Flux growth of CeCu$_2$Si$_2$, YbRh$_2$Si$_2$
and of layered Fe-pnictide systems

- CeCu$_2$Si$_2$: growth of large single crystals with precisely tuned physical properties

- YbRh$_2$Si$_2$ and YbIr$_2$Si$_2$: growth of high melting compounds with volatile Yb

- CeTPnO compounds (transition metal, Pn = P, As): Compounds with very reactive and volatile elements

Crystal grower:
- CeCu$_2$Si$_2$: *Micha Deppe*  *Hirale S. Jeevan*
- YbRh$_2$Si$_2$: *Octavio Trovarelli*  *Julia Ferstl*  *Sebastian Taube*
  *Zakir Hossain*  *Cornelius Krellner*  *Christoph Klinger*
- CeTPnO: *Nagesh Kini*  *Cornelius Krellner*  *Anton Jesche*
Our interest: Kondo lattice systems

- Kondo lattices: intermetallic compounds based on Ce, Yb

- Ce, Yb: unstable f shell
  ⇒ transition from a magnetic (Ce\(^{3+}\)) to a non-magnetic state (Ce\(^{4+}\))

- Tuning parameter: hybridization \( g \) between f and conduction electr.
  → can be changed by pressure or chemical composition
  → characteristic energy: Kondo temperature \( T_K \)

- Near crossover: ⇒ Strong correlation effects
  → Unconventional metallic states: * heavy quasi particles
    * Non-Fermi-liquid behavior
  → Unconventional superconducting states: * p- or d-wave symmetry
    * mediated by magnetic interactions?
CeCu$_2$Si$_2$

- First investigation: B.C. Sales and R. Viswanathan 1976
  - Kondo temp. $T_K = 10$ K
  - Sommerfeld coefficient $\gamma = 800$ mJ/K$^2$mol

- First Heavy Fermion superconductor (Steglich et al. 79)

  - $T_c = 0.6$ K
  - Large specific heat anomaly at $T_c$

  $\Delta C \approx \gamma T_c \Rightarrow 4f$ electrons forms SC state

Specific heat $C/T = f(\ln T)$
But there is a further ordered phase

- Y. J. Uemura et al. 1988 (μSR)
  Nakamura et al. 1988 (NMR)
- G. Bruls et al. 1994 (ultrasound)
- R. Feyerherm et al. 1995 (μSR)

→ observation of a further unconventional state (A-Phase)
  * magnetic?
  * but no magnetic Bragg peaks!
  * compete with superconductivity!

- Extreme sample dependence of physical properties
- Growth of single crystals with defined physical properties very difficult
Effect of composition

- Investigation of effect of composition using slightly off-stoichiometric polycrystalline material. → clear relation between composition and magnetic/superconductive properties

- Homogeneity region quite small
  * below accuracy of EDX
  * no clear changes in structural parameters

- Nevertheless
  → Different ground states within narrow homogeneity region

S: superconducting state
A/S: competition between magnetic and SC state
A: magnetically ordered state
X: disordered magnetic state
Origin of peculiar behavior of CeCu$_2$Si$_2$

- Investigation of the alloy CeCu$_2$(Si$_{1-x}$Ge$_x$)$_2$ replacing Si by Ge → negative chemical pressure
- Investigation of CeCu$_2$Si$_2$ under isostatic pressure

⇒ Phase diagram as function of f-hybridization $g$

⇒ CeCu$_2$Si$_2$ is located at a quantum critical point!

⇒ strong dependence on sample composition

Open questions:
- Nature of A-Phase
- Nature of superconducting phase
- Relation between magnetism and superconductivity
Growth of single crystals

- $\text{CeCu}_2\text{Si}_2$ forms peritectically at 1520 °C
  - growth from Cu-rich melt
  - control of composition?
  - evaporation of Cu!

- Previous work:
  - Aliev et al. [82], Schneider et al. [83]: Czochralski from stochiometric melt
  - Stewart et al. [83]: from In flux
    - no superconductivity
  - Batlogg et al. [84], from In, Sn, Cu flux: only Cu flux leads to SC crystals but large residual resistivity
  - Assmus et al. [84]: Bridgman from Cu-rich melt: very small SC single crystals, low residual resistivity
  - Onuki et al. [84]: Czochralski from Cu rich melt: larger single crystals but higher residual resistivity
Growth of single crystals

- Problems: - no single crystal large enough for neutron scattering experiments
  - no control of physical properties

- Our approach: growth from Cu flux (40mol% Cu, 60 mol% CeCu₂Si₂)
  → comparatively high growth temperatures( 1500 °C)

- How to control Cu : Si ratio in the presence of excess Cu?
  
