

Thermodynamic and transport experiments on the ground state of strongly correlated electron systems

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CoG





## **TU Dresden Technical University**



Population 580 000

#### **Our research**

#### **Research goal**

Find and explore exotic states in bulk crystals Unconventional metals, magnets and superconductors Topological states



#### 2 Postdoc positions in December!



#### S. Khim, J. Landaeta, ..., E. Hassinger, Science (2021)

#### **Experimental techniques**



High sensitivity bulk techniques Magnetic ac-susceptibility  $\chi$  (20 mK - 300 K, 18 T) Electrical transport ρ (20 mK - 300 K, 18 T) Thermal transport κ (30 mK - 300 K, 8 T) Quantum oscillations

> In extreme conditions Low temperature

0.02 K - 300 K

High magnetic field

17 T + high-field labs

#### **High pressure**

0.5 mm

Piston cylinder technique, 3 GPa ( $\rho$ , $\chi$ ) Uniaxial pressure ( $\rho$ , $\chi$ ) Slide 5

# Why study strongly correlated electron systems?

Present highly interesting unconventional properties: Superconductivity at the border of magnetic phases Non-Fermi liquid behaviour near quantum critical points Odd-parity (possibly topological) unconventional superconductivity Recently discovered examples: UTe<sub>2</sub>, CeRh<sub>2</sub>As<sub>2</sub>





Knebel et al. PRB 2001 Ran et al. Nat. Phys. 2019 <sub>Slide 6</sub> Underlying question: What can we learn from thermodynamic and transport experiments about the ground state of correlated electron systems?

- 1. Basics on Fermi liquids
- 2. Extreme case of strong interactions: Heavy-fermion systems, prototype materials to study quantum criticality, example CeRh<sub>2</sub>As<sub>2</sub>
- 3. Superconductivity in a locally non-centrosymmetric system, example CeRh<sub>2</sub>As<sub>2</sub>

After hearing this lecture, you will be able to

- Interpret experimental results from some of the macroscopic experimental techniques
- Explain the competition of Kondo effect and RKKY interaction
- Relate the thermodynamic and transport properties to the ground state
- Recognise properties of locally non-centrosymmetric superconductors

#### Fermi liquid theory



- Lev Davidovich Landau 1956
- Observation: <sup>3</sup>He behave like a free fermion gas
- Interactions are taken into account by introduction of an effective mass
- Quasiparticles are N-particle excitations with same charge and spin as free particles
- Describes normal state of most metals at low temperature

Free electron gas

$$c_V = \frac{\pi^2}{3} k_B^2 N\left(\varepsilon_F\right) T = \gamma_0 T.$$

Fermi liquid: specific heat

$$\frac{C}{T} = \gamma_0 \frac{m^*}{m}.$$
  $\frac{m^*}{m} = 1 + \frac{1}{3}F_1^s$ 

Magnetic susceptibility

Fermi temperature is lowered

$$T_{
m F} \propto rac{1}{m^*}$$

 $\chi = \chi_0 \frac{m^*}{m} (1/(1+F_0^a))$ 

9

Pauli susceptibility

#### **Heavy Fermion systems**

- Typically Ce or Yb intermetallic compounds (discovered 1975 CeAl<sub>3</sub>)
- 4f shell is partly filled => local magnetic moments
- Strong interaction between f electrons and conduction electrons via Kondo effect => hybridization => large density of states at the Fermi level
- Extreme examples of Fermi liquids, effective masses of 1000 times the free electron mass
- Enhanced specific heat and magnetic susceptibility



#### **Example material CeRh<sub>2</sub>As<sub>2</sub>**





Grown by Seunghyun Khim using Bi flux

Typical sample dimensions, but smaller is possible

The structure is not relevant for the explanation of the heavy-fermion behaviour, but for superconductivity

First report by R. Madar et al., J. Less-Common Metals (1987)

