi_0 \sim \ell \sim$ few Å

- Also, the critical region broadens in low-dimensions. For conventional superconductors only thin a-films could show the fluctuation effects under experimental conditions.

- Now, in High-T_c SC:

Coherence length $\xi_0 \sim$ 10 - 30 Å and also effectively low-dimension (layered) $\therefore$ We expect large fluctuation effects $\because$ generally

$$\tau^G \propto \left(\frac{1}{\xi_0}\right)^6$$

- For weakly coupled sc layers of separation $s \gg \xi_\perp \ll \xi_{\parallel}$:

$$\tau^G \approx \left(\frac{\Delta}{\epsilon_F}\right)^2 \left(\frac{\Delta}{k_B T_c}\right) \left(\frac{s}{\xi(0)_\perp}\right)^2$$

in clean limit in plane.

- Critical region of width $\sim 0.1\,K$ is estimated.

- If treated as an anisotropic sc, replace $\xi(0)$ by $\left(\xi(0)_\perp\, \xi^2_{\parallel}(0)\right)^{1/3}$.

C. J. Lobb Phys Rev. B 36, 3930 (1987)

Aharon Kapitulnik et al. (1987)

In the Critical Region $\tau \equiv \left|\frac{T-T_c}{T_c}\right| < \tau_G$, fluctuations (thermal) of Superconducting Order parameter $\Rightarrow$

1. Modification of mean-field Critical exponents (Universal feature)
2. Precursor effects (non-universal features)
   Enhanced conductivity (Paraconductivity)
   Enhanced diamagnetism
   Enhanced (suppressed) thermoelectric power

Essentially the system anticipates onset of SC Order $\Leftrightarrow$ regions the size of ξ develop transient SC order. The effect is larger the smaller the ξ. Hence its dominance for HTSC with $\xi \sim 10\,\text{Å}$, as also for superfluid ^4He, but not for LTSC with $\xi \sim 10^4\,\text{Å}$.

Thus HTSC provides the unique opportunity of studying these fluctuations in clean bulk samples.
→ Important experimental probe.

Complete treatment requires Time-Dependent-Ginzburg-Landau (TDGL) phenomenology (See M. Cyrot Rep. Prog. Phys. 36, 103 (1973)).

* <u>Pre-cursor</u> effects due to <u>Superconducting fluctuations:</u>

$$\sigma_{dc}(q) = \frac{1}{2k_B T} \int_{-\infty}^{+\infty} dt \, \langle J_q(t) J_q(0) \rangle$$
$$q \to 0$$

with current

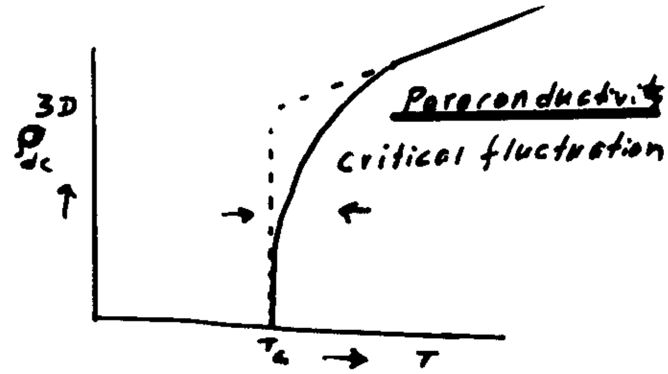
$$J_q(t) = \frac{e^* \hbar}{m} \sum_k (2k+q) \Psi_k^* \Psi_{k+q}$$

$\langle \cdots \rangle$ with respect to the GL-free energy

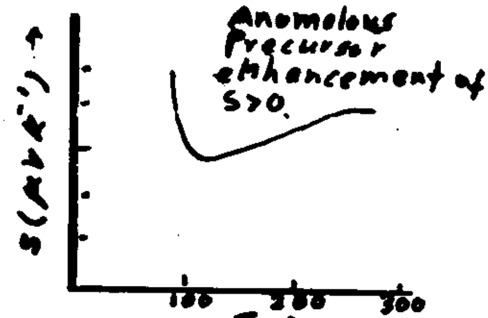
$$\Downarrow$$

$$\sigma_{dc}^{3D} \propto \left(\frac{T_c}{T - T_c} \right)^{1/2}$$

$$\sigma_{dc}^{2D} \propto \left(\frac{T_c}{T - T_c} \right)$$



Similar precursor effects for diamagnetic χ and Thermoelectric power S →



$YBa_2Cu_3O_{7-\delta}$
Mawdsley et al.
Nature <u>328</u>, 233 (1987).

* <u>ANISOTROPY:</u> HTSC are highly anisotropic (weakly coupled layers)

→ anisotropic mass

Kinetic term in GL free energy $\to \frac{1}{2} \sum_{\alpha,\beta} (-i\hbar \nabla_\alpha \Psi)^* \left(\frac{1}{m^*}\right)_{\alpha\beta} (-i\hbar \nabla_\beta \Psi)$

$\Rightarrow$ replace m^* by $(m_\perp^* m_\parallel^{*2})^{1/3}$

It is also possible that one has really <u>2D</u> <u>superconducting planes</u> with <u>weak Josephson Junction coupling</u> (<u>Kosterlitz-Thouless</u> 2D superconducting) This latter view has experimental support from measured paraconductivity in some HTSC.