TU Braunschweig

Kavli Institute for Theoretical Physics

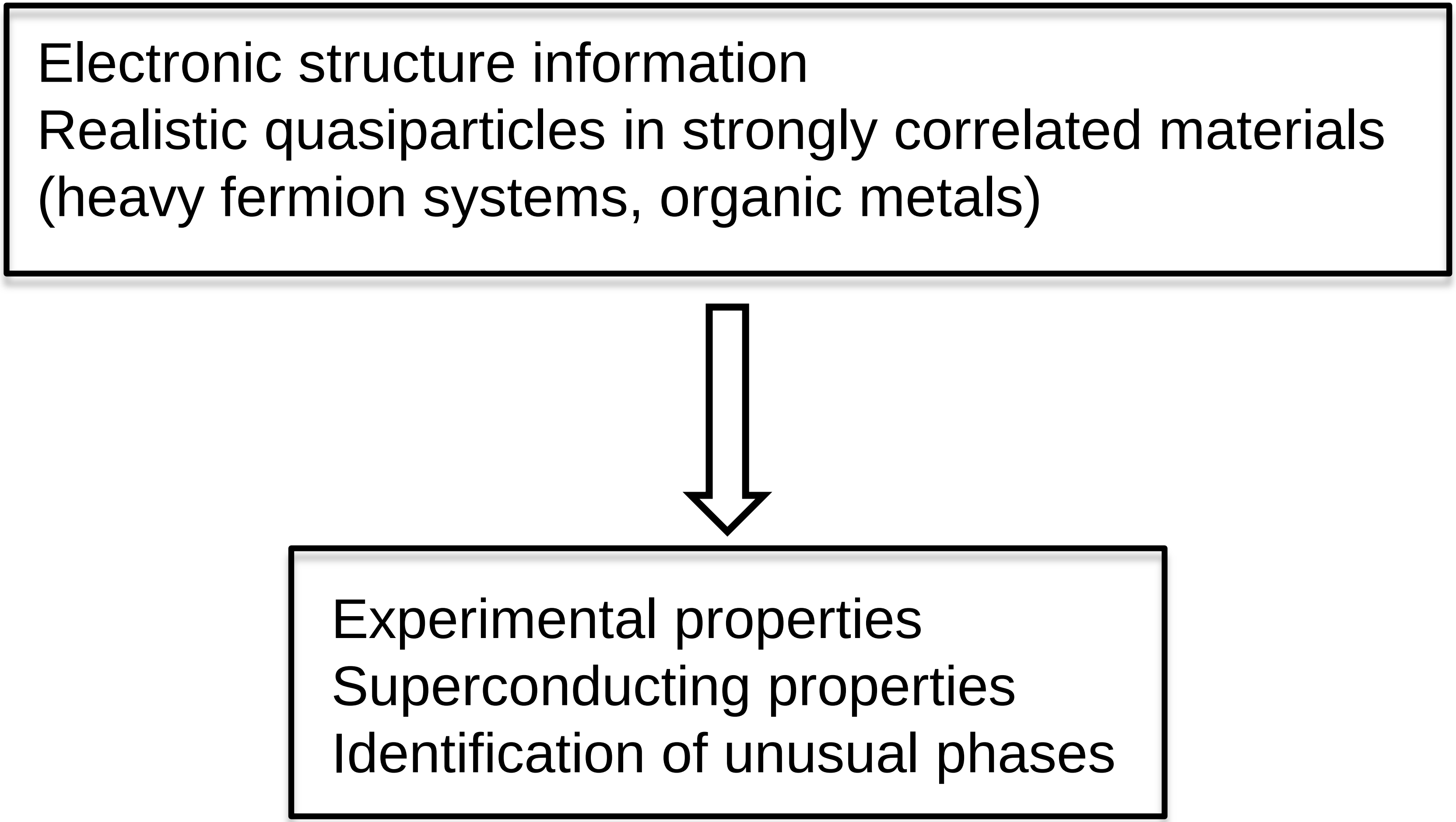
The Physics of Higher Temperature
Superconductors, August 20, 2009

Superconductivity in the Heavy-Fermion Compounds and Organic Metals: Competing orders and Novel Phases

Gertrud Zwicknagl

Institut für Mathematische Physik
Technische Universität Braunschweig

Theory supporting/guiding experiment



Electronic structure information
Realistic quasiparticles in strongly correlated materials
(heavy fermion systems, organic metals)

Experimental properties
Superconducting properties
Identification of unusual phases

Outline

I: Heavy fermion systems

1. Renormalized band method
2. Heavy fermions in Ce-based compounds
3. Instabilities of the Fermi liquid, unusual phases

II. Organic superconductors: ET Salts

1. Superconducting properties
2. FFLO (LOFF) states
3. Quasiclassical theory
4. Results
5. Summary and outlook

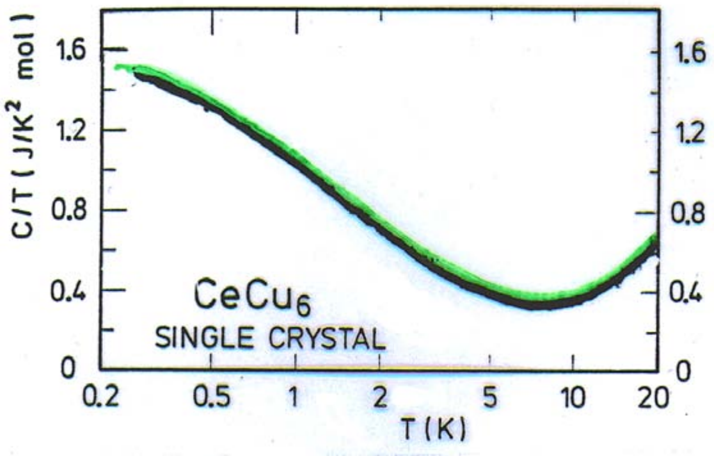
Heavy fermions: Lanthanide and actinide compounds

Anomalous behaviour of f electrons:

At low temperatures T < 10 K

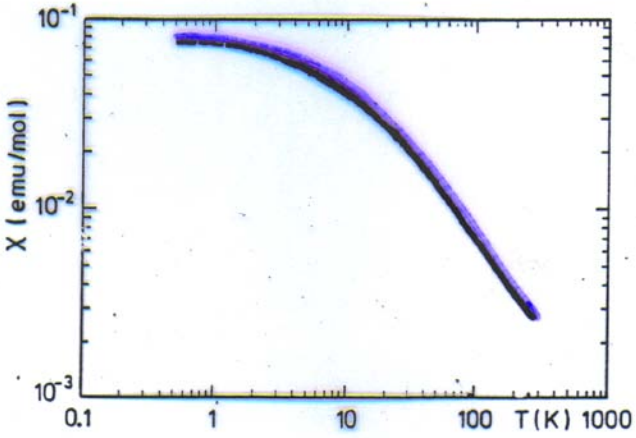
Specific heat

$$C(T) \rightarrow \gamma T \ ; \ \gamma \sim 1 J/(mole\, K^2)$$

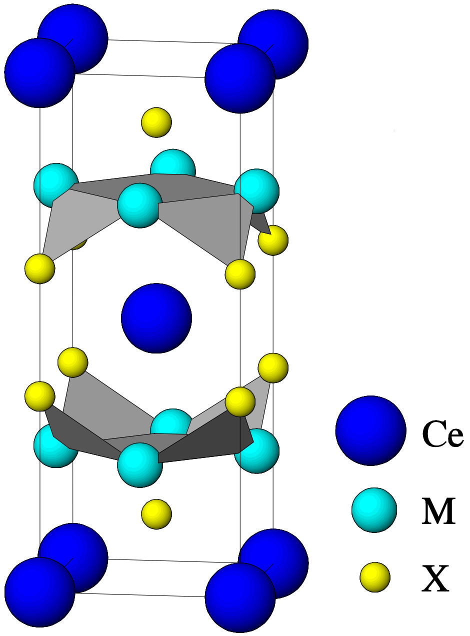


Susceptibility

$$\chi(T) \rightarrow const$$

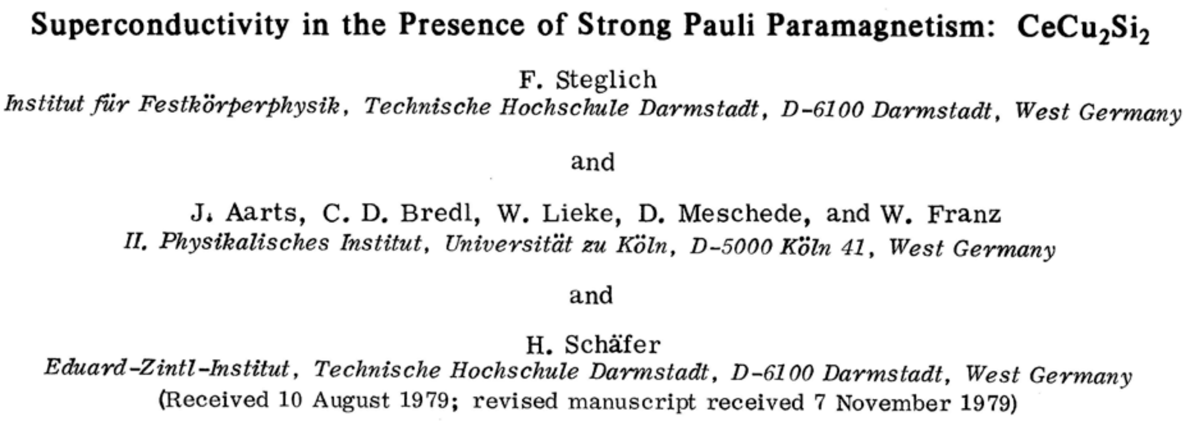


$CeCu_2Si_2$: “Mother” of Heavy Fermion Compounds



$ThCr_2Si_2$ structure

$$\gamma \sim 700 mJ/(mole\, K^2)$$



Superconductivity in the Presence of Strong Pauli Paramagnetism: $CeCu_2Si_2$

F. Steglich

Institut für Festkörperphysik, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

and

J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, and W. Franz

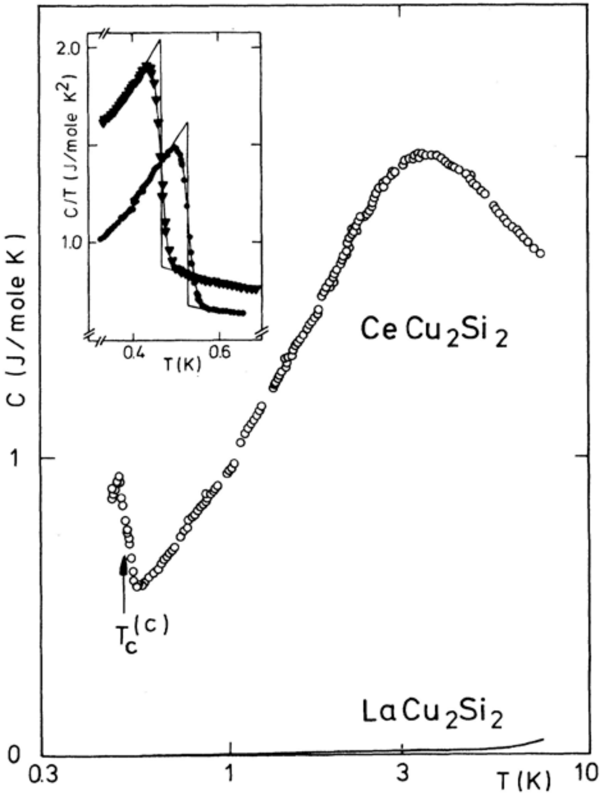
II. Physikalisches Institut, Universität zu Köln, D-5000 Köln 41, West Germany

and

H. Schäfer

Eduard-Zintl-Institut, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

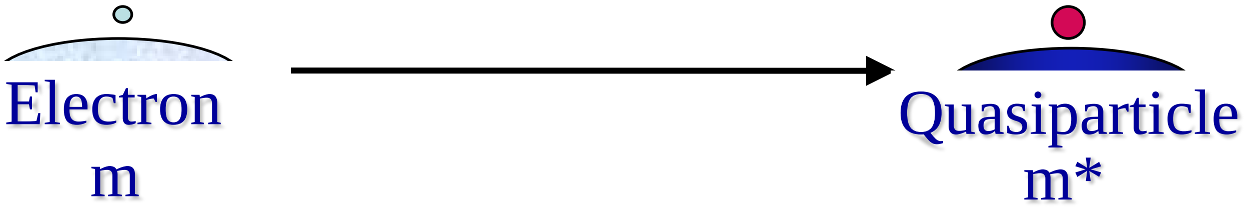
(Received 10 August 1979; revised manuscript received 7 November 1979)



Heavy fermions: Conjecture

Localized f-electrons behave like free electrons with high mass: $m^* \approx 1000 m_e$