## **Basic properties: Magnetic susceptibility**



- Ce: 1 electron in the f shell (L = 3, S = 1/2 => J = 5/2)
- for T > 50 K, weakly interacting moments, Curie Weiss
- effective moment very close to Ce<sup>3+</sup> value

Xo

10K

- *f*-electron localised at high temperature as in free atom
- at low T: no evidence for magnetic order, moments are screened by Kondo interaction

χ

 $\rightarrow$  trivalent Ce system with sizeable *c*-*f* hybridization



For  $T < T^*$ : Flat temperature response with high value, Pauli susceptibility of conduction electrons with large density of states at  $E_F$ 

$$\chi = \chi_0 \frac{m^*}{m} (1/(1+F_0^a))$$

## Kondo Effect

Experimental resistance

(Au with Fe impurities)





Jun Kondo '63

explanation



Conduction electrons form screening cloud around magnetic impurity Local moments are screened Non-magnetic ground state

 $T_K \sim D \exp(-1/JD(E_F))$ 



## From Kondo impurity to Kondo lattice



## **Basic properties: Magnetic susceptibility**



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- for T > 50 K, weakly interacting moments, Curie Weiss
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$$\chi = \chi_0 \frac{m^*}{m} (1/(1+F_0^a))$$

## **Electrical resistivity**



#### Resistivity

- T dependence typical for Kondo lattice systems
  - for T > 50 K: increase with decreasing T
- → Incoherent Kondo scattering (Kondo impurity model)
  - For T < 20 K: pronounced drop
- $\rightarrow$  formation of coherent Kondo lattice

#### However: Different to standard Fermi liquid at low T

- no T<sup>2</sup> above superconducting transition
- → Non-Fermi liquid behaviour



#### For $T > T^* \rho$ big and weakly Tdependent For $T \sim T^*$ maximum For $T << T^* \rho = \rho_0 + AT^2$ $A \sim \gamma^2$ is large: scattering of heavy quasiparticles<sub>Slide 16</sub>

## Specific heat



- Large, but smooth increase in C/T
- Large values of C/T  $\rightarrow$  heavy fermions
- However: Different to standard Fermi liquid at low T: No saturation => non-Fermi liquid behaviour
- → evidence for large critical fluctuations
- → Proximity to a QCP



#### **Another interaction: RKKY**



#### **RKKY** interaction

Magnetic interaction between f moments via conduction electrons magnetic ground state  $T_{RKKY} \sim J^2D(E_F) \cos(k_F r)/k_F r$ 

#### Rudermann, Kittel, Kasuya, Yosida

Local magnetic moment at x - 0, causes Friedel oscillations of the spin density of the electron gas (same coupling as Kondo), this polarises another local moment.

Weak type of exchange interaction, low transition temperatures

## Heavy Fermion systems under pressure

#### **RKKY** interaction

Magnetic interaction between f moments via conduction electrons magnetic ground state  $T_{RKKY} \sim J^2D(E_F) \cos(k_F r)/k_F r$   $m_f$ 



#### Kondo effect

m<sub>f</sub>

Conduction electrons screen f moment Non-magnetic ground state  $T_{K} \sim D \exp(-1/JD(E_{F}))$   $m_{f} \qquad s_{c}$ 

> Pressure tunes J => suppression of order at quantum critical point



Total

=0

moment

## **Classical and quantum phase transitions**



- Correlation time  $\tau \rightarrow \infty$  at  $2^{nd}$  order phase transitions
- energy of temporal OP fluctuations  $\hbar \omega = h/\tau \ll k_B T_c$ can be neglected close to  $T_c$
- However, if  $T_c = 0$ , inequality <u>never</u> holds in approach of the transition!
- Quantum critical regime: temporal OP fluctuations matter
- Criticality in effective dimension d<sub>eff</sub>=d+z with z: dynamical critical exponent
- New universality classes, different types of criticality with many unusual novel properties

• Experimental realisations: need material that displays different ground states dependent on the tuning of a non-thermal "control parameter"  $\delta$  (e.g. chemical substitution or doping, application of pressure, magnetic field, ...)

