Heavy Electrons: Electrons at the Brink of Magnetism Lecture I.

- Spin Entropy a driving force for new physics
- 2) Landau Fermi liquid theory
- (see viewgraphs for details.)
- 3) Local Fermi liquids with a single scale.
- 4) Kadowaki Woods Relation.

important clues (Curro *et al.*, 2005) to the ongoing quest to discover room-temperature superconductivity.

# 1.2 Key elements of heavy-fermion metals

Before examining the theory of heavy-electron materials, we make a brief tour of their key properties. Table 1 shows a selective list of heavy fermion compounds

# 1.2.1 Spin entropy: a driving force for new physics

The properties of heavy-fermion compounds derive from the partially filled f orbitals of rare-earth or actinide ions (Stewart, 1984; Lee *et al.*, 1986; Ott, 1987; Fulde, Keller and Zwicknagl, 1988; Grewe and Steglich, 1991). The large nuclear charge in these ions causes their f orbitals to collapse inside the inert gas core of the ion, turning them into localized magnetic moments.

Moreover, the large spin-orbit coupling in f orbitals combines the spin and angular momentum of the f states into a

Table 1. Selected heavy-fermion compounds.

Туре	Material	<i>T</i> * (K)	$T_c, x_c, B_c$	Properties	ρ	$ m J mol^{-1} K^{-2}  \gamma_n $	References
Metal	CeCu <sub>6</sub>	10	_	Simple HF metal	$T^2$	1600	Stewart, Fisk and Wire (1984a) and Onuki and Komatsubara (1987)
Super- conductors	CeCu <sub>2</sub> Si <sub>2</sub>	20	$T_c = 0.17 \mathrm{K}$	First HFSC	$T^2$	800-1250	Steglich <i>et al.</i> (1976) and Geibel <i>et al.</i> (1991a,b)
	UBe <sub>13</sub>	2.5	$T_c = 0.86 \mathrm{K}$	Incoherent metal→HFSC	$ ho_c \sim$ 150 u $\Omega$ cm	800	Ott, Rudigier, Fisk and Smith (1983, 1984)
	CeCoIn <sub>5</sub>	38	$T_c = 2.3$	Quasi 2D HFSC	T	750	Petrovic <i>et al.</i> (2001) and Sidorov <i>et al.</i> (2002)
Kondo insulators	Ce <sub>3</sub> Pt <sub>4</sub> Bi <sub>3</sub>	$T_{\chi} \sim 80$	_	Fully gapped KI	$\sim e^{\Delta/T}$	_	Hundley <i>et al.</i> (1990) and Bucher, Schlessinger, Capfield and Fick (1994)
	CeNiSn	$T_{\chi} \sim 20$	_	Nodal KI	Poor metal	_	Takabatake <i>et al.</i> (1994) and Izawa <i>et al.</i> (1999)
Quantum critical	$CeCu_{6-x}Au_x$	$T_0 \sim 10$	$x_c = 0.1$	Chemically tuned QCP	Т	$\sim \frac{1}{T_0} \ln \left( \frac{T_0}{T} \right)$	von Löhneysen et al. (1994) and von Löhneysen (1996)
	YbRh <sub>2</sub> Si <sub>2</sub>	$T_0 \sim 24$	$B_{\perp} = 0.06 \mathrm{T}$ $B_{\parallel} = 0.66 \mathrm{T}$	Field-tuned QCP	Т	$\sim \frac{1}{T_0} \ln\left(\frac{T_0}{T}\right)$	Trovarelli <i>et al.</i> (2000), Paschen <i>et al.</i> (2004), Custers <i>et al.</i> (2003) and Gegenwart <i>et al.</i> (2005)
SC + other order	UPd <sub>2</sub> Al <sub>3</sub>	110	$T_{AF} = 14 \text{ K},$ $T = -2 \text{ K}$	AFM + HFSC	$T^2$	210	Geibel <i>et al.</i> (1991a), Sato <i>et al.</i> (2001) and Tou <i>et al.</i> (1995)
	URu <sub>2</sub> Si <sub>2</sub>	75	$T_{sc} = 2.4$ $T_1 = 17.5$ K, $T_{sc} = 1.3$ K	Hidden order and HFSC	$T^2$	120/65	Palstra <i>et al.</i> (1985) and Kim <i>et al.</i> (2003)

Unless otherwise stated,  $T^*$  denotes the temperature of the maximum in resistivity.  $T_c$ ,  $x_c$ , and  $B_c$  denote critical temperature, doping, and field.  $\rho$  denotes the temperature dependence in the normal state.  $\gamma_n = C_V/T$  is the specific heat coefficient in the normal state.

state of definite J, and it is these large quantum spin degrees of freedom that lie at the heart of heavy-fermion physics.