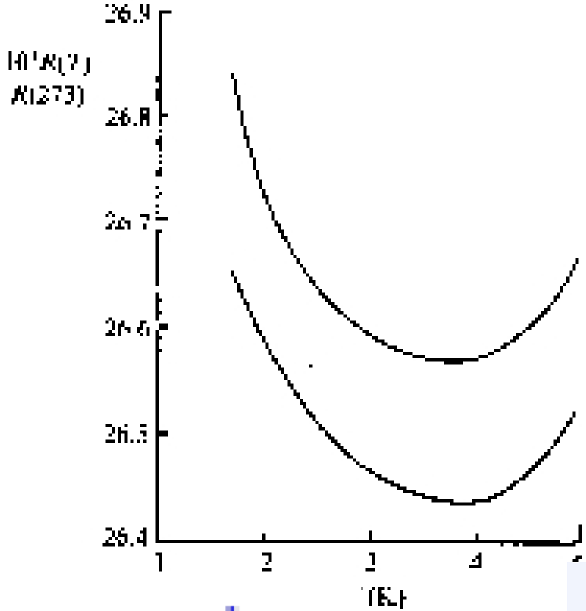
Landau: Fermi liquid
1-to-1 correspondence between excitations of interacting and free fermion systems implies $C(T) \to \gamma T; \chi(T) \to const$



Problem: Calculation of quasiparticles

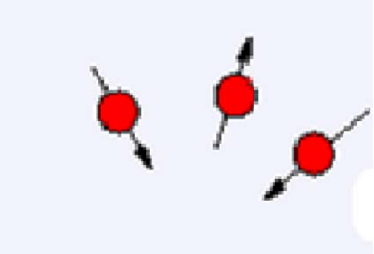
Heavy fermions in 4f systems: Kondo effect

“Confinement“



Minimum in electrical resistivity of dilute magnetic alloys

deHaas, deBoer, van den Berg (1934)



Low temperatures:

Heavy Quasiparticles

High temperatures

Free moments+conduction

electrons

Heavy quasiparticles in Ce compounds:

Conjecture:

Low temperatures:
f-degrees of freedom itinerant coherent fermions
Heavy quasiparticles
Fermi surface: conduction electrons +f-electrons
Confirmed by deHaas-vanAlphen

High temperatures:
4f electrons localized
Curie-Weiss behavior in $\chi(T)$,
Crystalline Electric Field Excitations in C(T)
Fermi surface: only conduction electrons?

Heavy fermions: Fermi liquid

Assumption:

1-to-1 correspondence between low-energy excitations of interacting and noninteracting Fermi system

Quasiparticles $$\tilde{E}_\sigma(\boldsymbol{k}) = E(\boldsymbol{k}) + \sum_{\boldsymbol{k}',\sigma'} f_{\boldsymbol{k}\sigma,\boldsymbol{k}'\sigma'}\,\delta n_{\boldsymbol{k}\sigma}$$

Dilute gas of quasiparticles

$$E(\boldsymbol{k}) = \boldsymbol{v}_F(\hat{k})\cdot\left(\boldsymbol{k}-\boldsymbol{k}_F\right)$$

Interactions

Isotropic system: Parametrization by effective mass m* and interaction parameters; k_F fixed by particle number

Anisotropic crystal:
Renomalized bands

Heavy fermions: Fermi liquid

Parametrization:

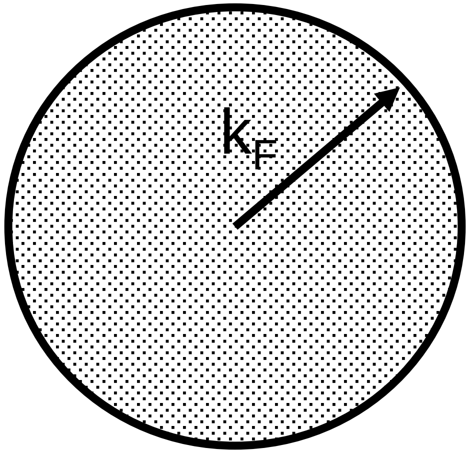
Proceed in close analogy to 3He

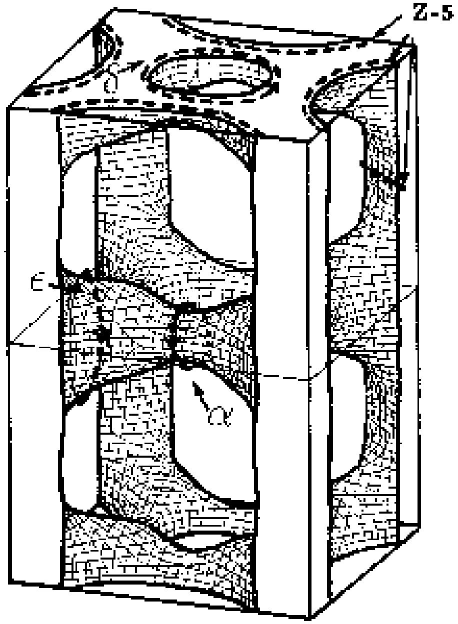
Isotropic system:

Parametrization by effective mass m* and interaction parameters; k_F fixed by particle number

Anisotropic crystal:

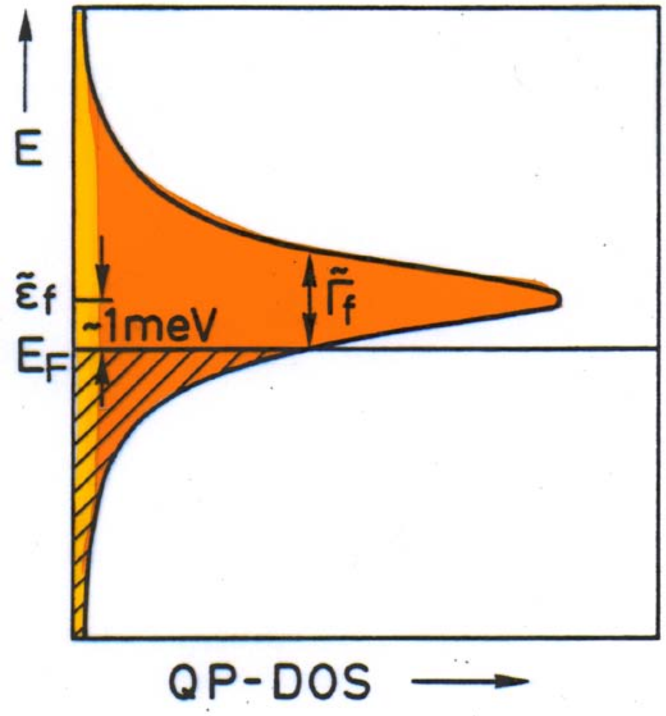
Renomalized bands





Renormalized band method

Quasiparticle bands



Phase shift:

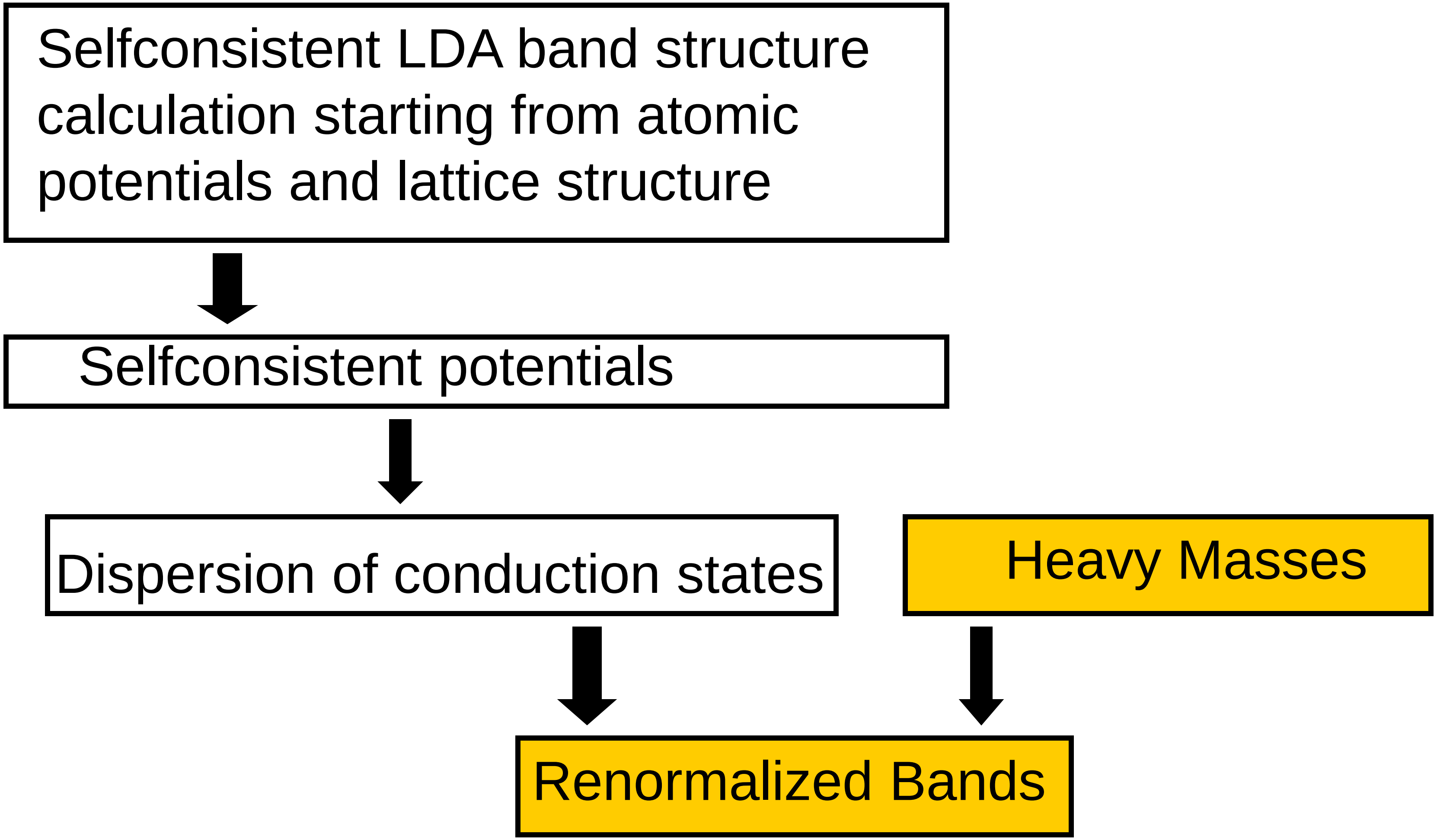
$$\tilde{\eta}_f = \arctan \frac{\tilde{\Gamma}_f}{\tilde{\varepsilon}_f - E}$$

Condition:
No re-distribution of charge $\Longrightarrow \tilde{\varepsilon}_f$

Single parameter $\tilde{\Gamma}_f$: adjusted to specific heat

Renormalised band method

Calculational scheme:



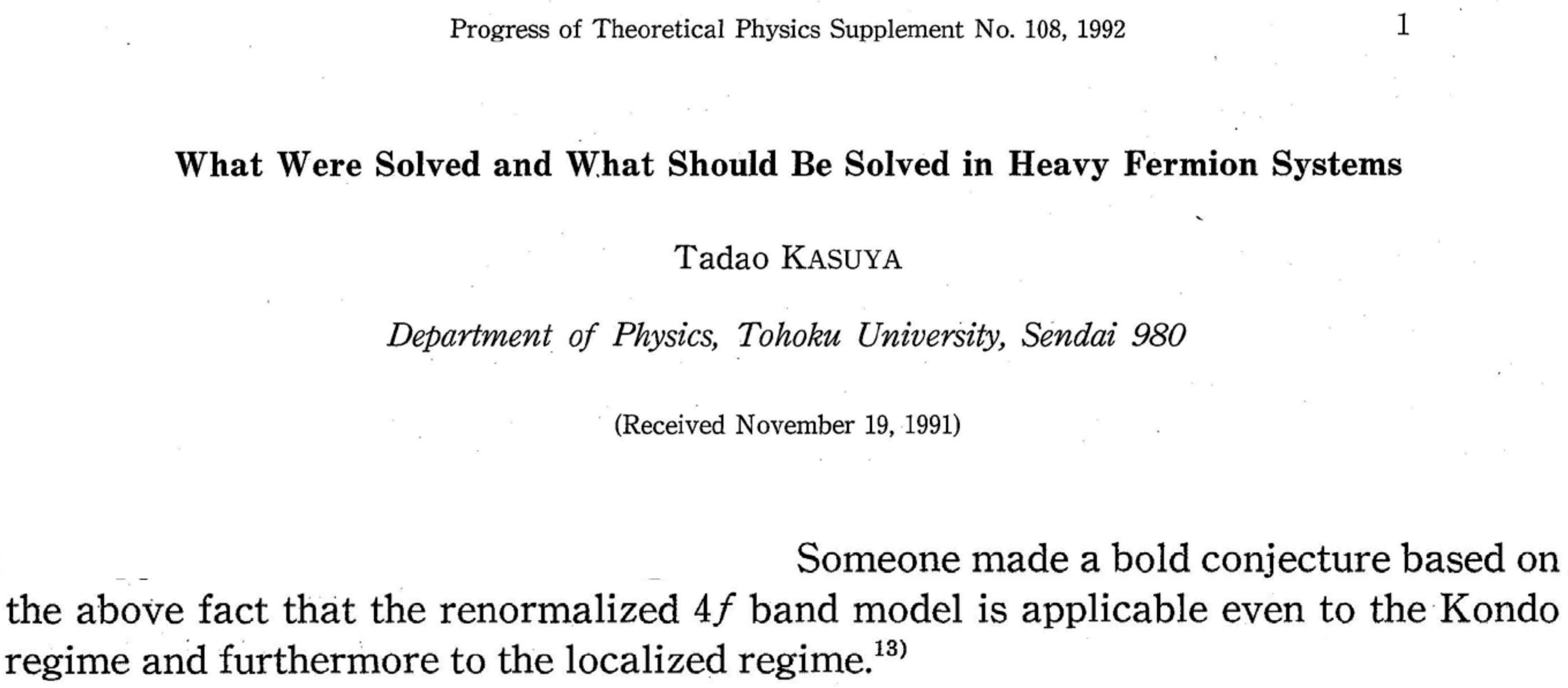
Selfconsistent LDA band structure calculation starting from atomic potentials and lattice structure