• Prime example: heavy-fermion metals

Slide 20 Slide P. Gegenwart

#### **Experimental signatures of quantum criticality**

Fermi-liquid:specific heat:  $C/T = \gamma_0$ <br/>electr. resistance:  $\rho - \rho_0 = AT^2$ Non-Fermi liquid: $C/T \sim \log (T_0/T)$ , or weak power<br/>law divergence<br/> $\rho - \rho_0 \sim T$ , or exponent below 2





v. Löhneysen et al., 1996

#### **Experimental signatures of quantum criticality**

Fermi-liquid: specific heat:  $C/T = y_0$ electr. resistance:  $\rho - \rho_0 = AT^2$  $C/T \sim \log (T_0/T)$ , or weak power Non-Fermi liquid: law divergence  $\rho - \rho_0 \sim T$ , or exponent below 2 Color is exponent of *T*-



P. Gegenwart, Q. Si, F. Steglich, Nature Phys. (2008)

 $\rho(T) = \rho_0 + AT^n$ 

# Unconventional

# ictivity near a quantum critical point





Mathur et al. Nature 1998

Knebel et al. PRB 2001

#### Possible origin of non-Fermi liquid behavior

Experiments: divergence of *C/T*, electrical resistance  $\Delta \rho \sim T^{\epsilon}$  with  $\epsilon < 2$ , different theoretical ideas:

- a) Magnetic correlations decay slowly near QCP, become strong
  - -> Quasiparticles undergo anomalous scattering & superconductivity mediated by spin fluctuations
- b) Quasiparticles disintegrate because f-electrons localize
  - -> mass divergence, change of Fermi surface from small (f-el localized) to large (f-el contribute)







Ac susceptibility, specific heat and resistivity of CeRh<sub>2</sub>As<sub>2</sub> at high temperature

- 1. Kondo-lattice system
- 2. No order down to 0.5 K
- 3. Non-Fermi liquid behavior at low temperature

-> Proximity to a quantum critical point (might be important for superconducting pairing mechanism)



#### Interesting ordered states at low temperature



# **T**<sup>0</sup> order (Phase I), non-magnetic or weakly magnetic

*T*<sub>0</sub> ~ 0.5 K

#### Heavy-fermion superconductivity

Large jump in specific heat => f electrons involved

*T*<sub>c</sub> ~ 0.35 K

- How can you recognise a heavy-fermion system from magnetic susceptibility/ resistivity/ specific heat? How do you explain their temperature dependence?
- How does the competition of Kondo interaction and RKKY interaction lead to quantum criticality in heavy-fermion systems?
- Which extraordinary phenomena can be observed near a quantum critical point?

#### Interesting ordered states at low temperature



**T**<sup>0</sup> order (Phase I), non-magnetic or weakly magnetic

*T*<sub>0</sub> ~ 0.5 K

#### **Heavy-fermion superconductivity** Large jump => f electrons involved

*T*<sub>c</sub> ~ 0.35 K

## CeRh<sub>2</sub>As<sub>2</sub> - a unique material



Switch from **SC1** to **SC2** only for H || c, large critical fields strongly exceeding Pauli limit

Unknown origin

Anisotropic in magnetic field

Switch to **Phase II** at 8 T

1. Superconductivity

## Pair breaking by magnetic field



#### Field suppression of superconductivity



## **Unusual critical fields**



### **Orbital limit**

*H* || ab Н || с 3  $CeRh_2As_2$ H || ab  $H \parallel c$  $H_{\rm orb} \sim 6 {\rm T}$ Horb 15 ★ □  $\Box \chi_{ac}(T)$  $\mathbf{F}$  $\stackrel{\sim}{\bigstar} \chi_{ac}(H)$   $\stackrel{\wedge}{\blacktriangle} M(H)$   $\stackrel{\sim}{\diamond} \lambda(H)$ \_\_\_\_\_\_ ★\_\_ 2 🖈 🙀  $\mu_0 H(T)$ 10 ₩  $\mu_0 H(T)$ 戽 1 5 0 └ 0.0 0 ∟ 0.0 0.2 0.3 0.2 0.3 0.1 0.1 *T* (K) T(K)

