Superconductivity
Heavy fermions are intermetallic compounds where the strong electronic correlations completely govern the low energy-low temperature properties. For example, the name of "heavy-fermion" has been coined thanks to the very strong renormalization of the effective mass of the quasi particles, by a factor which can be larger than 100. Nevertheless, for the pure compounds, a Fermi liquid picture can still describe the low temperature ground state. Some of these systems also become superconducting, with critical temperatures around 1 Kelvin. The interest of their superconducting state arise from two main question :

- is the pairing mechanism responsible for this state also governed by the strong electronic correlations (instead of the usual electron-phonon interaction) ?
- is the superconducting state of unconventional nature? If yes, what is the form (the symmetry) of the superconducting order parameter. We will try to give a simple overview only of the response brought to the second question. It is more complex than in the case of High-T$_c$, cuprates or Ruthenate compounds due to the fact that these materials have really 3D properties. So we will explain how the different types of possible superconducting order parameters have been classified in this case, and what kind of experimental tests of the theoretical models have yield fruitful responses, together with the actual limitation of our knowledge.
I.- Introduction:

All candidates for unconventional superconductivity are found among strongly correlated systems. One can make a short list of the various systems and of their peculiarities, starting with the oldest one: superfluid $^3$He, which is also the system for which the deepest knowledge of the unconventional superconducting order parameter has been achieved.

**Superfluid $^3$He: $T_c \sim 1$ mK (superfluidity discovered in 1972):**

It is a 3D isotropic system, and the superfluid state has been proved to be of a p-wave” type. This had been anticipated due to the importance of the hard core repulsion, which favors a state where the relative wave function of the Cooper pairs has a node at the origin.

**Heavy fermion systems (discovered in the 80’):**

Examples: CeCu$_2$Si$_2$ (1979), UBe$_{13}$ (1983), UPt$_3$ (1984)... They are 3D anisotropic (tetragonal, cubic, hexagonal) intermetallic systems, where the f electron magnetism has a predominant role in the low temperature properties. The superconducting state, depending on the compound, could be of “d-wave” or “f-wave” type (to be precised later on in the text).

**Organic superconductors:**

They have also been discovered in the same period, with compounds like : (TMTSF)$_2$ClO$_4$, $\kappa$-(BEDT-TTF)$_2$Cu(N(CN)$_2$)$_2$Br ... At high temperature, they have a pronounced 1D or 2D character, and are close to SDW, CDW instabilities. The nature of their superconducting state remains an open question: “p-wave”, “d-wave”, “s-wave”?..., with some recent indications of a p-wave state for the BEDT-TTF compound.

**High-$T_c$ cuprates (starting in 1986...):**

YBa$_2$Cu$_3$O$_7$ ... is the most well known representative of this well known family. They have an orthorhombic or tetragonal crystal structure, with a more or less pronounced to 2D character. For many compounds of this family, there is a microscopic evidence for a “d-wave” state
Ruthenates (1994...):

$\text{Sr}_2\text{RuO}_4$ has a crystal structure very similar to that of the cuprates, with a metallic 2D character. But contrary to the cuprates, its superconducting state could be of a “p-wave” type.

II.- Questions about unconventional superconductivity

Trying to understand an unconventional superconductor usually means trying to answer the two main questions:

1. **Why unconventional ?**

   This question is by far the most difficult, and is connected to the nature of the pairing mechanism. A pairing mechanism which leads to an unconventional superconducting state can arise:
   - either from usual electron-phonon interactions with strong Coulomb repulsion, favoring a higher orbital state (in order to avoid the repulsive potential). This effect is important in strongly correlated systems, due to the short superconducting coherence length ($\xi_0 \sim 10$ to $100$ Å) generally characterizing these systems.
   - or from new mechanisms, involving magnetic excitations, or other purely electronic pairing mechanisms, which by essence favor some peculiar "non s-wave" channel.

2. **How ?**

   This is answered by the knowledge of all symmetries of the order parameter, like for any other second order phase transition. These symmetries are classified:
   - either by the orbital momentum in an isotropic medium like superfluid $^3\text{He}$
   - or by the irreducible representations of the crystal point group in a lattice.
3. **Microscopic: “Unconventional Cooper pairs”**

A microscopic knowledge of an unconventional superconducting state amounts to the determination of the wave function ($\varphi$) of the Cooper pairs. They are themselves controlled by the pairing potential. In a simple model, neglecting retardation and many-body effects, the pairing potential is a function $V(r_1, r_2) = V(r_1 - r_2)$ which has the symmetry of the underlying medium (isotropic for a liquid, or the lattice symmetry in a superconductor). When solving the Cooper (or BCS) problem, the eigenstates of the Hamiltonian can be classified according to its symmetries. What is known from group theory is that each eigenstate of the Hamiltonian belongs to one of the irreducible representations of the symmetry group, and that the eigenstates inside the same irreducible subspace are degenerate. To summarize:

**The symmetries of $V(r)$ control those of $\varphi$ (list of possible I.R.)**
**The form of $V(r)$ controls the choice of the ground state IR**

So in an isotropic medium: $\varphi(k)$ can be chosen among spherical harmonics $Y^l_m(k)$, and the superconductor is said to be "s-wave" if the ground state is proportional to $Y^1_0 = Y_0^0 = 1$, "p-wave" if it is a combination of $Y^l_m$, $l=1$, d-wave if $l=2$... The orbital momentum $l$ characterizes the orbital state of the Cooper pairs (that is the relative wave function of two electrons), NOT the state of a single electron.

In a lattice, the irreducible representations of the crystal point group have to be used instead of the irreducible representations of the rotations group, and the names change accordingly. For example a superconducting state having the full lattice symmetry should be called an $A_{1g}$ state instead of an "s-wave" state.

4. **Order parameter of unconventional superconductors**

From a macroscopic point of view, a superconducting transition is a second order phase transition and it can be characterized by an order parameter.

For conventional superconductors:, this order parameter is a complex function $\varphi(R,T)$. This function is tightly related to the Cooper pair wave function:
− $|\phi(R,T)|^2$ is the local superfluid density (equivalent to the amplitude $|M|$ of the magnetization $M$ in a ferromagnet). It is temperature dependent and may vary slowly in space.