Selfconsistent potentials

Dispersion of conduction states

Heavy Masses

Renormalized Bands



Progress of Theoretical Physics Supplement No. 108, 1992 1

What Were Solved and What Should Be Solved in Heavy Fermion Systems

Tadao KASUYA

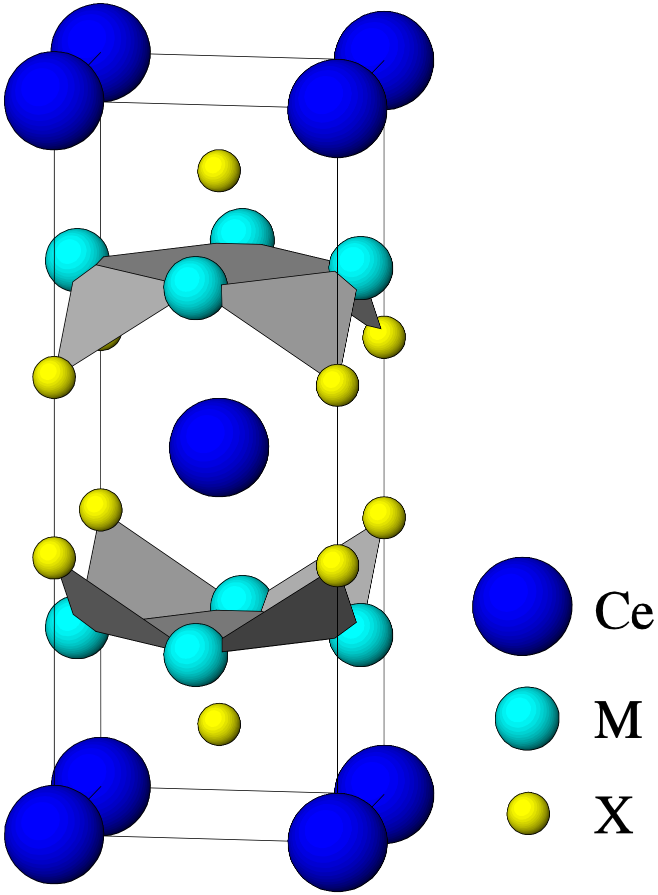
Department of Physics, Tohoku University, Sendai 980

(Received November 19, 1991)

Someone made a bold conjecture based on the above fact that the renormalized $4f$ band model is applicable even to the Kondo regime and furthermore to the localized regime.[13)]

Heavy fermions in Ce compounds

$CeRu_2Si_2$

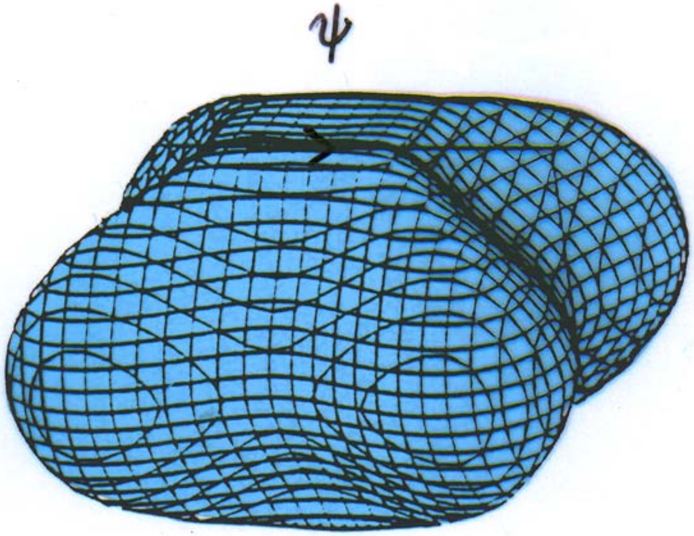


$$\gamma \sim 350 mJ/(mole\,K^2)$$

Heavy Fermions in Ce compounds

Confirmation of the quasiparticle model

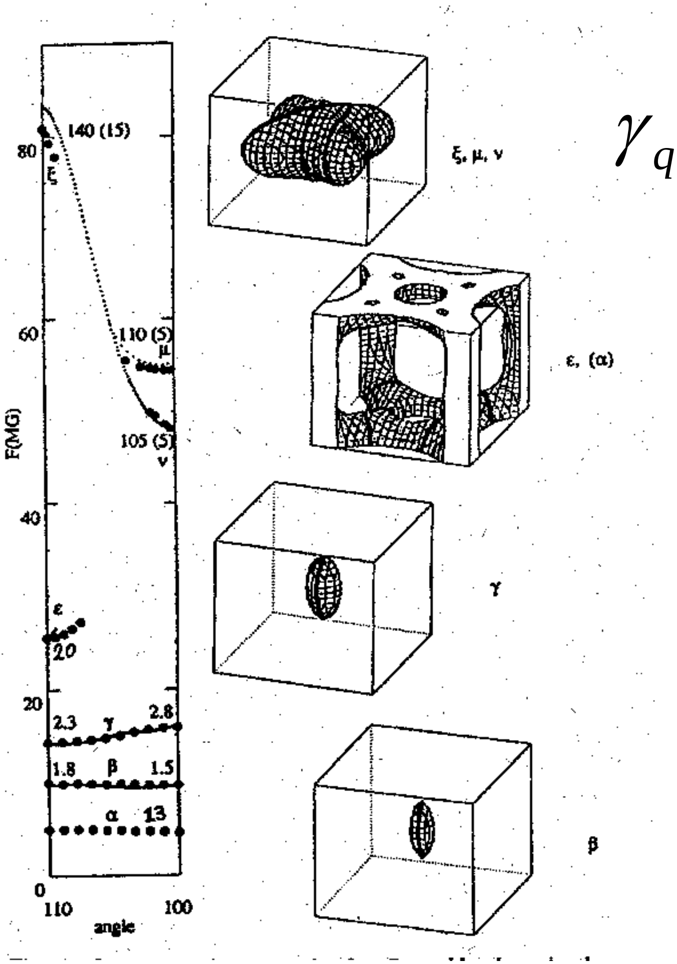
Fermi surface for Heavy Fermions in $CeRu_2Si_2$
(GZ, E. Runge, N. E. Christensen,
Physica B 163, 97 (1990))



Experimentally
confirmed
Aoki et al., PRL 72,797 (1992)

Heavy fermions in Ce compounds

Confirmation of the quasiparticle model : $CeRu_2Si_2$
Effective dHvA masses are consistent with specific heat



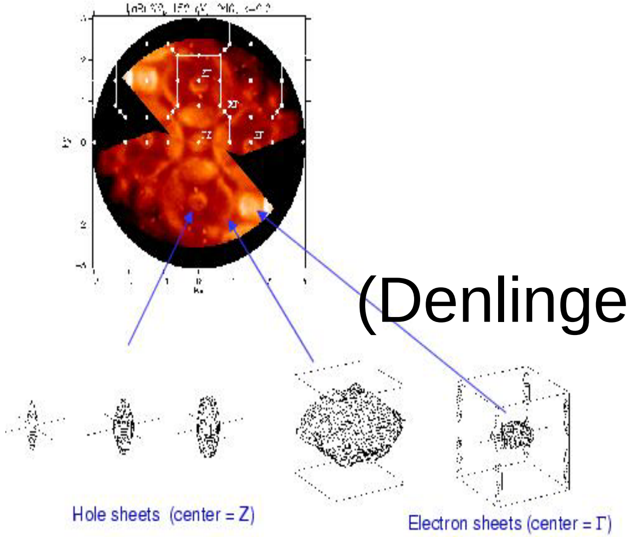
$$\gamma_{quasiparticle} \sim 260 \pm 50\, mJ/(mole\, K^2)$$

Exp.: Tautz et al., 1995

Heavy fermions: Change in Fermi surface

f states localized

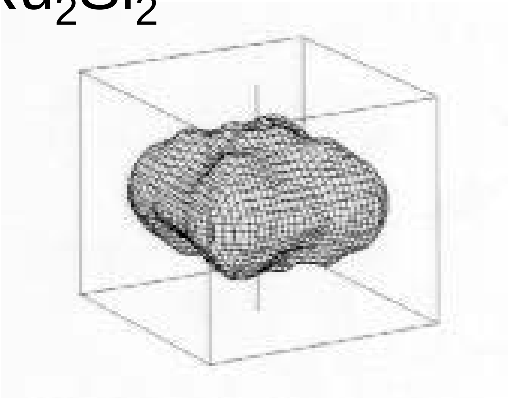
Fermi surface of $LaRu_2Si_2$



(Denlinger et al)

f states itinerant (low T)

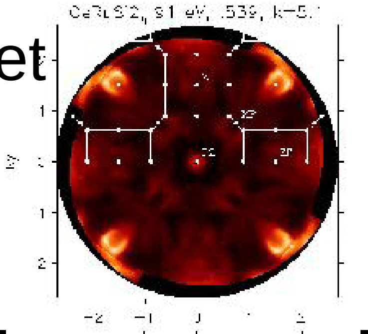
Fermi surface of $CeRu_2Si_2$



(Tautz et al)

Fermi surface of $CeRu_2Si_2$ at intermediate T

$T \sim 6T_K$:
Large Z hole pocket
like in La



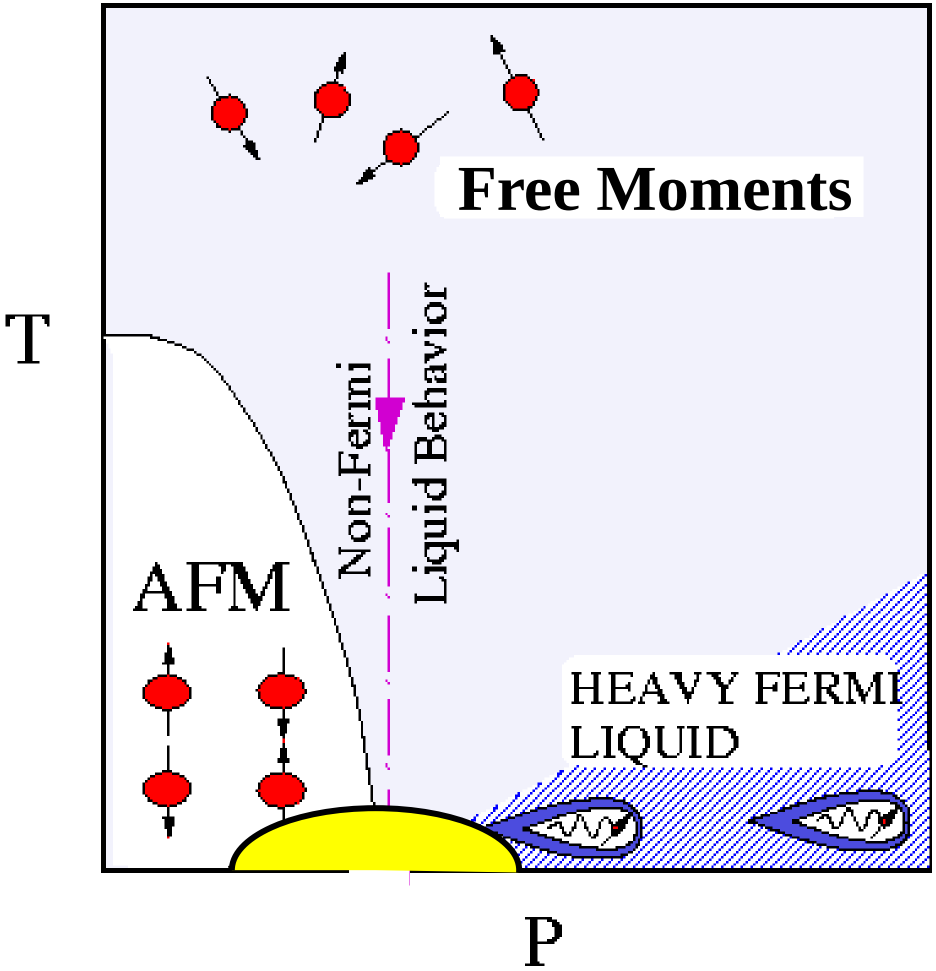
Hypothesis confirmed:
local f character at E_F
no (coherent)
quasiparticles

Instabilities of the heavy Fermi liquid

-Quantum critical points

competition

Antiferromagnetism ⟷ Fermi liquid

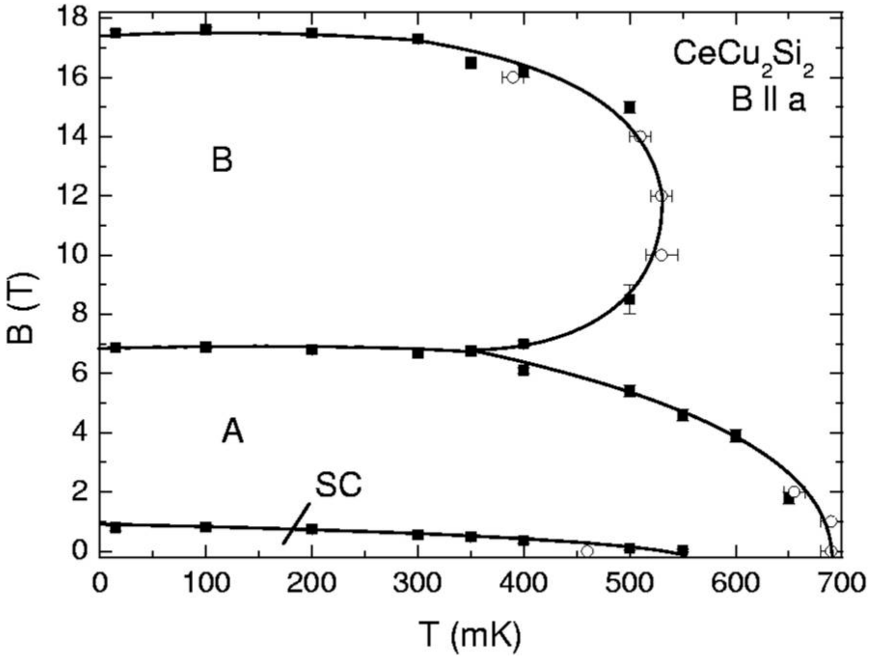


Superconductivity?