Above kink orbitally limited

#### Pauli limit



Enhanced Pauli limit

#### Anisotropy



Enhanced Pauli limit

Larger enhanced Pauli limit factor of 3 difference in the low-field region

#### Two superconducting states





#### **Comparison with non-centrosymmetric superconductors**



N. Kimura et al., PRL (2007) M. Sigrist, AIP conf. Proceed. (2005)

Local symmetry (non centrosymmetric) has strong impact on SC



## Non-centrosymmetric systems

Electric field => Effective magnetic field In the plane



Bauer et al. PRL (2004)

$$\vec{B} = -\frac{\vec{v}}{c} \times \vec{E} = \frac{E}{mc} (\vec{k} \times \hat{z})$$

Rashba spin-orbit coupling

$$\sum \alpha_R \, \vec{g}(\vec{k}) \cdot \vec{\sigma}_{ss'} c^{\dagger}_{\vec{k}s} c_{\vec{k}s'}$$

$$\vec{g}(\vec{k}) = k_x \hat{y} - k_y \hat{x}$$

Bands split



#### Non-centrosymmetric metals in a magnetic field



### Superconductivity in non-centrosymmetric systems

Absence of inversion symmetry => Parity is not well defined Even and odd functions mix => Singlet and triplet mixing possible

Gap equations of singlet and triplet are coupled, Since coupling is of order  $\,\alpha_R$  / E\_F channels can be studied separately



Bauer and Sigrist, Non-centrosymmetric superconductors, Lecture notes in Physics 2012

## Spin susceptibility in singlet superconductor



Singlet superconducting state

Frigeri et al. NJP 2004

Pauli susceptibility vanishes in SC state

## Spin susceptibility in singlet superconductor + Rashba



## Pauli limit in singlet superconductor + Rashba



Frigeri et al. PRL (2004)

#### Non-centrosymmetric superconductors versus CeRh<sub>2</sub>As<sub>2</sub>



Non-centrosymmetric superconductors

- Enhanced Pauli limit ("spin locking")
- Anisotropic Pauli limit with larger Pauli limit for H||c

#### But:

Kink not observed in non-centrosymmetric systems

How about locally non-centrosymmetric system?

#### Locally non-centrosymmetric superconductors

Large critical fields in layered superconductors

S. Goh, et. al. PRL (2012) Shimozawa, et. al., Rep. Prog. Phys. (2016)





#### Locally non-centrosymmetric superconductors

(a)  $-\nabla V_{loca'}$ WHH CeColn<sub>5</sub>(r CeColn<sub>5</sub>(5) Large critical fields in layered YbColn\_(5  $H_{c2\perp}/H_{c2\perp}^{orb}(T=0 \text{ K})$ YbColn<sub>5</sub>(5) superconductors MgF<sub>2</sub>-CeColn<sub>5</sub>(5) 0.5 YbColn<sub>5</sub>(5) S. Goh, et. al. PRL (2012) single crystal (strongly Pauli limited) Shimozawa, et. al., Rep. Prog. Phys. (2016) 0 0.5 0 Ce (  $T/T_{\rm c}$ AB- type (5:5) Two superconducting states Parity is well defined, no mixing 12 Even Odd Н u<sub>0</sub>H / k<sub>B</sub>T<sub>c0</sub> parity parity 8 Ν For intermediate  $+\alpha_R$  $-\Delta$  $\Delta$ Odd  $\frac{\alpha_R}{t_\perp}$ SC 4 parity  $-\alpha_R$  $\Delta$  $\Delta$ Even parity Ν ()0.5 0  $T/T_{c0}$ Yoshida, Sigrist, Yanase, PRB (2012)

. .