  → by changing the Ce : Si ratio
    - large Ce-content → Cu rich phase
    - small Ce-content → Si rich phase

  → magnetic and SC properties could be reproducibly tuned by changing starting composition

- Ce₀.₉Cu₂Si₂ + Cu flux → A
- Ce₀.₉₅Cu₂Si₂ + Cu flux → A/S
- Ce₁Cu₂Si₂ + Cu flux → S /A
- Ce₁.₀₅Cu₂Si₂ + Cu flux → S

Single crystals 0.5 - 5 g
Growth of single crystals

Element | Purity
--- | ---
Ce | 4N (99.99 %)
Cu | 6N
Si | 6N

Arc melting

Temperatur programm

- 2 Std.
-1.2°C/Std.
-2.2°C/Std.
-3.2°C/Std.
+300°C/Std.
-300°C/Std.

Time (hours)
different ground states evidenced by specific heat

$\text{Ce}_{0.90} \rightarrow \text{A-type, only AF order}$

$\text{Ce}_{0.95} \rightarrow \text{A/S-type (highest RRR)}$

$\text{Ce}_{1.00} \rightarrow \text{S/A-type}$

$\text{Ce}_{1.05} \rightarrow \text{S-type, only SC}$
Competition between Magnetism and superconductivity in A/S-CeCu$_2$Si$_2$

- $T_N \approx 700$ mK
- $T_c \approx 550$ mK
- $B_{c2} \approx 1$ T

- Superconductivity destroy magnetism
- No coexistence of AF and SC on microscopic scale
- Confirmation by $\mu$SR and NQR
  [R. Feyerherm, 97; K. Ishida, '99]

$Q \approx (0.22, 0.22, 1.47)$

$\chi_{ac}$ (arb. units)

- $B (T)$
- $T (K)$
**YbRh$_2$Si$_2$ and YbIr$_2$Si$_2$**

- Huge number of Ce-based Kondo lattices, but only few Yb-based ones
  - synthesis and crystal growth much more difficult: ← high Yb vapor pressure

- YbRh$_2$Si$_2$: known before:
  - structure (Rossi et al 1979)
  - one $\rho(T,p)$ study on polycrystal (Thompson et al. 1987)

- Our work; first growth of single crystals, O. Trovarelli et al., 2000, from In-flux
  - $\Rightarrow$ YbRh$_2$Si$_2$ extremely close to the quantum critical point where antiferromagnetic order disappears: $T_N$ only 70 mK

- In flux $\rightarrow$ small crystals, but high quality
  - later on adopted by further groups (Lapertot, Fisk, Petrovic)

- R. Hu et al. [07]: growth from Zn flux
  - $\Rightarrow$ larger single crystals but poor quality
  - $\Rightarrow$ Zn incorporation in 122 phase
Single crystal growth

Problem:
- Yb has a low boiling point: \( T_b = 1196 \, ^\circ\text{C} \)
- Rh, Ir have high melting points: \( T_{m,Rh} = 1966 \, ^\circ\text{C} \), \( T_{m,Ir} = 2410 \, ^\circ\text{C} \)

➤ Indium flux growth with 96 at% In using Bridgman technique

Excess In-flux is dissolved in diluted HCl

\( \text{Al}_2\text{O}_3 \)-crucible

Closed Ta-crucible

Ta-crucible

Xerion 2-zone furnace
YbRh$_2$Si$_2$-Tuning the temperature profile

- DTA => Formation of YbRh$_2$Si$_2$ at 1480 °C (with 96 at% In)
- Linear cooling down at higher $T$ yields better crystallinity
  $RR_{1.8K} = 30$

a. homogenization at 1520 °C

b. linear cooling down of lower zone
  => $T$ gradient

c. Bridgman
YbRh$_2$Si$_2$-Tuning the initial composition

- Excess Yb compared to Rh and Si yields thicker crystals
- Excess Rh compared to Si yields better crystallinity

Starting composition: 3 at% Yb : 2.2 at% Rh : 1.8 at% Si : 93 at% In
YbRh$_2$Si$_2$ single crystals

- Size of single crystal increased to
  - surface 50 mm$^2$
  - d = 0.8 mm

- high quality: $\rho_0 = 0.45$ $\mu\Omega$cm  
  (RRR = 150)
  $\Rightarrow$ extremely sharp transition despite very low $T_N = 70$ mK

Specific heat near $T_N$

![Specific heat graph]

J. Custers et al., Nature 424, 524
YbIr$_2$Si$_2$ - Polymorphism

- Crystallizes in 2 different structures (depending on growth conditions)
- Similar to polymorphism in LaIr$_2$Si$_2$ or CeIr$_2$Si$_2$

**I-type (ThCr$_2$Si$_2$)**

- Tuning parameters of YbRh$_2$Si$_2$ are not applicable
- Excess Yb favors the P-type Structure
- Annealing (150 hrs @ 1000 °C) yields the I-type structure
YbIr$_2$Si$_2$ and YbCo$_2$Si$_2$ single crystals

- Method extended to YbIr$_2$Si$_2$, YbCo$_2$Si$_2$ and Yb(Ir$_1$-xCox)$_2$Si$_2$