- the phase of $\phi$ is the relative phase of the Cooper pairs (equivalent to the direction of $M$ in a ferromagnet)

The appearance of a well defined phase in the superconducting state is the signature of the symmetry broken by any superconducting or superfluid state, the so-called "gauge" symmetry. Such a fact is possible only because the ground state of a superconductor is a linear combination of states of different particle numbers. In a conventional superconductor, the gauge symmetry is the only broken symmetry.

By definition, an unconventional superconductor is one that breaks not only gauge symmetry, but also one of the following:

− either parity (singlet/triplet or even/odd)
− or time reversal symmetry
− or a symmetry of the crystal point group

The order parameter of an unconventional superconductor has to give account of these additional broken symmetries. For an even parity (<> singlet) superconductor, instead of a unique function $\phi(R,T)$, the order parameter may be now be a linear combination of various basis functions $f_i(k)$, which depend on an internal degree of freedom: a wave-vector on the Fermi surface. The case of a conventional superconductor is one for which there is only one function $f_i(k)$, equal to 1 or having the full lattice symmetry. More generally, the order parameter is now written:

$$\Psi (P,T,\kappa) = \sum_{\kappa,\kappa'} \phi_{\kappa,\kappa'} \phi_{\kappa,\kappa'} (P,T) = \sum_i \phi_i (P,T) \phi_i (\kappa)$$

the required number of $f_i(k)$ is equal to the dimension of the IR ($2l+1$ for a superconductor with Cooper pairs of orbital momentum $l$ for example). In a lattice, because the number of symmetries is much lower than in an isotopic medium, the dimensions of the IR is small (there are less symmetry induced degeneracies):

maximum dimension = 3 for a cubic lattice,
2 for a 3D tetragonal or hexagonal lattice,
1 only for a 2D square or rectangular lattice...
For temperatures lower than $T_c$, the precise combination of $f_i(k)$ determines all the symmetries preserved by the O.P. (the new reduced symmetry group of the superconducting state).

One important fact about these additional broken symmetries is that they might enforce nodes of the order parameter for some directions of $k$, due to a change of sign under reflections, rotations... The microscopic models for the superconducting state show that these nodes of the order parameter will enforce the same nodes of the excitation gap: so the symmetry analysis may not only reveal degeneracies of the order parameter which can give rise to multiple transitions, but also nodes of the excitation gap which have direct consequences on the excitation spectrum, influencing the thermodynamic and transport properties in the superconducting state. An examination of the case of the High-$T_c$ cuprates may help to clarify this point.

V.- Order parameters for High-$T_c$

<table>
<thead>
<tr>
<th>$R_{\pi/2}$</th>
<th>$I_{\pi/4}$</th>
<th>name</th>
<th>I.R.</th>
<th>$f(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>x</td>
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<td>$s$</td>
<td>$A_{1g}$</td>
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<tr>
<td>-</td>
<td>x</td>
<td>-</td>
<td>$d_{x^2-y^2}$</td>
<td>$B_{2g}$</td>
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<tr>
<td>-</td>
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<td>x</td>
<td>$d_{xy}$</td>
<td>$B_{2g}$</td>
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<tr>
<td>x</td>
<td>-</td>
<td>-</td>
<td>$s^*$</td>
<td>$A_{2g}$</td>
</tr>
</tbody>
</table>
Let us assume a simple tetragonal symmetry in a 2D system. It is then easy to enumerate all possible point group symmetries (the symmetries of the square). There are only 4 one-dimensional irreducible representation for even-parity states, classified by the 3 symmetry operations of the square (2 are enough): see figure below.

"d" states break rotational symmetry.
The \(d_{x^2-y^2}\) state seems to be the "good one" (now widely accepted) for YBCO, BSCCO...

The \(d_{x^2-y^2}\) order parameter (drawn in green), has nodes enforced by the change of sign imposed by the breaking of symmetry under reflection with respect to the diagonals.

1. **Order parameters for the Heavy fermion UPt₃**

Being 3D systems, the heavy fermion superconductors have more complicated order parameters. For UPt₃, a 3D hexagonal system, theorist have established that there were;
- 4 1-dimensional IR (\(A_1, A_2, B_1, B_2\))
- 2 2-dimensional IR (\(E_1, E_2\))

Experimentally, the study of UPt₃ has been guided by the discovery of its complex superconducting phase diagram, which displays several different superconducting phases, separated by well marked second order phase transitions.
2. Phase diagram & symmetries

The lines of the phase diagram of UPt$_3$ correspond to phase transitions observed in all thermodynamic or transport measurements. At these transitions, only the superconducting properties change. This suggests:

– that the transitions occur between superconducting states of different symmetries.

– that one should look for scenarios based on the classification of possible order parameters based on the irreducible representations of the hexagonal group.

Essentially all theoretical scenarios involve 2 different basis functions $f_A(k)$ and $f_B(k)$ for the A and C phase, and a mixture of the two for the B phase. $f_A(k)$ and $f_B(k)$ can be:

– either basis functions of two different irreducible representations

– or the basis functions of a 2D IR

At present, the most "popular" $E_{2u}$ model is of the last kind, with a choice for the functions $f_A(k)$ and $f_B(k)$:

$$f_A(k) = k_z (k_x^2 - k_y^2), \quad f_B(k) = k_z k_x k_y$$

The next figures summarize the behavior of the order parameter and of its components in the H-T phase diagram and as a function of temperature in zero applied field respectively. The figure above shows, for each phase, the gap structure with the various symmetry enforced nodes.
3. Questions & answers for UPt₃

The main questions that one would like to answer for UPt₃ are:
• An identification of the order parameter in each phase (A,B,C), which can be decomposed by the physical properties which can be tested:
  - the parity of the order parameter (even/odd, singlet/triplet)
  - the position of the nodes of the gap
  - eventually, the complete symmetry of each state (fᵢ(κ)…)
• What are the origin of the A→B and B→C transitions:
  - accidental quasi degeneracy of 2 IR?
  - 2D IR with a weak symmetry breaking field: magnetism, defects…?
  - a change in the vortex (lattice) structure (B→C)?