## **Crystal structure**



Locally non-centrosymmetric at Ce position Two Ce atoms per unit cell Alternating Ce environment Alternating Rashba interaction Globally inversion symmetric

=> Parity is well defined, no mixing

Local *C*<sub>4v</sub> point group Overall centrosymmetric

R. Madar et al., J. Less-Common Metals (1987)

#### Locally non-centrosymmetric superconductors





#### Model



 $\label{eq:HN} \begin{array}{ll} \mbox{In-plane hopping} & \mbox{Rashba SO term} \\ \hline H_N = & t_1[\cos(k_x) + \cos(k_y)] - \mu + \alpha_R \tau_z [\sin(k_x) \sigma_y - \sin(k_y) \sigma_x] \\ & + t_{c,1} \tau_x \cos(\frac{k_z}{2}) \cos(\frac{k_x}{2}) \cos(\frac{k_y}{2}) + t_{c,2} \tau_y \sin(\frac{k_z}{2}) \cos(\frac{k_x}{2}) \cos(\frac{k_y}{2}) \\ & + \lambda \tau_z \sigma_z \sin k_z (\cos k_x - \cos k_y) \sin k_x \sin k_y. \end{array}$ 

(much smaller than Rashba) => set to 0

#### **Even- to odd-parity transition**



Phase transition from even-parity to odd-parity superconductivity

SC1 Pauli limited with enhanced Pauli limit Anisotropy given by ratio  $\alpha_{
m R}/t_{
m c}$ 

Cavanagh *et al.,* PRR (2021) Large ratio from non-symmorphicity

Nogaki *et al.,* PRR (2021) Odd-parity state predicted to be **topological crystalline superconducting state** 



Hafner et al. PRX (2022)

#### Local inversion symmetry breaking A common motif

#### Inversion partner atoms Sublattice degree of freedom



Anderson, PRB (1984)



Appel and Hertel, PRB (1987) Hazra and Coleman, PRL (2023) Fischer *et al.*, Ann. Rev. Cond. Mat. (2023). <— Review paper on locally noncentrosymmetric superconductors

#### Symmetry is not everything The case of LaRh<sub>2</sub>As<sub>2</sub>



- Same structure
- Weak correlations

Landaeta et al. PRB (2022)



- Same *T*<sub>c</sub>
- Conventional Phonon coupling
- Low critical fields (orbitally limited)
- Correlations are needed!



# 2. Relation of superconductivity with Phase I

Pressure experiments

Pressure effective tuning parameter for quantum materials

What stabilises two-phase superconductivity?

Proximity to quantum critical point?

Resistivity and specific heat

*P* up to 2.67 GPa in piston cylinder pressure cell

Information on both normal and superconducting state properties

M. Pfeiffer, K. Semeniuk, J. Landaeta, R. Borth, C. Geibel, M. Nicklas, M. Brando, S. Khim, E. Hassinger, arXiv:2312.09728 (2023) K. Semeniuk, M. Pfeiffer, J. Landaeta, M. Nicklas, C. Geibel, M. Brando, S. Khim, E. Hassinger, arXiv:2312.09729 (2023)



#### Proximity to a quantum critical point



#### Specific heat

Huge Sommerfeld coefficient => Large effective mass

Non-Fermi liquid behaviour

#### Resistivity

~ **7**0.5

Low ordering temperature *T*<sup>0</sup> Phase I QCP?

Is superconductivity stabilised by quantum fluctuations of Phase I?