YbIr$_2$Si$_2$ (I type)

- Investigation of physical properties
  * YbIr$_2$Si$_2$, is on the non-magnetic side of the quantum critical point
  * YbCo$_2$Si$_2$ is deep in the magnetic region

⇒ alloys between 3 compounds cover whole range of the phase diagram
CeTPnO compounds

- Discovered by Zimmer et al., 1995
- Tetragonal ZrCuSiAs structure type
  - Layered structure
  - Alternating CeO and TP layers
  - Intermediate between oxide and intermetallic compounds
- Our original interest: search for ferromagnetic Kondo lattice systems
  - Strong ferromagnetic exchange in RTX compounds with related CeFeSi or CeScSi structure
- Since February 2008:
  - High Tc (up to 55 K) superconductivity in doped RFeAsO (R = rare earth)
  - First single crystals of RTPnO
- Using Sn flux
  - Polycrystals for T = Ru, Os, Fe, Co
  - Kamihara et al. [08], Ren et al., [08]
  - Now CeRuPO, CeFePO, CeFeAsO
Synthesis — CeTPO

Problems:

- P  ⇒  high vapor pressure, very reactive
- Ru, Os  ⇒  high melting points:  
  \[ T_{m,Ru} = 2310 \, ^\circ\text{C}, \ T_{m,Os} = 3045 \, ^\circ\text{C} \]
- Fe, Co  ⇒  magnetic impurity phases

- Sn flux technique
- Sealed in evacuated Quartz ampoule
- Excess Sn is dissolved in diluted HCl
Tuning the crystal growth - CeRuPO

- Tuning the initial composition
  \[ 8_{\text{at}}\% \text{Ce} : 6_{\text{at}}\% \text{P} : 4_{\text{at}}\% \text{RuO}_2 : 82_{\text{at}}\% \text{Sn} \]
- Tuning the temperature profile
  \[ \Rightarrow \text{Higher temperatures (T~1500°C, Al}_2\text{O}_3\text{- in Ta-crucible) with pre-reacted Sn-P} \]
- Small plate-like single crystals (2 x 1 x 0.1 mm\(^3\) ~ 1 mg)
- Side products: single crystals of CeRu\(_2\)P\(_2\), Ce\(_3\)Ru\(_4\)Sn\(_{13}\)

Largest RTepnO single crystals available today
EDX & XRD — CeRuPO

- EDX & XRD: no foreign phases
  ⇒ Ce:Ru:P ≡ 1:1:1
- Oxygen occupancy:
  PC: carrier gas-hot extraction
  ⇒ \( x_O = (25.0 \pm 0.7) \) at%
  SC: no change of \( c \)-parameter
  expected if \( x_O \) different to PC

<table>
<thead>
<tr>
<th>Material</th>
<th>Poly crystal CeRuPO</th>
<th>Single crystal CeRuPO</th>
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<td>( c [\text{Å}] )</td>
<td>8.256(2)</td>
<td>8.259(1)</td>
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<tr>
<td>( c/a )</td>
<td>2.050(1)</td>
<td>2.051(1)</td>
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CeFePO and CeFeAsO

- Similar synthesis and growth process
  - but lower flux content
    - higher solubility of Fe
    - lower melting points of binary R-As

Temperature profile

1. pre-reaction of Sn an $Pn$

2. synthesis at $T = 1500 \, ^\circ\text{C}$
Extraction of single crystals

- With hydrochloric acid: works well for CeRuPO and CeFePO - but attacks CeFeAsO
- With centrifuge: problem for small single crystals

Presently largest available RFePnO single crystals
Crystal characterization

XRD: $\Rightarrow$ P4/nmm, no foreign phases

EDX $\Rightarrow$ Ce:Fe:Pn 1 : 1 : 1
Resistivity — CeRuPO

- Typical for Kondo lattice systems
  - strong decrease well above $T_C$
- High residual resistivity ratio (RRR = 50)
  ⇒ good sample quality
- Well resolved anomaly at $T_C$
CeFeAsO: Fe magnetism

- ReFeAsO: at $T_0 \approx 150$ K: structural transition tetragonal $\rightarrow$ Orthorhombic
  at $T_N \approx 140$ K: columnar AF ordering of weak Fe moments

- Our single crystals: * pronounced sharp anomaly in $\rho(T)$ at $T_0$, $T_N$
  * much larger $\text{RRR} \approx 11$ than in polycrystals ($\text{RRR} \approx 2$)
  * for $T < T_0$ pronounced metallic behavior, no MI transition

\[ \text{resistivity} \]

\[ \text{specific heat} \]

- $C(T)$: at $T_0$, $T_N$: broad, double peaked anomaly
  * larger than in polycrystals
  * peak separation smaller
Summary

- Flux technique well adapted for growth of single crystals with volatile and/or very reactive elements for fundamental research purpose

- Tuning of starting composition important for growth of larger, high quality single crystals

- Physical properties can be controlled quite precisely by starting composition