Some of these questions were already partly answered, mainly compatible with the E₂ᵤ scenario:
  – the parity would be odd. This has been deduced from the anisotropic Pauli limitation of Hc₂ (Choi93, Shivaram 86), and from the absence of a large change of the Knight shift below Tc (Tou 96-98)
  – nodal structure: it would be hybrid in the B phase, with at least nodes along the c-axis, and in the basal plane. This was inferred from transport measurements probing the gap anisotropy: λ(T) (Broholm90), κ(T) (Behnia90, Luchier94-96, Suderow95-97), ultrasound (Adenwalla90, Elleman96).
  – symmetries: the experimental results on the gap structure and on the parity are consistent with an E₂ᵤ scenario (at least in the A and B phases) for κ and ultrasound (Graf 99)
  – origin of the various transitions: there is a support for a coupling to the weak magnetic order (appearing below 5K) but with still many unknowns:

4. Phase diagram & AF order

In heavy-fermion U-based superconductors, an antiferromagnetic (AF) order often coexist with superconductivity. In UPt₃, a short range magnetic order, which might also be only dynamical, is observed by neutron scattering below Tₙ ~5K. The ordered moment is very tiny, of about 0.01μₜ only, and it coexists with the superconducting state. In the E₂ᵤ model, a coupling between this magnetic ordering (which induces an orthorhombic deformation of
the hexagonal lattice structure) and the superconducting order parameter is supposed to lift the degeneracy between the two basis function $f_A(k)$ and $f_B(k)$ and be responsible for the $A \rightarrow B$ transition (Mineev, Sauls...).

Experimental evidence for such a coupling is given by the correlations between the splitting of the double transition and the amplitude of the ordered moment, measured by neutron scattering:

- pressure studies (Trappmann 91, Hayden 92) show a decrease of $T_c$ and $M$ with pressure.
- doping studies (Keizer 99) show an increase of $\Delta T_c$ and $M$ with increasing Pd concentration.

(figure from Keizer et al, cond. mat. 9903333)

5. Parity of the order parameter

NMR Knight-shift measurements are a key tool to probe the parity of the order parameter. Indeed, they are insensitive to the large diamagnetic jump of the electronic susceptibility at $T_c$ (which comes from surface currents), and they probe the Pauli susceptibility of the conduction electron at the nucleus site, inside the bulk sample. Odd parity states are characterized by a triplet state of the spin of the Cooper pairs, so that the occurrence of superconductivity changes little the Pauli susceptibility, and therefore the Knight shift.

This has been widely used for the various possible unconventional superconductors, giving as a result that:
– superfluid $^3$He has an odd (triplet) state, with no changes of the Knight shift in the A phase.
– the high-$T_c$ cuprates are even parity (singlet) superconductors, with a pronounced change of the Knight shift below $T_c$.
– for heavy fermions, the experiments were more difficult due to pair breaking, surface effect..., which become even more relevant when the samples are crashed into powders (for a good penetration of the radio frequency field). It could nevertheless be established that:
  UPd$_2$Al$_3$ is an even parity superconductor.
  UPt$_3$ is an odd parity superconductor. On this compound, the latest experiments have been performed on single crystals (Tou et al 96-98) on single crystals (see figure below).

(figure from Tou et al., PRL 77 (1996) 1374)

6. **Nodal structure of UPt$_3$: thermodynamic measurements**

We have already mentioned that nodes of the gap ($\Delta$) change the excitation spectrum. As a matter of fact, a characteristic feature of conventional superconductors is a vanishing density of states at low temperature, from the Fermi level up to excitations of energy. This is changed when the gap has nodes on the Fermi surface, because they produce a finite energy dependent density of states ($\rho_d$). This effect is easily observed on all thermal properties.
Indeed, the number \( N_{th} \) of thermal excitations varies roughly like \( \rho_d(E=k_B T) \sim k_B T \) for \( T/T_c <<1 \). For a conventional superconductor, \( N_{th} \) vanish like \( e^{(-\Delta/k_B T)} \), whereas it is proportional to \( T^2 \) for line of nodes of the gap, and to \( T^3 \) for point nodes of the gap.

This implies that in an unconventional superconductor, thermal properties (\( C_p, \kappa, \lambda, T_1 \ldots \)) have power laws behaviors at low temperature (typically \( T/T_c<0.3 \)).

Heavy fermions are a very good case to probe the gap nodes with low temperature thermodynamic or transport measurements because a Fermi liquid regime is generally well established at \( T_c \) (as opposed to High-\( T_c \) compounds), they are characterized in the normal state by a huge electronic density of states (strong mass renormalization of the electrons), and \( T_c \) is low, meaning that the phonons. Will have little contributions to these properties.

1) Specific heat of \( \text{UPt}_3 \)

The specific heat is one of the simplest thermodynamic quantities. In \( \text{UPt}_3 \) it is completely governed by the electronic contribution below 1 K (\( T_c=0.56\text{K} \)) and it has provided with a direct interpretation of raw data two important pieces of information:

– there is a double transition in zero field (Fisher 89), which can be followed under magnetic field (Hasselbach 89) revealing the A->B line of the phase diagram.

– it has a \( T^2 \) behavior at low temperature (\( 0.1<T<0.3\text{K} \)), characteristic of the presence of at least a line of nodes of the gap, possibly due to additional broken symmetry ?
These two facts already point toward an unconventional superconducting state. But specific heat also has its limitations: in particular, there is a low T anomaly (below 0.1K), which is not related to superconductivity, and might be a precursor of a true AF order? Moreover, it cannot probe gap anisotropy, so that one needs other probe of the low T behavior.

VI.- Transport properties

1. Impurity effects

Transport properties do offer some advantages at low temperature over specific heat, because they can be directional, probing preferentially excitations with wave-vector $k//\text{current}$, and they are also not sensitive to non itinerant (local) excitations like hyperfine contributions, paramagnetic impurities... They have the draw-back of including scattering effects on impurities or defects, which have to be studied in detail.

For $s$-wave superconductors, normal impurities (with no chemical pressure effects) have no effects on $T_c$, $\rho_d$, ... and only magnetic impurities have subtle pair-breaking effects:

- in the Born approximation (Abrikosov-Gor'kov theory, valid for small impurity phase shifts), impurity effects are described by only one parameter (like the scattering time). A strong drop of $T_c$ is predicted, and eventually, for large enough concentrations, a gapless state appears before $T_c$ vanishes (see the first graph of the figure below).