Heavy-fermion materials display properties which change qualitatively, depending on the temperature, so much so, that the room-temperature and low-temperature behavior almost resembles two different materials. At room temperature, high magnetic fields, and high frequencies, they behave as local moment systems, with a Curie-law susceptibility

$$\chi = \frac{M^2}{3T} \qquad M^2 = (g_J \mu_B)^2 J (J+1) \qquad (5)$$

where M is the magnetic moment of an f state with total angular momentum J and the gyromagnetic ratio  $g_J$ . However, at temperatures beneath a characteristic scale, we call  $T^*$  (to distinguish it from the single-ion Kondo temperature  $T_K$ ), the localized spin degrees of freedom melt into the conduction sea, releasing their spins as mobile, conducting f electrons.

A Curie susceptibility is the hallmark of the decoupled, rotational dynamics of the f moments, associated with an unquenched entropy of  $S = k_{\rm B} \ln N$  per spin, where N = 2J + 1 is the spin degeneracy of an isolated magnetic moment of angular momentum *J*. For example, in a Ceriumheavy electron material, the 4f<sup>1</sup> (*L* = 3) configuration of the Ce<sup>3+</sup> ion is spin-orbit coupled into a state of definite J = L - S = 5/2 with N = 6. Inside the crystal, the full rotational symmetry of each magnetic f ion is often reduced by crystal fields to a quartet (N = 4) or a Kramer's doublet N = 2. At the characteristic temperature  $T^*$ , as the Kondo effect develops, the spin entropy is rapidly lost from the material, and large quantities of heat are lost from the material. Since the area under the specific heat curve determines the entropy,

$$S(T) = \int_0^T \frac{C_V}{T'} \mathrm{d}T' \tag{6}$$

a rapid loss of spin entropy at low temperatures forces a sudden rise in the specific heat capacity. Figure 5 illustrates this phenomenon with the specific heat capacity of UBe<sub>13</sub>. Notice how the specific heat coefficient  $C_V/T$  rises to a value of order 1 J mol<sup>-1</sup>K<sup>2</sup>, and starts to saturate at about 1 K, indicating the formation of a Fermi liquid with a linear specific heat coefficient. Remarkably, just as the linear specific heat starts to develop,  $UBe_{13}$  becomes superconducting, as indicated by the large specific heat anomaly.

### 1.2.2 'Local' Fermi liquids with a single scale

The standard theoretical framework for describing metals is Landau–Fermi liquid theory (Landau, 1957), according to which the excitation spectrum of a metal can be adiabatically



**Figure 5.** Showing the specific heat coefficient of  $UBe_{13}$  after (Ott, Rudigier, Fisk and Smith, 1985). The area under the  $C_V/T$  curve up to a temperature *T* provides a measure of the amount of unquenched spin entropy at that temperature. The condensation entropy of HFSCs is derived from the spin-rotational degrees of freedom of the local moments, and the large scale of the condensation entropy indicates that spins partake in the formation of the order parameter. (Reproduced from H.R. Ott, H. Rudigier, Z. Fisk, and J.L. Smith, in W.J.L. Buyers (ed.): *Proceedings of the NATO Advanced Study Institute on Moment Formation in Solids, Vancouver Island*, August 1983, Valence Fluctuations in Solids (Plenum, 1985), p. 309. with permission of Springer Science and Business Media.)

connected to those of a noninteracting electron fluid. Heavyfermion metals are extreme examples of Landau–Fermi liquids which push the idea of adiabaticity into an regime where the bare electron interactions, on the scale of electron volts, are hundreds, even thousands of times larger than the millivolt Fermi energy scale of the heavy-electron quasiparticles. The Landau–Fermi liquid that develops in these materials shares much in common with the Fermi liquid that develops around an isolated magnetic impurity (Nozières, 1976; Nozières and Blandin, 1980), once it is quenched by the conduction sea as part of the Kondo effect. There are three key features of this Fermi liquid:

- Single scale: T\* The quasiparticle density of states ρ\* ~ 1/T\* and scattering amplitudes A<sub>kσ,k'σ'</sub> ~ T\* scale approximately with a single scale T\*.
- Almost incompressible: Heavy-electron fluids are 'almost incompressible', in the sense that the charge susceptibility  $\chi_c = dN_e/d\mu \ll \rho^*$  is unrenormalized and typically more than an order of magnitude smaller than the quasiparticle density of states  $\rho^*$ . This is because the lattice of spins severely modifies the quasiparticle density of states, but leaves the charge density of the fluid  $n_e(\mu)$ , and its dependence on the chemical potential  $\mu$  unchanged.

• *Local:* Quasiparticles scatter when in the vicinity of a local moment, giving rise to a small momentum dependence to the Landau scattering amplitudes (Yamada, 1975; Yoshida and Yamada, 1975; Engelbrecht and Bedell, 1995).