Instabilities of the heavy Fermi liquid

Unusual long-range order in $CeCu_2Si_2$

Pathologies in thermodynamic and transport properties



magnetic correlations

small magnetic moments

Bruls et al (1990), Weickert et al (2003)

Nature of the A- and the B-phase?

Instabilities of the heavy Fermi liquid

Interacting Fermi liquid

$$H = H_0 + H_{\text{int}}$$

Non-interacting quasiparticles

(Renormalized bands)

Interaction

Short-range repulsion

Spin density wave

$$H_{\text{int}} \to H_{SDW} = -\sum_{\vec{k},\sigma} \sigma \frac{1}{2} \sum_{\vec{Q}_j} \left(h\left(\vec{Q}_j\right) c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} + h.c. \right)$$

Instabilities of the heavy Fermi liquid

Interacting Fermi liquid

Spin density wave instability: Maxima in the static susceptibility c_0 of non-interacting quasiparticles

Calculate Lindhard function for heavy quasiparticle band

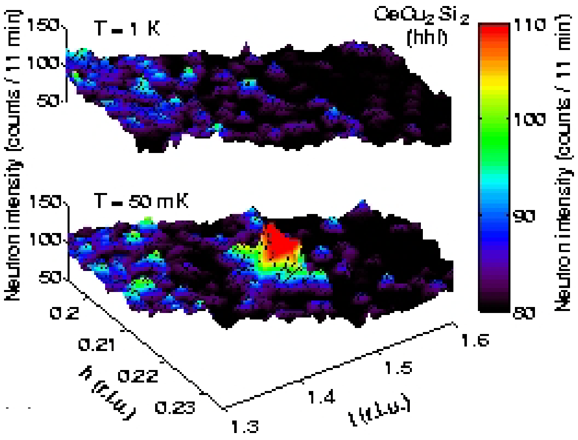
$$\chi_0\left(\vec{q}\right) = -\sum_{\vec{k}} \frac{f\left(E_{\vec{k}+\vec{q}}\right) - f\left(E_{\vec{k}}\right)}{E_{\vec{k}+\vec{q}} - E_{\vec{k}}}$$

Instabilities of the heavy Fermi liquid

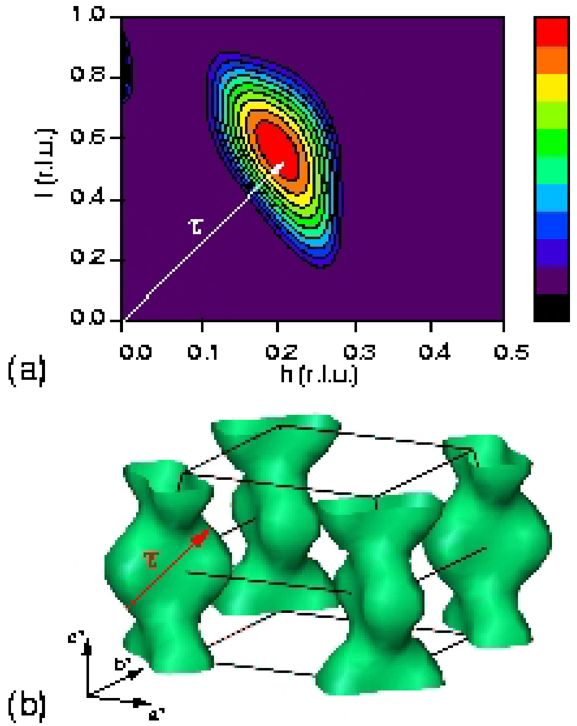
Spin density wave of heavy fermions in $CeCu_2Si_2$

(E. Faulhaber et al PRL **92**, 136401(2004))

Inelastic neutron scattering



Calculated susceptibility of the heavy quasiparticles



Instabilities of the heavy Fermi liquid

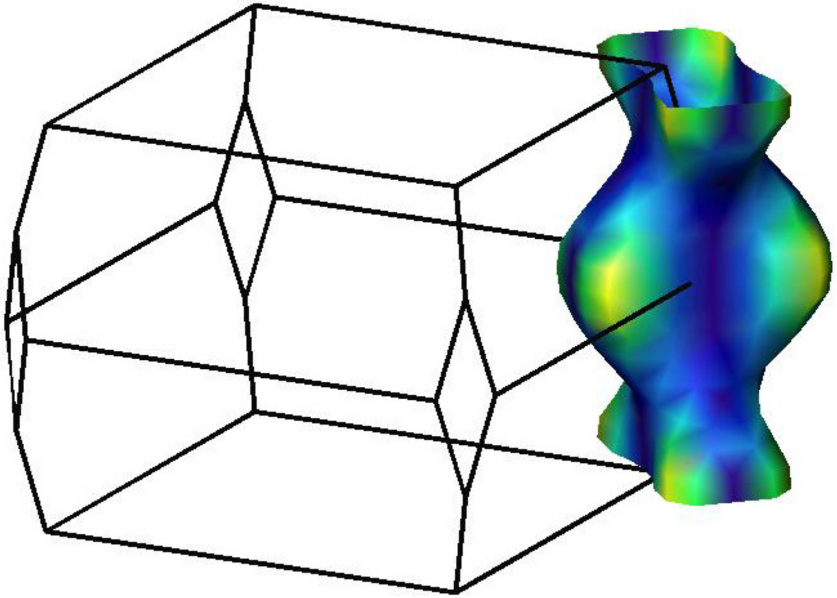
Resonance peak in superconducting $CeCu_2Si_2$

(I. Eremin et al PRL **101**, (2008))

Symmetry of the superconducting order paramete?r

Co-existence with SDW

$$\Delta(\boldsymbol{k}) = \cos k_x - \cos k_y$$



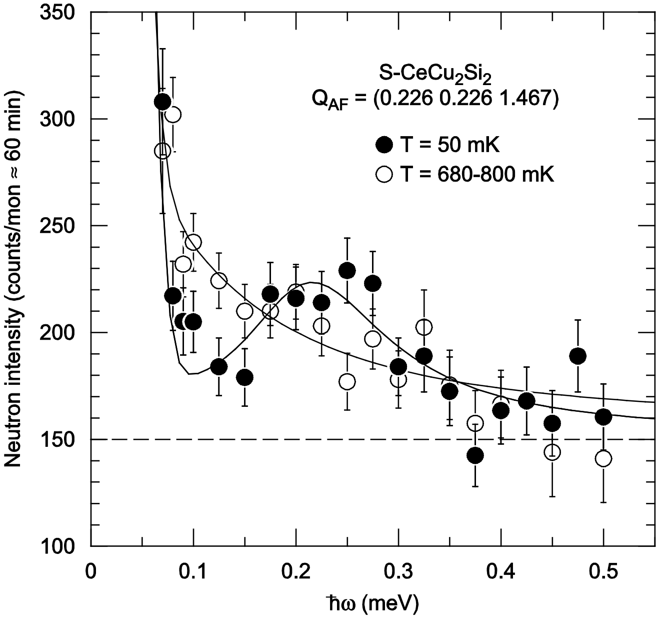
Instabilities of the heavy Fermi liquid

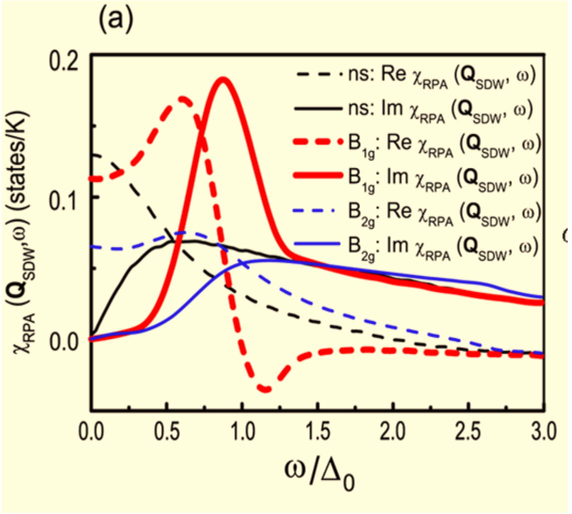
Resonance peak in superconducting $CeCu_2Si_2$

(I. Eremin et al PRL **101**, (2008))

Identification of the superconducting order parameter?

$$\Delta(\boldsymbol{k}) = \cos k_x - \cos k_y$$





Expt: O. Stockert et al, 2008)

•Summary I: Heavy fermions

-Heavy fermions :
f-degrees of freedom form narrow bands
Contribute to Fermi surface at low temperatures

-Standard methods of electronic structure calculation cannot be applied

-Renormalized bands:
Realistic quasiparticle bands by combining material-specific ab-initio calculations and semi-phenomenological description of strong correlations

-Quantum phase transitions and cooperative phenomena of heavy quasiparticles

Novel Phases in Quasi-2D-Organic Superconductors

Collaboration with:

R. Lortz
Y. Wang
A. Demuer
P. H. M. Böttger
B. Bergk
Y. Nakazawa
J. Wosnitza

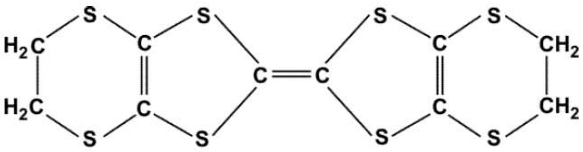
PRL **99**, 187002 (2007)

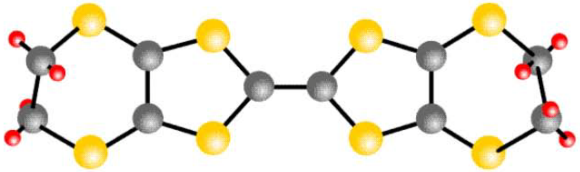
LNCMI
HLD
OSAKA UNIVERSITY
UNIVERSITÉ DE GENÈVE
香港科技大學
THE HONG KONG UNIVERSITY SCIENCE AND TECHNOLOGY
CAROLO-WILHELMINA BRAUNSCHWEIG

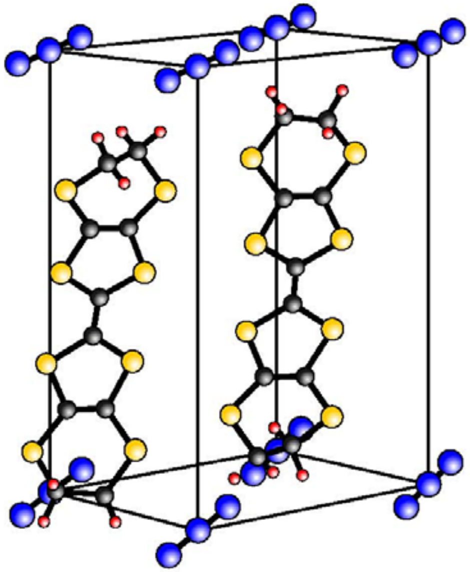
ET-Salts: Quasi-2D-Organic Superconductors