- for Kondo impurities (strong phase shift), 2 independent parameters are needed to describe the impurities: their concentration and their phase shift ($\delta\sim\pi/2$ for $T_K\sim T_c$). In such a case, bound states are induced in the gap, spatially localized on the impurity sites. Their position in energy is controlled by the phase shift: close to the gap edge for $\delta\sim0$ (one recovers the AG result), close to the Fermi level for resonant scattering ($\delta\sim\pi/2$): graph in the middle of the figure below.

For unconventional superconductor ($<\Delta_k>_\text{FS}=0$), any kind of impurities have pair-breaking effects. Moreover, in strongly correlated systems, impurities are often in the resonant scattering limit. So one has results similar to those of Kondo impurities in conventional superconductors, except that the bound states are now only virtual bound states due to their coupling with the finite density of states in case of gap nodes (last graph of the figure below).
The 2 main features to remember are that in heavy fermion (or high-T\textsubscript{c} cuprates):

- impurities are characterized by a phase shift δ \sim \pi/2 (Pethick and Pines 86)
- the appearance of virtual bound states means that the scattering time \( \tau \) has a strong energy dependence.

2. **Thermal conductivity in UPt\textsubscript{3}: a directional probe**

The thermal conductivity is a good probe of thermal excitations in the superconducting state. Simple kinetic arguments yield that \( \kappa(T) \sim 1/3 \ C_V \ \nu_F^2 \tau \). Also this formula is too simple in the superconducting state, it gives physical intuition on the behavior of \( \kappa(T) \):

- **in the normal state**, it is inversely proportional to the resistivity (Wiedeman-Franz law): \( \kappa/T \sim L_0/(\rho_0 + A T^2) \)
- in the superconducting state:
  - at low \( T/T_c \), it probes the gap close to the nodes
  - it is directional directional, sensitive to excitations with wave-vector \( k \) in the direction of the heat current \( J_0 \).
  - it is sensitive to scattering time (\( \tau \)), and in heavy-fermion, impurities are in the resonant scattering limit, close to the unitary limit (\( \delta \sim \pi/2 \)).

Experimental results:

The Wiedeman-Franz law is well obeyed in UPt\textsubscript{3} below 1K, even if e\textsuperscript{-}-e\textsuperscript{-} inelastic collision are still very important at \( T_c \). They become negligible for \( T/T_c \ll 1 \). The phonon contribution also remains negligible in the whole temperature range below \( T_c \). So like for the specific heat, it is possible to give...
a direct interpretation of the raw data at low T, in terms of purely electronic contributions.

The results (Suderow 96-98) probe the resonant scattering hypothesis and the isotropy of the scattering. At low T (below Tc/7), a T^3 power law is observed both for J_Q//b and J_Q//c, indicating the presence of nodes along the c axis and in the basal plane.

A slight change of regime is also observed below 30mK, which could be due to the contribution of the band of impurity induced bound states, expected for an order parameter having a vanishing average on the Fermi surface (<Ψ>FS = 0) and resonant impurity scattering (δ~π/2).

Quantitative comparison with theory indicates that the low T-behavior is consistent with an E_{1g} or E_{2u} scenario (Graff et al., JLTP 114 (1999) 257). Impurity effects are also prediction of a "universal behavior", meaning that the residual κ/T term induced by the impurity band would be independent of impurity concentration (Graf 96) has failed, and may indicate that impurity effects at finite concentrations are not yet so well understood (irradiation studies, (Suderow 99)).

VII.- Conclusion

Unconventional superconductivity in heavy fermion systems has mainly probed by macroscopic measurements. In UPt$_3$, it has been demonstrated by a combination of several properties, the most remarkable being the discovery of the phase diagram, an evidence for symmetry changes of the superconducting order parameter. The (odd) parity of the order parameter has been demonstrated by NMR and $H_{c2}$ measurements. The nodal structure of the gap has been revealed by transport properties, which also probed phase sensitive impurity effects. The future belongs to microscopic measurements of the gap. Up to now, it could only be measured by point contact spectroscopy (Goll 93-de Wilde 94), revealing weak Andreev reflection. But recently, planar Nb-UPt$_3$ junctions displayed Josephson coupling (Sumiyama 98), as demonstrated by the observation of Shapiro steps, a significant progress toward clean tunnel spectroscopy.

VIII.- References:

1. **Symmetries and High-T$_c$ cuprates:**

2. **Symmetries and Heavy-Fermions:**
   - Review on Heavy-Fermions:

3. **Unconventional superconductivity in superfluid $^3$He**
   - Book (recent and excellent !) on unconventional superconductivity
   - Introduction to Unconventional superconductivity, V. Mineev and K. Samokhin, Gordon and Breach Science publishers

4. **Impurity effects**
Imaging unconventional vortices with a Scanning Squid Microscope

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Scanning SQUID microscopes can image magnetic fields with a sensitivity of a few tenths of a microgauss, at a spatial resolution of a few microns. This paper briefly describes these instruments, and then discusses two applications: 1) The first observation of magnetic vortices with half of the superconducting quantum of flux, in specially designed tricrystal samples of the high critical temperature cuprate superconductors. The presence of these vortices is the best evidence to date for unconventional pairing symmetry in these superconductors. Measurements of the temperature dependence of the half-flux quantum effect in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ indicates that $d$-wave pairing predominates, with little if any imaginary component, at all temperatures from 0.5K through $T_c \sim 90K$. 2) Measurement of the magnetic penetration depth perpendicular to the planes in layered superconductors, by imaging vortices emerging parallel to the layers from single crystals of these materials. These measurements show that the inter-layer tunneling model for the mechanism of superconductivity in these materials cannot supply enough condensation energy to account for the high critical temperatures observed in several layered superconductors.
This paper is intended as an introduction to studies of unconventional vortices with the scanning SQUID microscope, with references to further reading. The general field of scanning SQUID microscopy has been reviewed recently in Reference 1. Briefly, a Superconducting Quantum Interference Device (SQUID) is a superconducting ring that is interrupted by one or more Josephson weak links. The d.c. SQUID, which is used most often for scanning magnetic microscopy applications, has two weak links. The dependence of the current of superconducting Cooper pairs $I_c$ through the weak link on the quantum mechanical phase difference $\phi$ across the link ($I_c=I_0\sin(\phi)$), when combined with the relationship between $\phi$ and the vector potential $\vec{A}$ threading the ring, leads to a modulation of $I_c$ (the maximum amount of current that can be driven through the SQUID before a voltage develops) with the total magnetic flux threading through the ring. The period of this modulation is $\Phi_0 = h/2e = 2.07 \times 10^{-15} \text{Wb}$, the superconducting flux quantum.[2, 3] Present day low-$T_c$ SQUIDs have effective magnetic flux noises of about $10^{-6}\Phi_0/H z^{1/2}$, making them the world's most sensitive magnetic field sensors (at least for pickup areas greater than $\sim 1 \mu m^2$). A SQUID microscope scans a sample relative to a specially designed SQUID to image the magnetic fields above the sample.