## Experimental signatures of the transition at $T_0$



No anomaly observed at  $T_0$  in susceptibility and magnetization

Weak magnetic or non-magnetic order

Microscopic information missing

Mishra *et al.,* PRB (2022) D. Hafner *et al.*, PRX (2022)

0

0.5

(b)

(c)

1.5

1.5

1.0

1.0

*T* (K)

# Anisotropy of $T_0$ in field with strong enhancement for $H \perp c$



Hafner, *et al.,* PRX (2022) K. Semeniuk, et al., PRB (2023) Kibune et al. PRL (2022) Ogata et al. PRL (2023) Machida, PRB (2022) Schmidt and Thalmeier, arxiv (2024) Strong increase of  $T_0$  for inplane fields not expected for AF order

NQR/NMR Onset of AF order below 0.25 K = bulk *T*<sub>c</sub> of that sample

Third order parameter? Accidentally same critical temperature as SC?

Possibility that H\* is a magnetic transition???

Here, we focus on  $T_c$  and  $T_0$ no evidence for extra AF state in our measurements.

## Suppression of *T*<sub>c</sub>





Monotonous decrease of  $T_c$  by factor of 2

# T<sub>0</sub> suppressed by pressure

![](_page_59_Figure_1.jpeg)

![](_page_59_Figure_2.jpeg)

#### Suppression of T<sub>0</sub>

#### T<sub>0</sub> suppressed by pressure

![](_page_60_Figure_1.jpeg)

## Quantum critical point of Phase I and superconducting dome

*H* = 0

![](_page_61_Figure_2.jpeg)

Quantum critical point of Phase I

 $P_0 = 0.5 \text{ GPa}$ 

Dome of superconductivity around  $P_0$ 

Quantum critical fluctuations of Phase I are driving superconductivity

#### **Temperature dependence of resistivity**

![](_page_62_Figure_1.jpeg)

Power-law analysis  $\rho(T) = \rho_0 + A^* (T/T_{ref})^n$ , with  $T_{ref} = 0.3$  K. Increase of exponent to n = 2 at 2.67 GPa => Recovery of Fermi liquid behavior below  $T^* = 0.2$  K at 2.67 GPa

A\* coefficient decreases for  $P > P_0$ Corresponds to  $\rho(T_{ref}) - \rho(T = 0)$ 

When  $T_{ref}$  = const

=> Decrease of correlations with pressure (A  $\sim$  m<sup>\*</sup><sup>2</sup>)

Confirmation of quantum critical behavior!

# Critical field *H* || *c*

![](_page_63_Figure_1.jpeg)

Two superconducting states survive up to 2.67 GPa

Strong decrease of *H*\* What does that mean for model?

3

# Critical field *H* || *c* : comparison with model

![](_page_64_Figure_1.jpeg)

#### $T_{\rm c}$ (SC2) approaches $T_{\rm c}$ (SC1)

Strong pressure dependence is quite interesting.

How can this be explained?

## Critical field *H* | | *c* : Model expectations

![](_page_65_Figure_1.jpeg)

Yoshida, Sigrist, Yanase, PRB (2012)

![](_page_66_Figure_1.jpeg)

Extrapolation:  $T_c$  (SC2) will become equal to  $T_c$  (SC1) very quickly at 3 GPa

 $T_{\rm c}$  (SC2) >  $T_{\rm c}$  (SC1) is impossible within current model

Extension of current theory

1. Odd parity interaction becomes stronger with pressure, phase transition in zero field as a function of pressure from even-parity to odd-parity state

To be tested...

#### **Pressure dependence - summary**

#### Rather traditional pressure phase diagram with

Quantum critical point of Phase I at 0.5 GPa (but unknown order)

Superconducting dome

#### Two-phase superconductivity

 $T_c$  suppressed but two states survive

Odd-parity superconductivity is stabilised by pressure Prospect for odd-parity superconductivity in zero field? Beyond the current theoretical understanding.

For more microscopic understanding, direct measurements of the order parameter of Phase I and of the Fermi surface (and its changes with pressure) are necessary.

![](_page_67_Figure_8.jpeg)