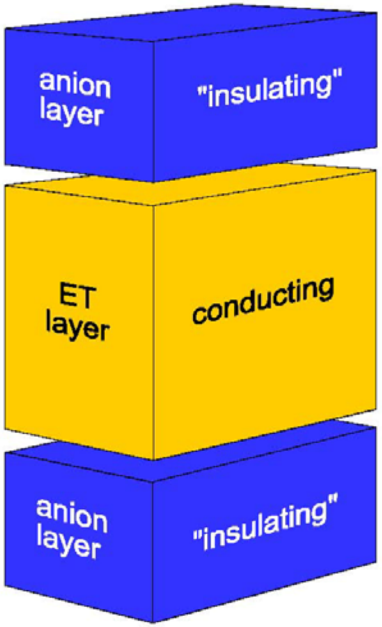
BEDT-TTF = ET

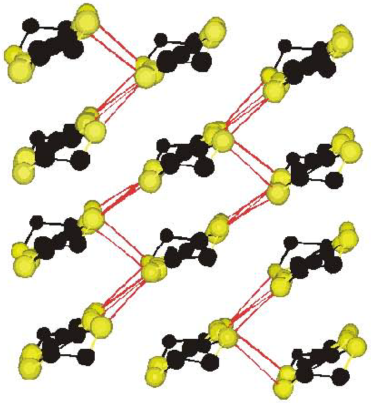
Bisethylendithio-tetrathiafulvalen

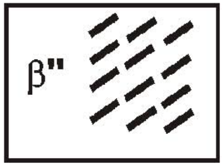


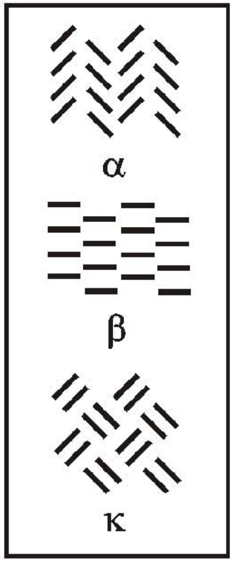








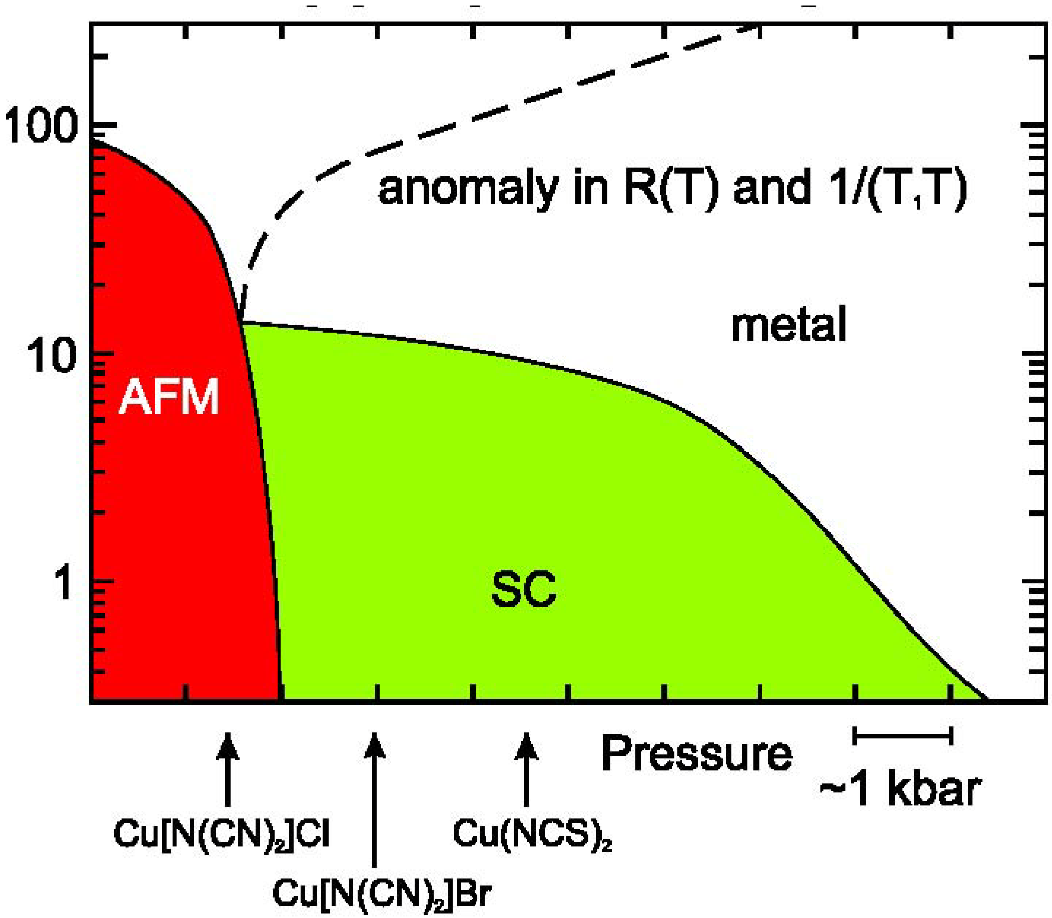




~ 100 organic superconductors of which ~ 50 are based on ET

κ-(ET)2Cu[N(CN)2]Cl: Tc≈13 K
In-plane ET structure: greekletters

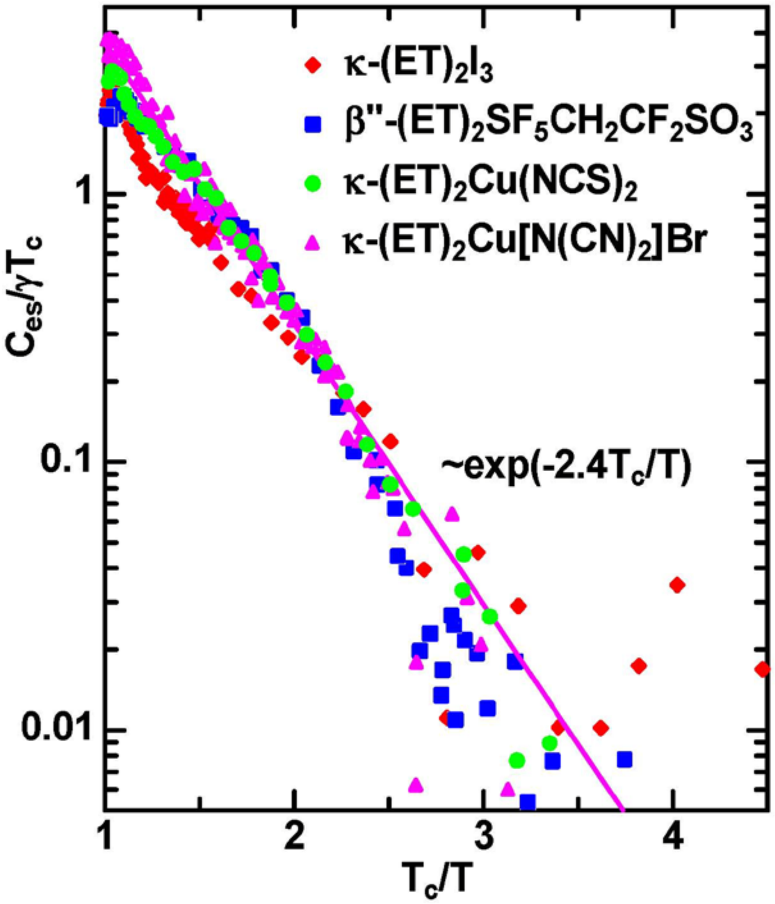
ET-Salts: Schematic phase diagram of κ-(BEDT-TTF)$_2$X



ET Salts: Symmetry of the superconducting order parameter?

Highly controversial

- Knight shift
- Tunnelling/point contact spectroscopy
- Angular dependences in magnetic field
- …

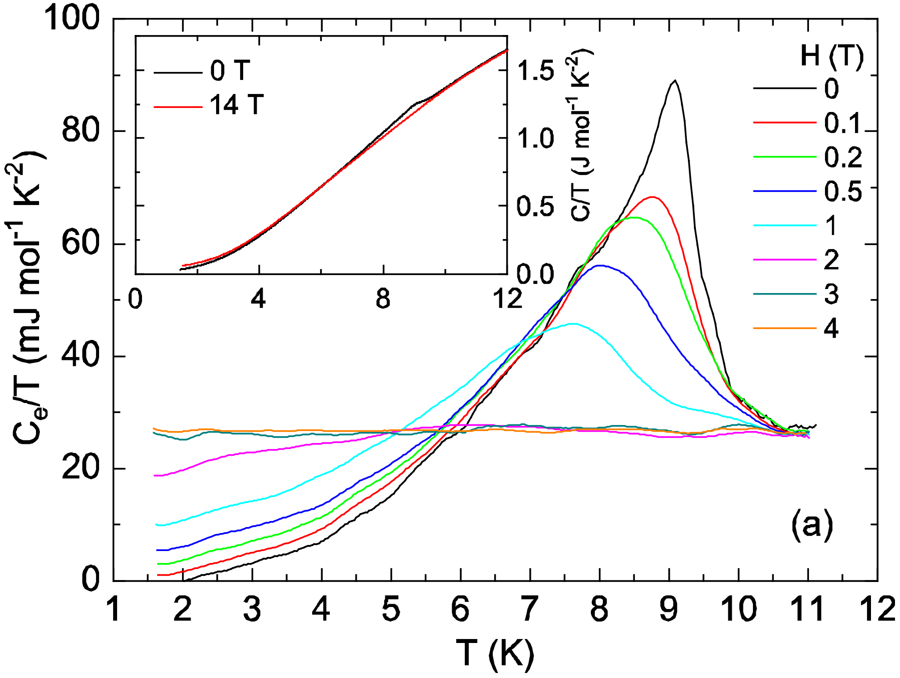


Specific heat

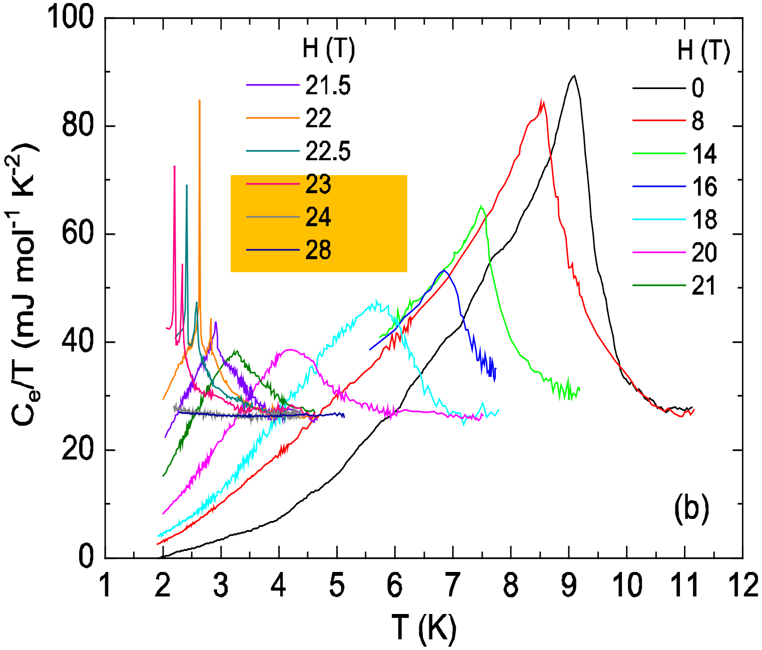
ET-Salts: Superconducting phase transitions in high magnetic fields

No orbital pairbreaking for magnetic fields perpendicular to the superconducting layers

In addition: Phase transitions within the superconducting state



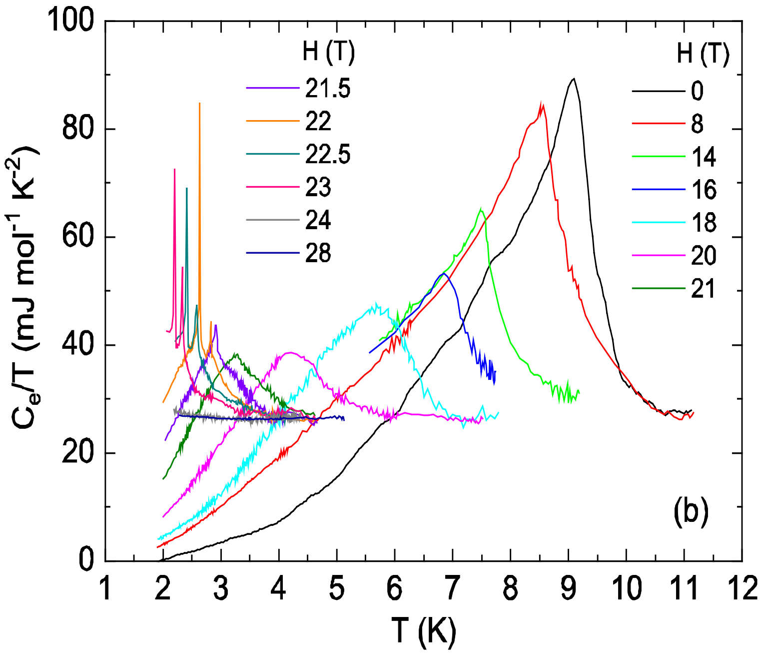
(a) H perpendicular



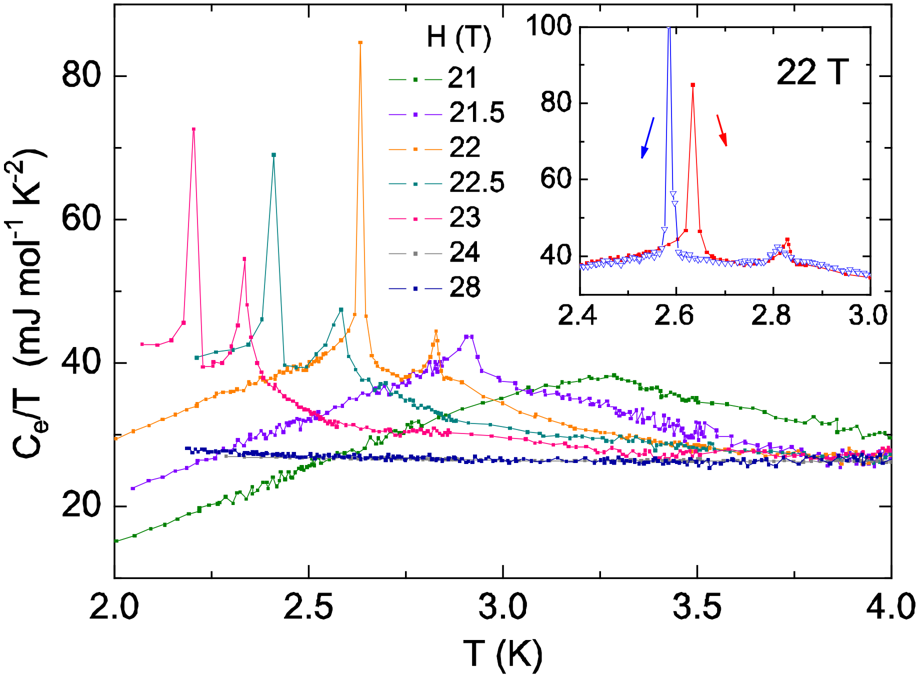
(b) H parallel

ET Salts: Superconducting phase transitions in high magnetic fields

Electronic specific heat contribution for magnetic fields perpendicular to the superconducting layers