Although the scanning SQUID microscope has been used in a number of fields, including non-destructive evaluation, biomagnetism, and corrosion science,[1] the most striking applications have been to the study of unconventional superconductors. Although the high-critical temperature cuprate superconductors were discovered almost 14 years ago,[4] there is still no agreement on the mechanism for superconductivity in these materials. However, significant progress has been made in one area: the symmetry of the pairing. It is well known that conventional superconductivity comes about by the formation of (Cooper) pairs of charge carriers with opposite momentum and spin, mediated by interactions of the carriers with lattice vibrations. In conventional superconductors, the pairing wavefunctions are nearly isotropic.[5] There is now substantial evidence from a number of experimental techniques that the pairing in the cuprates is highly anisotropic.[6] Further, phase sensitive measurements [7]-[12] have shown that there are sign changes in the pairing wavefunction, consistent with $d_{x^2-y^2}$ pairing symmetry.
These tests sense this sign change by tunneling Cooper pairs into different crystalline orientations of the high-\(T_c\) cuprates, either from conventional \([7, 8, 11, 12]\) superconductors or from other high-\(T_c\) superconductors \([9, 10]\). Phase differences in the pairing wavefunction phases are detected either by measuring a modulation of the total supercurrent through the device as a function of magnetic field,\([7, 8, 10, 11, 12]\) or by sensing spontaneously generated magnetic fields.\([9]\) These spontaneously generated fields arise from supercurrents resulting from a relaxation of a high energy state built into the sample by taking advantage of the sign changes in the pairing wavefunction.\([13, 14, 15]\) An example of such a frustrated geometry is shown in Figure 1(a). A (001) oriented SiTiO₃ substrate is formed from three crystals to make three \(0^\circ/30^\circ\) misorientation grain boundaries meeting at a central point. The high-\(T_c\) cuprate superconductors grow epitaxially on such a substrate, forming a thin-film tricrystal with grain boundaries with the same geometry. It is well known that such grain boundaries are Josephson weak links.\([16]\) If the cuprate is a \(d_{x^2-y^2}\) superconductor, and if the pairing wavefunctions are aligned with the crystalline axes (as indicated by the polar plots in Figure 1(a)), then the central point must have a sign change in the normal component of the wave-function across one of the grain boundaries. This sign change costs Josephson coupling energy, which is relaxed by generating a supercurrent around the tricrystal point. Assume for the moment that the pairing wavefunction has no imaginary component (time-reversal symmetry invariance is satisfied). Then if the supercurrent around the tricrystal point is confined to a ring, and if \(L_L/\Phi_0 \gg 1\), where \(L\) is the inductance of the ring, and \(I_c\) is the critical current of the ring, then the total flux threading the ring will be a half-integer multiple of the superconducting flux quantum, \(\Phi = (n + 1/2)\Phi_0\), \(n\) an integer.\([9]\) If the superconductor is not patterned around the tricrystal point, the frustration is relaxed by generated a Josephson vortex with \(\Phi_0/2\) total flux at the tricrystal point.\([17]\) The half-integer flux quantum effect has been observed in optimally doped YBa₂Cu₃O₇₋\(\delta\) (YBCO),\([9]\) Tl₂Ba₂CuO₆+\(\delta\) (Tl-2201),\([18]\) Bi₂Sr₂CaCu₂O₈+\(\delta\) (BSCCO),\([19]\) and GdBa₂Cu₃O₇₋\(\delta\) (GBCO).\([20]\) This indicates that these optimally hole-doped cuprates have predominantly \(d\)-wave pairing symmetry.

If there is an imaginary component to the pairing wavefunction,
it is expected that the total flux at the tricrystal point will be slightly different from $\Phi_0/2$, roughly in proportion to the relative size of the imaginary component. Careful measurements[21, 11] have shown that the imaginary component in YBCO is less than a few percent of the total wavefunction amplitude at low temperatures. This not only implies that there is little time reversal symmetry breaking in the bulk of these superconductors, but also, since these geometries include several Josephson weak links, that there is little if any imaginary component to the wave function induced by interactions at the surfaces of the superconductors.

However, a number of questions remain. Although there is evidence that the $s$-wave component in optimally doped BSCCO[22, 19] and Tl-2201[23] is insignificant compared with the $d$-wave component, it is believed that YBCO may have an appreciable $s$-wave component[12]. Further, there is evidence that the electron-doped cuprate superconductors may have $s$-symmetry,[24] and there have been reports of a change in gap anisotropy with temperature[25] and doping,[26] and the possible development of an imaginary component to the order parameter at low[27, 28] or high[29] temperatures.