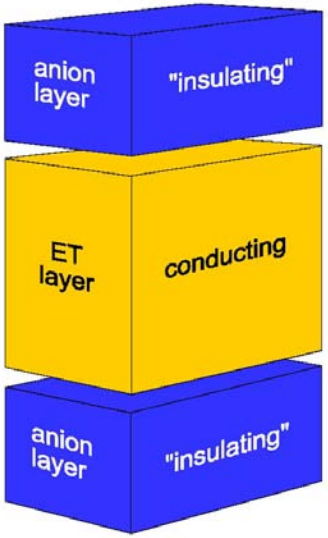


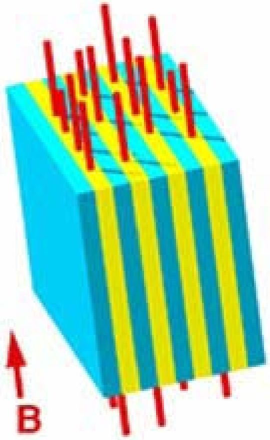
(a)

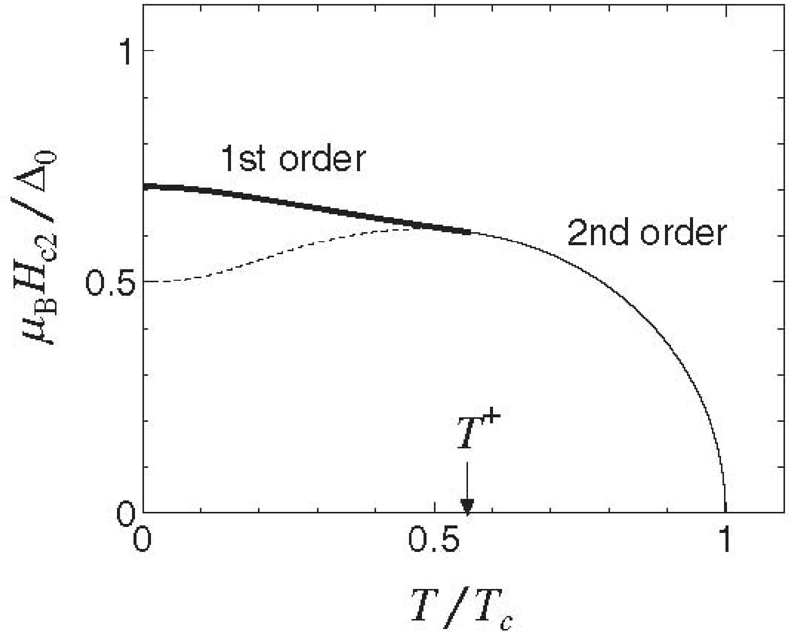


(b)

ET-Salts: Pauli limiting field in homogeneous superconductors







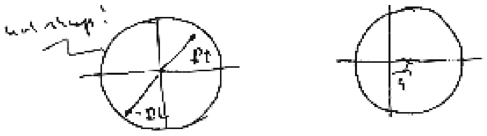
Estimated Clogston limit for κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ ~23T

First order transition at low T

Conjecture: Novel phases – spatially nonuniform superconducting states

Fulde-Ferrell-Larkin-Ovchinnikov st (FFLO or LOFF)

(1) Current carrying

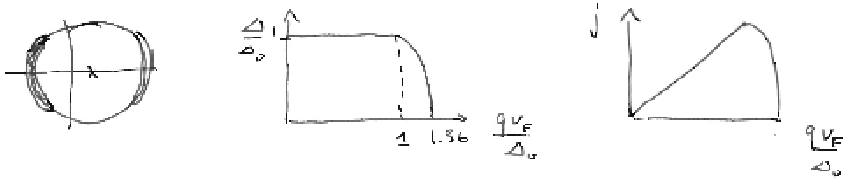


$E_p = \sqrt{\epsilon_p^2+\Delta_0^2}$

$E_p = \sqrt{\epsilon_p^2+\Delta_0^2} - \frac{q\cdot p}{m}$

$q v_F > \Delta_0$
unstable

for $v_F q > \Delta_0 \Rightarrow E_p$ can become negative



(2) Zeeman term:

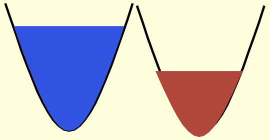
$H = H_{BCS} + \sum_i \mu_B \underline{\sigma}_i \cdot \underline{H}$

$E_{p\sigma} = \sqrt{\epsilon_p^2+\Delta_0^2} - \mu_B \sigma H \qquad \sigma = \pm 1$

$E_{p\sigma} < 0$ for $\boxed{\frac{\mu H}{\Delta_0} = 1}$

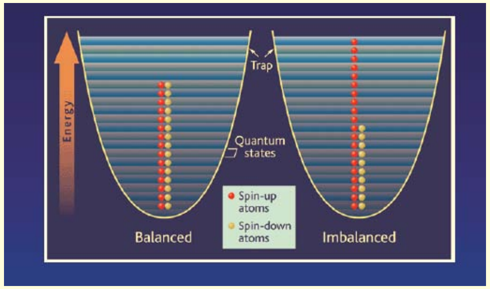
FFLO: Spontaneous breaking of translational symmetry

Paired states with imbalance => crystalline superconductivity

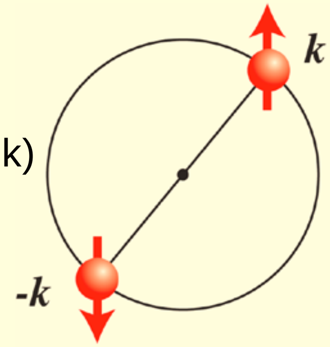


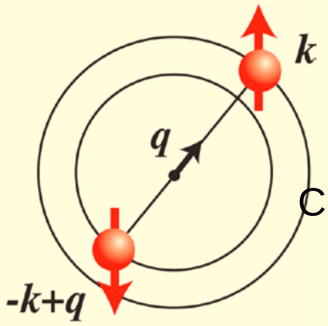
Many examples in nature

- Electrons in magnetic fields
- Ultra-cold atoms
- Neutron-proton pairs in neutron stars
- Color superconductivity in quark systems



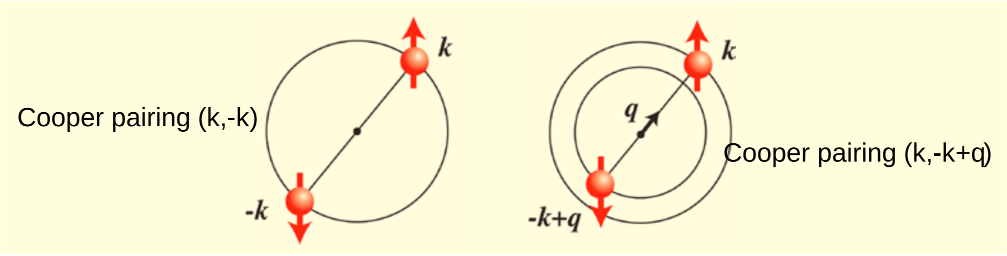
Cooper pairing (k,-k)

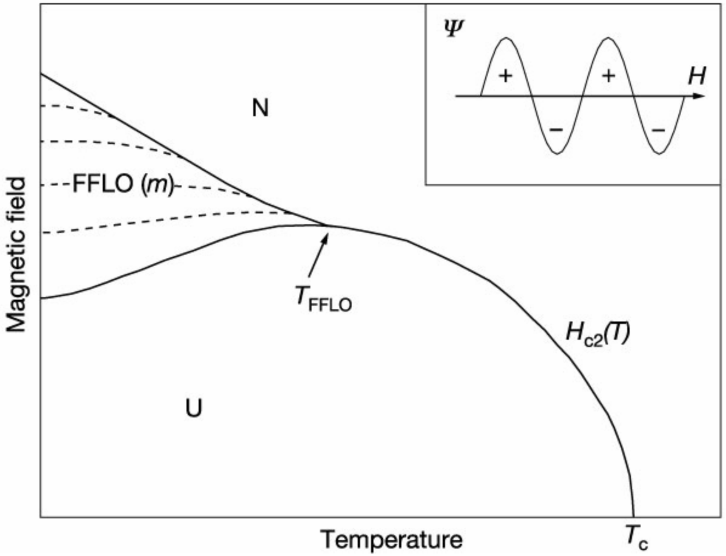




Cooper pairing (k,-k+q)

FFLO: Spontaneous breaking of translational symmetry



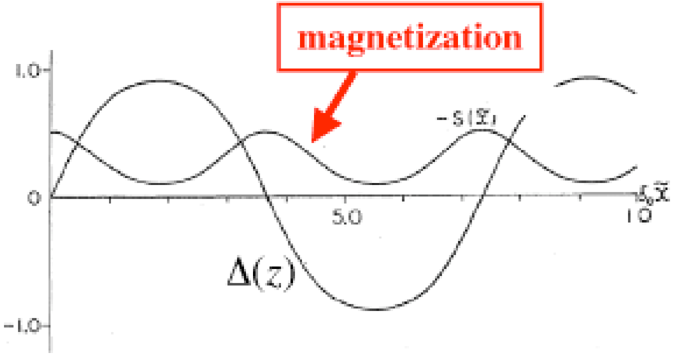


Degeneracy with respect to **q** => combinations,
Complicated spatial structures, phase transitions

$(k\uparrow, -k+q\downarrow)$: spatially inhomogeneous pairing field

$\Delta(z) \sim \exp(iqz)$ FF state

$\Delta(z) \sim \sin(qz)$ LO state



Strong influence of Fermi surface geometry

FFLO in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$?