Some of these questions can be addressed by measuring the temperature dependence of the half-integer flux quantum effect. We did this by building a scanning SQUID microscope in which the sample was heated, while keeping the low-$T_c$ SQUID cold, by having a high thermal conductance path to the liquid helium bath.[30] Some results from this microscope are shown in Fig. 1(c).[31] These are images of an un-patterned thin film of YBCO epitaxially grown on a SiTiO$_3$ substrate with the geometry of Fig. 1(a), designed to show the half-integer flux quantum effect for a $d$-wave superconductor. Above $T_c \sim 89$K there is no magnetic feature at the tricrystal point, but as the temperature is lowered localized magnetic flux develops at this point. Close to $T_c$ this localized flux is distributed over an area of several tens of microns, due to the relatively long penetration depths, but as the temperature is reduced the peak becomes more sharp, until it is resolution limited (to the size of the pickup loop). The height of the Josephson vortex at the tricrystal point is independent of the sign of the vortex (magnetic fields into or out of the sample surface), indicating time reversal symmetry invariance. Modelling of such data using the total flux in the Josephson vortex at the
Figure 1: (a) A (100) SrTiO$_3$ substrate tricrystal geometry for testing $d$-wave pairing symmetry in cuprate superconductors. Also shown are polar plots indicating the orientation of the assumed $d_{x^2-y^2}$ order parameters aligned with the substrate crystallographic axes. (b) Schematic of the pickup loop geometry of the SQUID used for imaging the half-flux quantum Josephson vortex as a function of temperature. In this case the pickup area was a square 17.8 microns on a side. (c) Scanning SQUID microscope images of the tricrystal point of a YBa$_2$Cu$_3$O$_{7-\delta}$ thin film epitaxially grown on a SrTiO$_3$ substrate with the geometry given in (a), for various temperatures.
Figure 2: Values for the total flux spontaneously generated at the tricrystal point of the sample of Fig. 1 as a function of temperature. The dashed line, for reference, is for total flux one-half of the conventional superconducting flux quantum $\Phi = \Phi_0/2 = hc/4e$.

tricrystal point as a fitting parameter[31] (Fig. 2) indicates that the total flux is very close to $\Phi_0/2$ at all temperatures from 0.5K through $T_c \sim 90K$. This in turn implies that $d$-wave pairing symmetry predominates, with little if any imaginary component, at all temperatures in YBCO.

One of the models for the mechanism for high-$T_c$ superconductivity is the Inter-Layer Tunneling (ILT) Model.[32, 33, 34, 35] This model was motivated by the belief that although the charge and spin carriers in the normal state in the cuprates are highly localized within the planes, they become delocalized upon the formation of pairs when the superconducting state is formed. However, as pointed out by Leggett[36, 37], the essential feature of the model is that the superconducting condensation energy arises from the reduction in kinetic energy associated with this delocalization. This energy gain can be inferred from the strength of the inter-layer Josephson current density, which is in turn related to the inter-layer penetration depth. It is generally agreed that the most direct
<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{ILT}$</th>
<th>Our measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}_2\text{SrCuO}_4$</td>
<td>$\sim 4\mu m$</td>
<td>$5\pm 1\mu m$</td>
</tr>
<tr>
<td>$(\text{Hg,Cu})_2\text{Ba}<em>2\text{CuO}</em>{4+\delta}$</td>
<td>$\sim 1-2\mu m$</td>
<td>$8\pm 1\mu m$</td>
</tr>
<tr>
<td>$\text{Tl}_2\text{Ba}<em>2\text{CuO}</em>{6+\delta}$</td>
<td>$\sim 1-2\mu m$</td>
<td>$18\pm 3\mu m$</td>
</tr>
<tr>
<td>$\kappa-(\text{BEDT}$-$\text{TTF})_2\text{Cu(NCS)}_2$</td>
<td>$\sim 10\mu m$</td>
<td>$63\pm 15\mu m$</td>
</tr>
</tbody>
</table>

Table 1: Comparison of predictions of the Inter-Layer Tunneling Model for the inter-layer penetration depth with scanning SQUID microscope measurements, obtained by fitting the magnetic fields from inter-layer vortices to an anisotropic Ginzburg-Landau model.

test of the ILT model is made with cuprates with a single copper-oxygen plane per unit cell: $\text{La}_2\text{SrCuO}_4(\text{LSCO})$, Tl-2201, and HgBa$_2$CuO$_{4+\delta}$(Hg-1201). The predictions of the ILT model for these compounds are shown in Table I. Optical measurements on LSCO[38, 39, 40] show good agreement with the predictions of ILT. However, the first test in Tl-2201[39] placed an upper limit in Tl-2201 of $\lambda_c \sim 15\mu m$, in serious disagreement.

A direct way to measure the inter-layer penetration depth is to image vortices emerging parallel to the planes in these compounds. A summary of our experiments is shown in Fig. 3. As can be seen from Fig. 3, the vortices are resolution limited perpendicular to the planes (horizontal), but show appreciable spreading parallel to the planes (vertical). These images were modelled as anisotropic Ginzburg-Landau vortices[41] with the inter-layer penetration depth as a fitting parameter, with results shown in Table I. Our results are in reasonable agreement with optical measurements for LSCO,[42] and Tl-2201[43] but show a serious discrepancy with the predictions of the ILT model for Tl-2201,[44] Hg-1201,[45] and the organic superconductor $\kappa-(\text{BEDT}$-$\text{TTF})_2\text{Cu(NCS)}_2$.[46] Since the condensation energy scales like the inverse of the inter-layer penetration depth squared, it appears unlikely that the inter-layer tunneling model, at least as presently formulated, can provide enough condensation energy to account for the high critical temperatures observed in these materials.
Figure 3: Scanning SQUID microscope images of vortices emerging parallel to the planes from several layered superconductors. The superconducting planes are oriented vertically in these images. The overlays show scaled schematics of the pickup loops used in each image. The inserts in (a) and (c) show for comparison images of conventional Abrikosov vortices emerging perpendicular to the planes.
In summary, the scanning SQUID microscope has proved to be a valuable tool for studying the fundamental properties of unconventional superconductors through magnetic imaging of unusual vortices.

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Non-uniform superconductivity under high magnetic field

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Usually the behaviour of a superconductor under magnetic field is determined by the orbital effect (the interaction of superconducting order parameter with a vector-potential). However, the magnetic field also acts on the spins of the electrons and this gives an additional mechanism of Cooper pairs’ destruction - the paramagnetic effect. When the orbital effect is suppressed, which is the case when there is a thin superconducting film in a parallel field, heavy fermion, or magnetic superconductors, the paramagnetic effect becomes important. In these cases, as it was predicted a long time ago by Larkin and Ovchinnikov and also by Fulde and Ferrell, a non-uniform superconducting state (so-called FFLO state) appears. Up to now, the question of experimental observation of FFLO state is still open. We discuss on the simple qualitative level the physical reasons of the FFLO state appearance and demonstrate that a generalised Ginzburg-Landau theory for FFLO superconductors may be proposed - it provides an adequate description of non-uniform states near the tricritical point on the (H, T) phase diagram. We note that for quasi-2D superconductors, the situation is very peculiar; in the presence of the orbital effect, the non-uniform state formation leads to the appearance of a new type of solutions for the superconducting order parameter. This gives rise to an unusual oscillatory temperature dependence of the upper critical field.
I.- Introduction