System fulfils requirements for formation of FFLO

- Strongly type II superconductor κ=100-200
- Maki parameter $\alpha = \sqrt{2} H_{orb} / H_P \approx 8$
- Long mean-free path

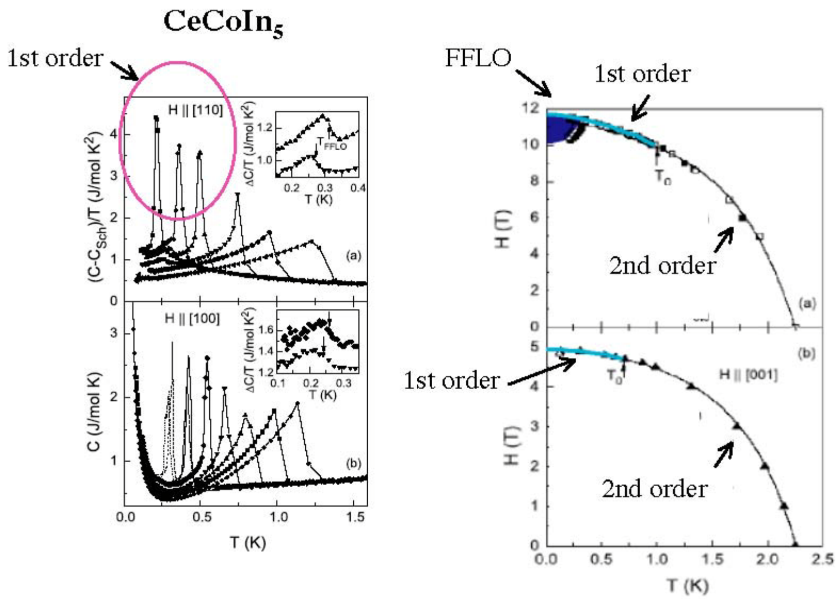
$$\xi_0 >> l \; ; \; l \sim 100nm \; ; \; \xi_0 \sim 9nm$$

Identification of FFLO states

Characteristic feature:

Modulated state with wave length ~$\xi_0 >> a$
Wave vector and structure dependent on magnetic field

$\Rightarrow$Criterion rules out heavy fermion superconductor $CeCoIn_5$ as candidate for FFLO state



A. Bianchi, et al, PRL 91, 18700 (03).

Identification of FFLO states
Comparison with theoretical predictions

However: Phase diagram, order of transitions etc depend
sensitively on detailled electronic structure
Candidates are not „free“ electron gas =>

Need flexible method + detailled information about the normal state

Extend work of Burkhardt and Rainer (1994) and Vorontsov and Graf (2006)

Theoretical ansatz:

Normal state

Detailled deHaas-vanAlphen experiments show

- Fermi liquid state
- Elementary excitations are weakly interacting fermionic quasiparticles characterized by wave vector **k** and spin σ
- Energies $\varepsilon(\mathbf{k},\sigma)$ quasi-2D-dispersion
- Extremely long mean-free path => pure system

Use realistic quasiparticle dispersion

Include quasiparticle interactions as parametrized by the Landau-parameter F_0^a

Theoretical ansatz:

Superconducting state:

BCS-Ansatz (pairing hypothesis)

Use Nambu-Gorkov formalism

4-spinor accounting for coherence in particle-hole and spin-space

$$\Psi_{\vec{k}} = \begin{pmatrix} c_{\vec{k}\uparrow} \\ c_{\vec{k}\downarrow} \\ c^{\dagger}_{-\vec{k}\downarrow} \\ c^{\dagger}_{-\vec{k}\uparrow} \end{pmatrix} \quad ; \quad \Psi^{\dagger}_{\vec{k}} = \begin{pmatrix} c^{\dagger}_{\vec{k}\uparrow} & c^{\dagger}_{\vec{k}\downarrow} & c_{-\vec{k}\downarrow} & c_{-\vec{k}\uparrow} \end{pmatrix}$$

Theoretical ansatz:

Separation of length and energy scales:

$$\xi_0 >> a \; ; \; k_B T_c >> E_F$$

Focus on low-energy and long-wavelength phenomena in inhomogeneous systems

Integrate out high-energy / short-wavelength contributions

=> Quasiclassical theory of superconductivity (Eilenberger.Larkin-Ovchinnikov-Eliashberg)

Quasiclassical theory:

Quasiclassical propagator:

$$\hat{g}\left(\hat{\boldsymbol{k}}, \boldsymbol{R}; \varepsilon\right) = \frac{1}{Z\left(\hat{\boldsymbol{k}}\right)} \int d\xi_k \int d^3\boldsymbol{r}\, e^{-ik.r}\, \hat{G}\left(\boldsymbol{R}+\frac{\boldsymbol{r}}{2}, \boldsymbol{R}-\frac{\boldsymbol{r}}{2}; \varepsilon\right)$$

Relative variable (s-,p-,d-wave etc)

Center of gravity variable (spatial modulation of order parameter etc)

4x4 matrix propagator with normal (diagonal) and anomalous (off-diagonal) propagators

Quasiclassical theory:

(Eilenberger.Larkin-Ovchinnikov-Eliashberg)

Transport-like equation:

$$\left[\varepsilon\hat{\tau}_3-\left(\hat{\sigma}+\hat{v}\right),\hat{g}\right]+i\hbar\vec{v}_F\cdot\nabla_{\vec{R}}\hat{g}=0$$

Normalization condition:

$$\hat{g}^2=-\pi^2\hat{1}$$

Selfconsistency equation:

$$\hat{\sigma}\left\{\hat{g}\right\}$$

Order parameter, impurities, Fermi liquid corrections,…

External field(s): Zeeman term $\hat{v}$

Quasiclassical theory:

Free energy:

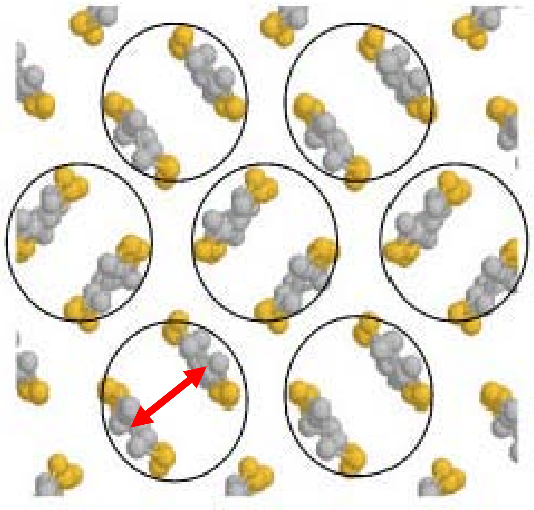
$$\Omega = \int d^3\boldsymbol{R}\ \Omega(\boldsymbol{R})$$

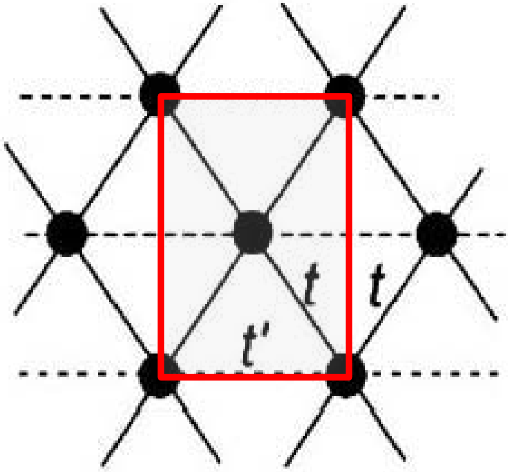
$$\Omega(\boldsymbol{R}) = \Omega_{qp}(\boldsymbol{R}) - \left\{ \begin{array}{l} \text{corrections for double counting} \\ \text{of interaction energies in quasiparticle contributions} \end{array} \right\}$$

Selfconsistency equations for superconducting order parameter and magnetization

Comparison with experiment: Electronic properties of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

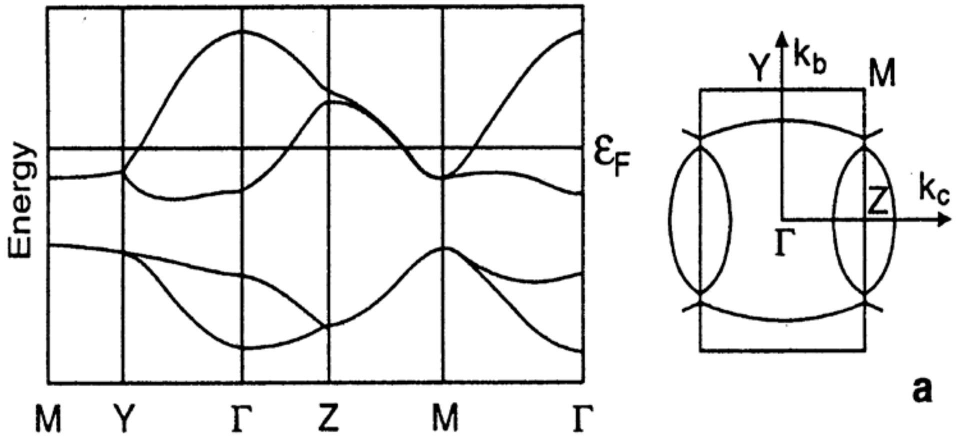
Strongly anisotropic (quasi-2D) system





Bonding-
anti-bonding bands

Comparison with experiment: Electronic properties of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$



- Strongly anisotropic (quasi-2D) system
- Effective masses are strongly anisotropic
- Nesting features
- Strongly interacting quasiparticles: pronounced electron-phonon- and electron-electron interactions
- Superconducting T_c~9-11 K

Comparison with experiment: Strategy

- **First step:** Determine model for normal state (quasiparticle interactions)

Consider upper critical field for the transition from the normal to the superconducting phase

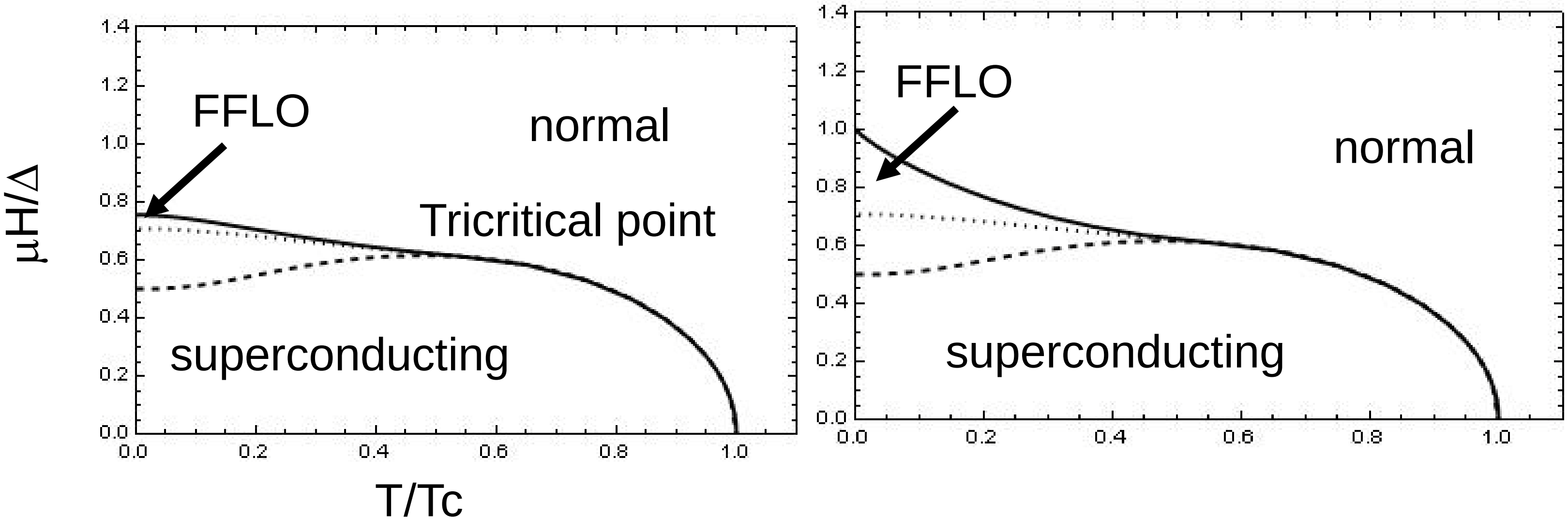
Semi-quantitative analysis: assume second order transition

- **Second step:** Detailled analysis of the superconducting phases (work in progress)

B-T- phase diagram

Isotropic system, s-wave order parameter,
no Fermi liquid interactions

3dD vs 2D



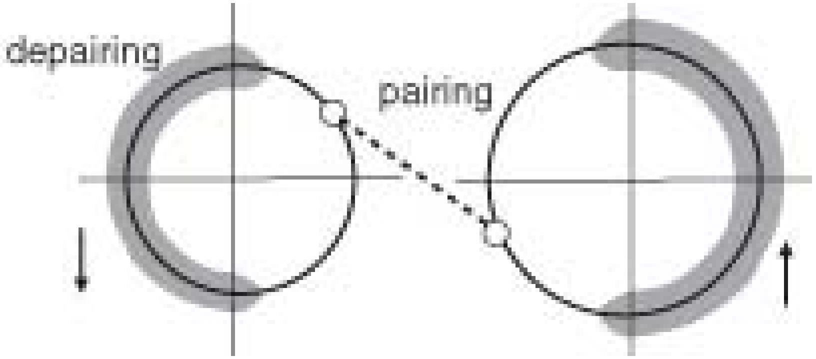
—— Transition normal – superconducting

······ 1st order transition into normal state

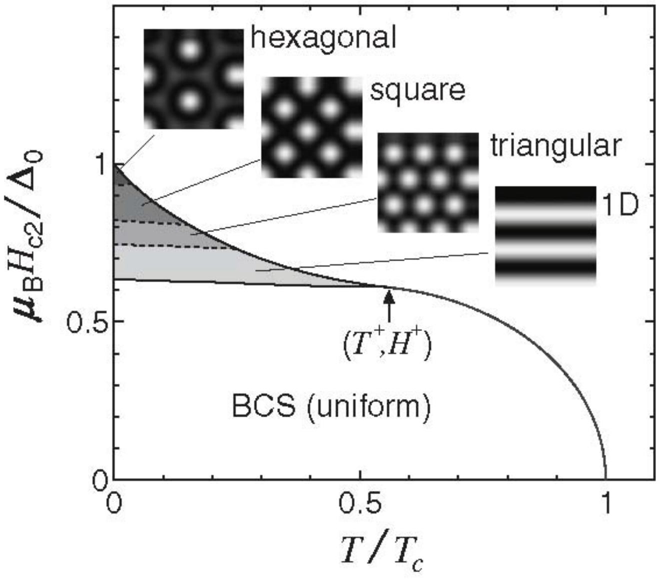
- - - - Supercooling field

B-T phase diagram: Dimensionality effect

Stability of FFLO states is enhanced in low dimensions

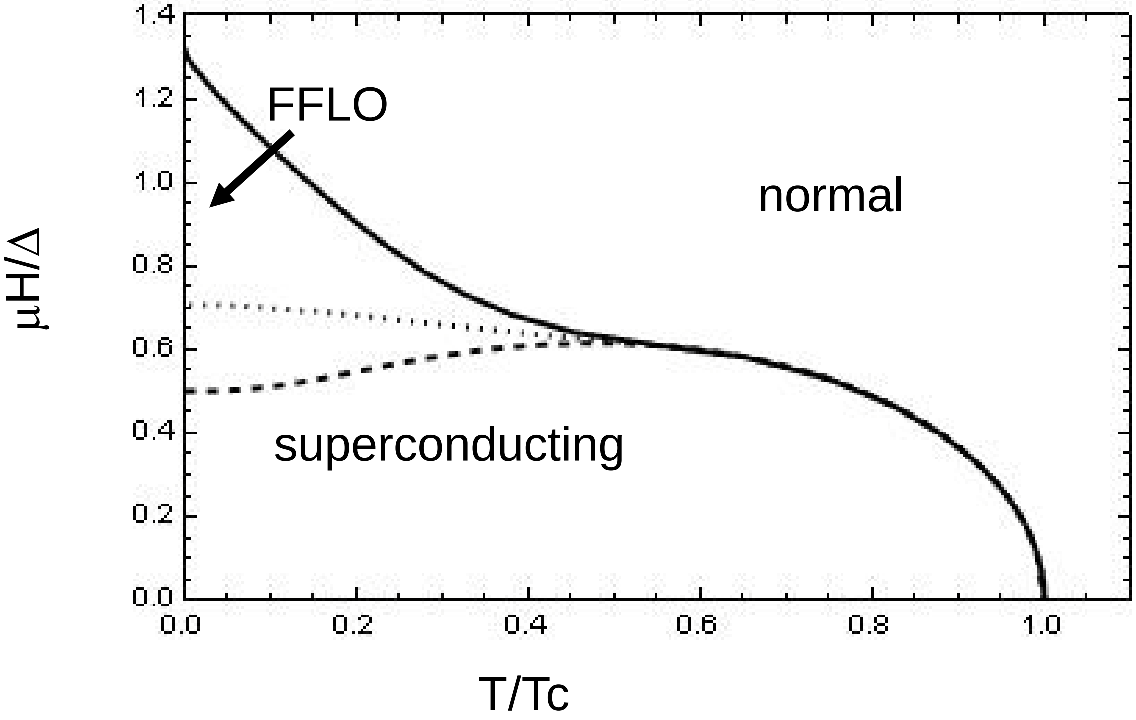


Complex phase diagram
Cylindrical FS



B-T phase diagram

Fermi surface and effective masses of
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, weak-coupling approximation
no interaction corrections
s-wave (d-wave analogous)



B-T phase diagram

Low-T upper critical magnetic field:
Influence of Fermi surface

Cylindrical FS vs model for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,
weak-coupling approximation
Strong enhancement by anisotropy in effective mass

$\frac{\frac{g}{2}\mu_B H}{\Delta(T=0)}$	s-wave	d-wave
Cylindrical FS	1.00	1.28
Model FS	1.32	1.85

B-T phase diagram: Influence of Fermi surface

Vicinity of tricritical point

Expand free energy (see Mora and Combescot)

Evaluate coefficients with quasiparticle dispersion

=> Transition stays second order in the absence of quasiparticle interactions

B-T phase diagram: Comparison with experiment

Experimental Fermi surface and effective masses from deHaas-vanAlphen experiments

s-wave (and d-wave)

Account for strong electron-phonon coupling:
Solve Eliashberg-equations
electron-phonon-spectral function chosen so as to reproduce strong-coupling corrections in gap ratio and specific heat discontinuity

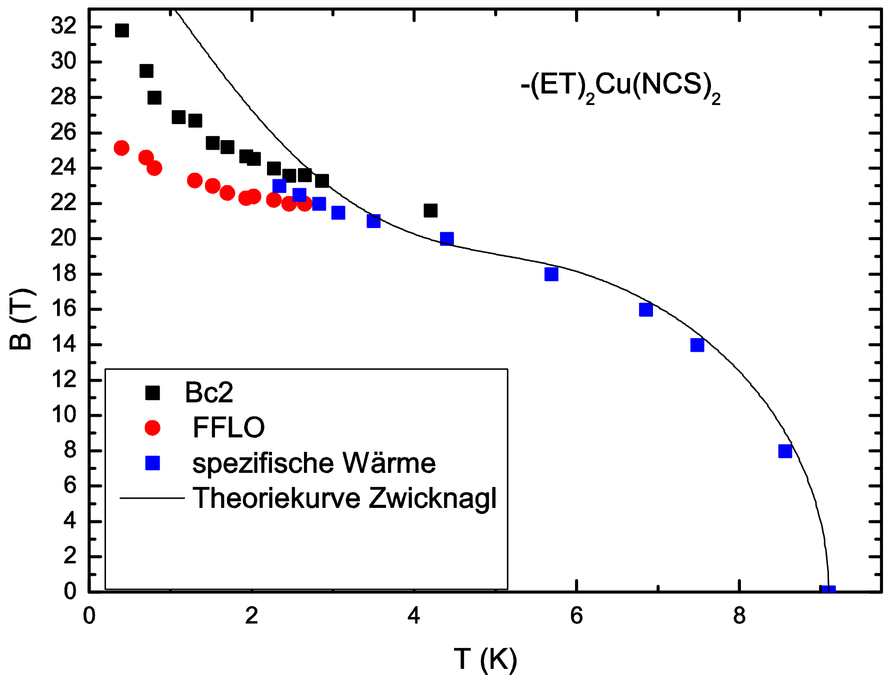
Pure system

B-T phase diagram: Preliminary result

Quasiparticle bands, s-wave superconductor, weak-coupling approximation

Additional pairbreaking at low T/ high fields

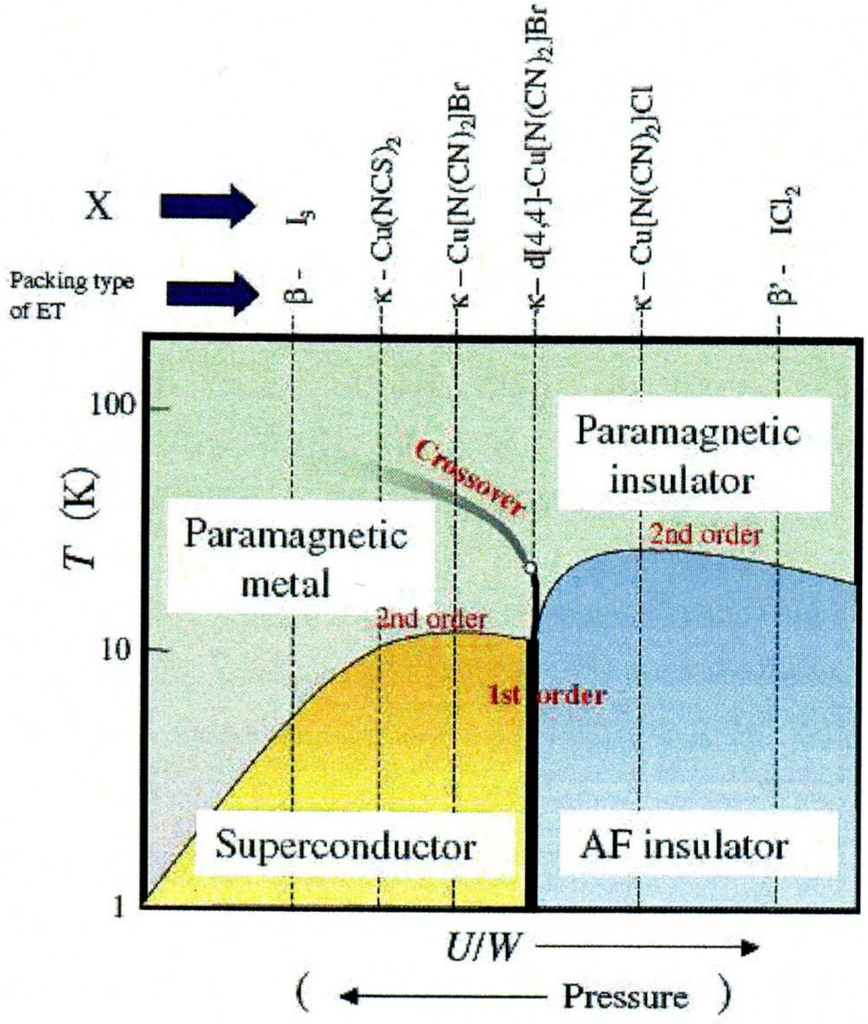
(orbital effect?)



Phase diagram B. Bergk

Work in progress: Quasiparticle interactions

Schematic phase diagram of κ-(BEDT-TTF)$_2$X



Work in progress: Magnetic quasiparticle interactions

Critical field for second order transition:
Simple rescaling

$$\mu_B B_{c2}(T;F_0^a) = \left(1+F_0^a\right)\mu_B B_{c2}(T;0$$

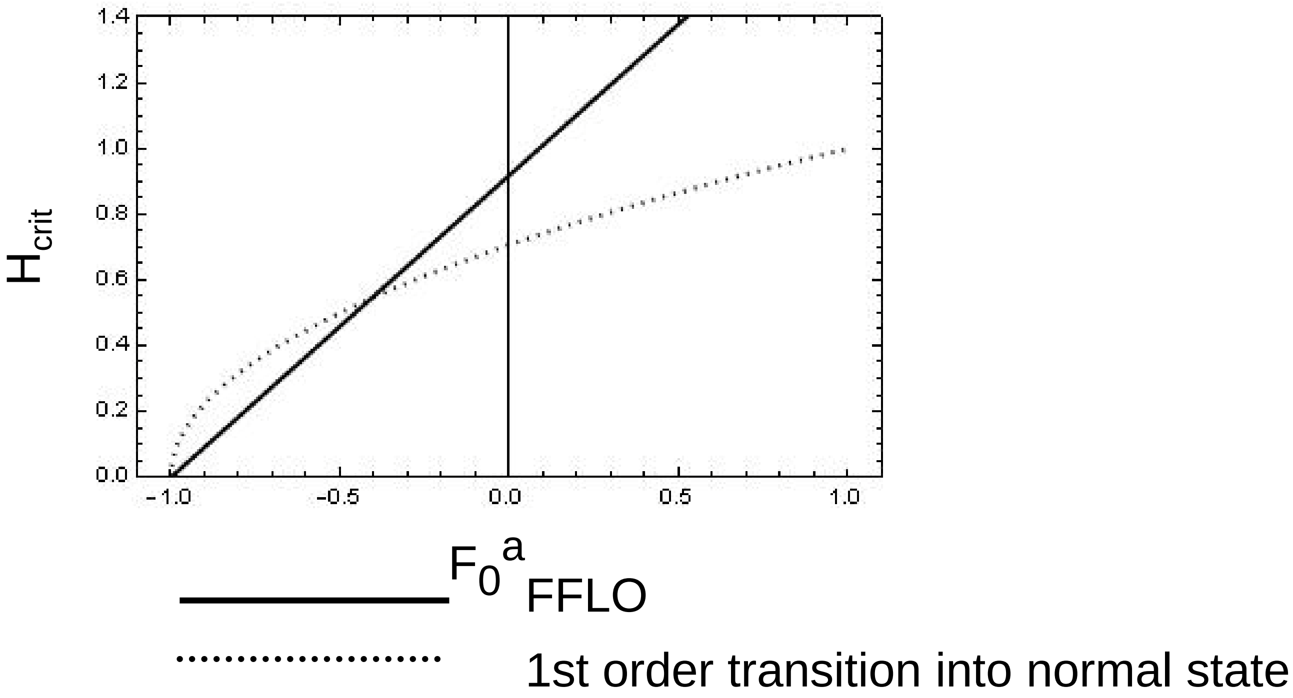
Pauli-limiting field at low T

$$\mu_B B_P(T;F_0^a) = \sqrt{1+F_0^a}\,\mu_B B_P(T;0$$

Work in progress: Magnetic quasiparticle interactions

B(T=0) for model κ-(BEDT-TTF)$_2$Cu(NCS)$_2$:

Pronounced interaction effects
Ferromagnetic interactions destabilize FFLO
Antiferromagnetic interactions stabilize FFLO



Work in progress: “Unbiased“ minimization of Free energy

$\Omega\{\hat{g},\hat{\sigma}\}$ Stationarity with respect to variations in $\hat{g},\ \hat{\sigma}$

Turn Ω into functional of self-energy
(superfluid order parameter)
Minimize numerically:

Serene/Rainer
Simplifying assumptions:
Self-energies frequency-independent
Gradient expansion

=>Detailled analysis of interaction effects,
structure of the inhomogeneous phases, orbital effect,
vortex lattice …

Summary II: Organic superconductors

- Novel superconducting phases in layered organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$
Inhomogeneous FFLO?

- Anisotropy in effective mass strongly enhances stability of inhomogeneous phase

- Quasiclassical theory for realistic model

- Experiment qualitatively reproduced

- Work in progress: Detailled analysis of interaction effects, structure of the inhomogeneous phases, orbital effect, vortex lattice …