It is well known that in type II superconductors when the magnetic field is higher than the lower critical field $H_{c1}$ the Abrikosov vortex lattice appears (see for example [1]). With the rise of the magnetic field, the vortex density increases and finally when the field reaches the value of the upper critical field $H_{c2}$ the second order transition into normal state occurs. Near the critical temperature the upper critical field is given by the expression $H_{c2}(T) = \phi_0/2\pi\xi^2(T)$, where $\phi_0 = \hbar/2e$ - flux quantum and $\xi(T) = 0.18(v_F/T_c)\sqrt{T_c/(T_c - T)}$ is the temperature dependent superconducting coherence length for pure superconductors. Such behaviour of superconductor under magnetic field is determined by orbital effect (interaction of superconducting order parameter with a vector-potential $A$ of the magnetic field $H = \text{rot}A$). However the magnetic field acts also on the spins of the electrons and this gives an additional mechanism of Cooper pairs destruction - paramagnetic effect. Usually it is an orbital effect and not a paramagnetic one which is responsible for the superconducting destruction by the magnetic field and in such case theory [2] gives an exact solution for superconducting order parameter on the upper critical field line $H_{c2}(T)$ at all temperatures. For pure paramagnetic effect the critical field $H_p$ at $T = 0$ may be found from the comparison of the energy gain $\Delta E_n$ due to electron spin polarization in normal state and superconducting condensation energy $\Delta E_s$. We find

$$\Delta E_n = -\chi_n H^2/2, \quad (1)$$

where $\chi_n = 2\mu_B^2 N(0)$ is the spin susceptibility of the normal metal, $\mu_B$ is the Bohr magneton, $2N(0)$ is the density of electron states at Fermi level (per two spin projections) and electron $g$ factor is supposed to be equal to 2.

On the other hand

$$\Delta E_s = -N(0) \Delta_0^2/2, \quad (2)$$

where $\Delta_0 = 1.76T_c$ superconducting gap at $T = 0$ and from the equation $\Delta E_n = \Delta E_s$, we find the Chandrasekhar-Clogston limit (paramagnetic
limit at $T=0$).

$$H_p(0) = \frac{\Delta_0}{\sqrt{2\mu_B}}.$$  

Note that it is the field of the first order phase transition from normal to superconducting state. The full analysis [3] demonstrates that at $T = 0$ such critical field is higher than the field of the second order phase transition $H_{p}^{II}(0) = \Delta_0/2\mu_B$ and the transition from normal to uniform superconducting state is of second order at $T^* < T < T_c$ only, where $T^* = 0.56T_c$, $H^* = H(T^*) = 0.61\Delta_0/\mu_B = 1.05T_c/\mu_B$. However Larkin, Ovchinnikov [4] and Fulde, Ferrell [5] predicted in the framework of the model of pure paramagnetic effect the appearance of the non-uniform state with sinusoidal modulation of superconducting order parameter (FFLO state).

The critical field of the second order transition into FFLO state goes somewhere above the first order transition line into a uniform superconducting state [3]. At $T = 0$ it is $H_{FFLO}^{II}(0) = 0.755\Delta_0/\mu_B$ (whereas $H_p = 0.7\Delta_0/\mu_B$). This FFLO state appears only in the temperature interval $0 < T < T^*$ and it is sensitive to impurities [6] - in dirty limit it is suppressed and the first order transition into uniform superconducting state takes place instead.

The phase diagram for 3D superconductors in the model of pure paramagnetic effect is presented in Fig.1 [3].

II.- Qualitative explanation of non-uniform phase formation

The appearance of modulation of the superconducting order parameter is related with the Zeeman’s splitting of electron’s level under magnetic field acting on the electron spins. To demonstrate this let us consider the case of 1D superconductor.

In the absence of field the Cooper pair is formed by two electrons with momenta $+k_F$ and $-k_F$ and spins ($\uparrow$) and ($\downarrow$) respectively. The resulting momentum of Cooper pair $k_F + (-k_F) = 0$. Under magnetic field due to Zeeman splitting the momentum at the Fermi level of the electron with spin ($\uparrow$) will shift from $k_F$ to $k_1 = k_F + \delta k_F$ where $\delta k_F = \mu_B H/\nu_F$, and of electron with spin ($\downarrow$) from $-k_F$ to $k_2 = -k_F + \delta k_F$ (see Fig.2). Then the resulting momentum of the Cooper pair will be $k_1 + k_2 =$
Figure 1: Phase diagram for 3D superconductor. The dashed line corresponds to a second order transition between normal and uniform superconducting state.
2 \delta k_F \neq 0 \) which just means the modulation of the superconducting order parameter with a wavevector \( 2 \delta k_F \). This type of reasoning explains the origin of the non-uniform superconducting state formation in the presence of the field acting on electron spins and at the same time it demonstrates the absence of paramagnetic limit at \( T \to 0 \) for the 1D superconductor. For 2D or 3D superconductor, it is not possible to choose wave vector \( \delta k_F \) to compensate Zeeman splitting for all electrons on the Fermi surface (\( \delta k_F \) depends on direction of \( v_F \)) and paramagnetic limit is preserved. However the critical field for non-uniform state at \( T = 0 \) is always higher than for uniform one.

It is straightforward to analyze the non-uniform phase in the framework of generalized Ginzburg-Landau expansion. The standard Ginzburg-Landau functional is (see for example [1]):

\[
F = a |\psi|^2 + \gamma \left| \nabla \psi \right|^2 + \frac{b}{2} |\psi|^4 ,
\]

(4)

where \( \psi \) is the superconducting order parameter and the coefficient \( a \) becomes zero at the transition temperature \( T_c \). At \( T < T_c \) the coefficient \( a \) is negative and the minimum of (4) is achieved for uniform superconducting state with \( |\psi|^2 = -\frac{a}{\gamma} \). If we take into account the paramagnetic effect of the magnetic field, all the coefficients in (4) will depend on field \( H \) (note that we neglect the orbital effect that is why there is no vector-potential \( A \) in (4)). What is most important is that the coefficient \( \gamma \) changes sign at the point \( (H^*, T^*) \) of the phase diagram. The negative sign of \( \gamma \) means that the minimum of the functional does not correspond to an uniform state anymore. To describe such a situation it is necessary to add a higher order derivative in the expansion (4) and the generalized Ginzburg-Landau expansion will be:

\[
F_G = a(H, T) |\psi|^2 + \gamma(H, T) \left| \nabla \psi \right|^2 + \frac{\lambda(H, T)}{2} \left| \nabla^2 \psi \right|^2 + \frac{b(H, T)}{2} |\psi|^4 ,
\]

(5)

Near the tricritical point \( (H^*, T^*) \) the wavevector of modulation is small in comparison with \( \xi_0^{-1} \) and it is justified to use Ginzburg-Landau expansion. For negative \( \gamma \) the most favorable is to have a non-uniform
Figure 2: Schematic representation of the Cooper pair formation in 1D superconductor. Zeeman’s splitting provokes the change of the Fermi momenta for electrons with spins $\uparrow$ and $\downarrow$. 
solution $\Delta \sim e^{i\mathbf{q}_0 \cdot \mathbf{r}}$ with the wave vector $\mathbf{q}_0$ corresponding to the minimum of $q$ dependent part of (5): $-|\gamma| q^2 + \frac{\lambda}{2} q^4$, i.e. $q^2 = \frac{|\gamma|}{\lambda}$.

In principle, near the tricritical point $(H^*, T^*)$ it is possible to develop the full description of the non-uniform state on the basis of the expansion (5). The vector-potential $\mathbf{A}$ may be incorporated by the substitution $\nabla \to \nabla - \frac{2e}{\hbar} \mathbf{A}$. However the peculiar property of the BCS model is that the coefficient $b$ becomes equal to zero at the same point $(H^*, T^*)$ and then it is needed to add to (5) the terms $\sim |\psi|^2 \nabla^2 \psi^2$. This made the analysis of the properties of the non-uniform phase on the basis of (5) rather complicated [7].

III.- Quasi-1D superconductors

As it has been mentioned a special situation in regard to the paramagnetic limit occurs in quasi-1D superconductors. In the limit $T \to 0$ in the absence of impurities, there is no paramagnetic limit and the region in which the non-uniform state exists becomes significantly broader for $T < T^*$ (see Fig. 3) [10]. In this case it is possible to find a complete description of the non-uniform phase for all the temperature region of its existence. It is a soliton lattice phase described by the Jacobi elliptic function [10],[11]. The boundary between uniform and soliton lattice phase is depicted by dotted lines in Fig. 3. Note also that the phase $(H, T)$ diagram of the non-uniform 1D superconducting state is appropriate for the description of the completely different system, the spin-Pierls transition in the 1D insulating antiferromagnetic $s = 1/2$ Heisenberg chain [12],[13] under the magnetic field.

IV.- Quasi-2D superconductors

In layered superconductors in the purely paramagnetic limit the critical field for FFLO state at $T = 0$ is $H^{FFLO}_{2D}(0) = \Delta_0/\mu_B$ [8] and the curve $H^{FFLO}_{2D}(T)$ [9] goes higher than that for 3D case. Such purely paramagnetic limit is realized when the external magnetic field is parallel to the superconducting layers. When the magnetic field is tilted from the parallel orientation, the orbital effect starts to play a role. At the critical field the solution for the superconducting order parameter is the Landau
Figure 3: Phase diagram for 1D superconductor.
level eigenfunction [2], which may be written as

\[ \psi_m(\vec{\rho}) = \exp(-im\varphi) \cdot \exp(-\frac{\rho^2eH}{2c}) \cdot \rho^m, \]  

(6)

where \( m \) is the orbital momentum and in polar coordinates \( \vec{\rho} = (\rho, \varphi) \). Usually it is the lowest level \( m = 0 \) eigenfunction which gives the solution corresponding to the upper critical field. However in the case when the paramagnetic effect is predominant the situation changes and higher level eigenfunctions become relevant at \( T < T^* \) [8]. Calculation of the temperature dependence of the upper critical field has been performed in [9] and they reveal an unusual oscillatory temperature dependence of the critical field, Fig. 4.

The critical field is given by a sequence of curves corresponding to solutions for the superconducting order parameter with different orbital momenta. Experimentally, the resulting unusual oscillatory temperature dependence of the critical field can be a decisive evidence for the formation of the non-uniform state. The structure of the mixed state is very peculiar [7]. The line of first-order transition must separate the states with different orbital momenta. It is clear that such transitions will be accompanied by a jump of the magnetic moment and the critical current. These transition may be provoked by a magnetic field and/or a temperature change and also by a variation of the angle between the field and the superconducting layers.

Let us stress that all these particular features must be observed in the region of the non-uniform phase appearance, i.e. at \( T < 0.55T_c \). For an experimental test of this \( H_{c2}(T) \) behaviour, it is important to keep in mind that low-\( T_c \) superconductors are required in order to have reasonable values of \( H_{FFLO}(0) : H_{FFLO}(0)/T_c \approx 2.4T/K \).

V. 3D superconductors

At the present time even in the framework of the model of purely paramagnetic effect the structure of the FFLO state in 3D superconductors is known only near the tricritical point \( (H^*, T^*) \). It is the non-uniform state with one-dimensional modulation and the transition between normal and FFLO states occurs to be the slightly first-order one [14]. When
Figure 4: Temperature dependence of the critical field in layered superconductor for fields inclined toward the superconducting planes [9]. Full line: \( H_{c2} \) taking into account both the Pauli limit and an orbital effect parametrized by a slope at \( T_c \) of \(-30 \ T/K\). The orbital limit is large enough to promote transitions up to the Landau level \( m = 2 \).
the temperature decreases the period of modulation of FFLO state grows and it steadily transforms into uniform superconducting state. At low temperature the transition from normal to FFLO state becomes strongly first-order and corresponding critical field is not known. The critical field of the second-order transition in the presence of orbital effect was calculated in [15] for lowest Landau level, but later on it has been demonstrated that the superconducting states with higher orbital momenta may appear in clean 3D superconductors too [16]. Note that not too much is known about the mixed state of FFLO phase yet.

References