Landau–Fermi liquid theory relates the properties of a Fermi liquid to the density of states of the quasiparticles and a small number of interaction parameters (Baym and Pethick, 1992). If  $E_{\mathbf{k}\sigma}$  is the energy of an isolated quasiparticle, then the quasiparticle density of states  $\rho^* = \sum_{\mathbf{k}\sigma} \delta(E_{\mathbf{k}\sigma} - \mu)$  determines the linear specific heat coefficient

$$\gamma = \operatorname{Lim}_{T \to 0} \left( \frac{C_V}{T} \right) = \frac{\pi^2 k_{\rm B}^2}{3} \rho^* \tag{7}$$

In conventional metals, the linear specific heat coefficient is of the order  $1-10 \text{ mJ mol}^{-1} \text{ K}^{-2}$ . In a system with quadratic dispersion,  $E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m^*}$ , the quasiparticle density of states and effective mass  $m^*$  are directly proportional

$$\rho^* = \left(\frac{k_F}{\pi^2 \hbar^2}\right) m^* \tag{8}$$

where  $k_F$  is the Fermi momentum. In heavy-fermion compounds, the scale of  $\rho^*$  varies widely, and specific heat coefficients in the range 100–1600 mJ mol<sup>-1</sup> K<sup>-2</sup> have been observed. From this simplified perspective, the quasiparticle effective masses in heavy-electron materials are two or three orders of magnitude 'heavier' than in conventional metals.

In Landau–Fermi liquid theory, a change  $\delta n_{\mathbf{k}'\sigma'}$  in the quasiparticle occupancies causes a shift in the quasiparticle energies given by

$$\delta E_{\mathbf{k}\sigma} = \sum_{\mathbf{k}'\sigma'} \mathbf{f}_{\mathbf{k}\sigma,\mathbf{k}\sigma'} \delta n_{\mathbf{k}'\sigma'} \tag{9}$$

In a simplified model with a spherical Fermi surface, the Landau interaction parameters only depend on the relative angle  $\theta_{\mathbf{k},\mathbf{k}'}$  between the quasiparticle momenta, and are expanded in terms of Legendre Polynomials as

$$\mathbf{f}_{\mathbf{k}\sigma,\mathbf{k}\sigma'} = \frac{1}{\rho^*} \sum_{l} (2l+1) P_l(\theta_{\mathbf{k},\mathbf{k}'}) [F_l^s + \sigma \sigma' F_l^a] \quad (10)$$

The dimensionless 'Landau parameters'  $F_l^{s,a}$  parameterize the detailed quasiparticle interactions. The s-wave (l = 0)Landau parameters that determine the magnetic and charge susceptibility of a Landau–Fermi liquid are given by Landau (1957), and Baym and Pethick (1992)

$$\chi_s = \mu_{\rm B}^2 \frac{\rho^*}{1 + F_0^a} = \mu_{\rm B}^2 \rho^* \left[ 1 - A_0^a \right]$$

$$\chi_c = e^2 \frac{\rho^*}{1 + F_0^s} = e^2 \rho^* \left[ 1 - A_0^s \right]$$
(11)

where the quantities

$$A_0^{s,a} = \frac{F_0^{s,a}}{1 + F_0^{s,a}} \tag{12}$$

are the s-wave Landau scattering amplitudes in the charge (s) and spin (a) channels, respectively (Baym and Pethick, 1992).

The assumption of local scattering and incompressibility in heavy electron fluids simplifies the situation, for, in this case, only the l = 0 components of the interaction remain and the quasiparticle scattering amplitudes become

$$A_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} = \frac{1}{\rho^*} \left( A_0^s + \sigma \sigma' A_0^a \right) \tag{13}$$

Moreover, in local scattering, the Pauli principle dictates that quasiparticles scattering at the same point can only scatter when in opposite spin states, so that

$$A_{\uparrow\uparrow}^{(0)} = A_0^s + A_0^a = 0 \tag{14}$$

and hence  $A_0^s = -A_0^a$ . The additional assumption of incompressibility forces  $\chi_c/(e^2\rho^*) \ll 1$ , so that now  $A_0^s = -A_0^a \approx 1$  and all that remains is a single parameter  $\rho^*$ .

This line of reasoning, first developed for the single impurity Kondo model by Nozières and Blandin (1980) and, Nozières (1976) and later extended to a bulk Fermi liquid by Engelbrecht and Bedell (1995), enables us to understand two important scaling trends amongst heavy-electron systems. The first consequence, deduced from equation (11), is that the dimensionless Sommerfeld ratio, or 'Wilson ratio' W = $\left(\frac{\pi^2 k_{\rm B}^2}{\mu_{\rm B}^2}\right) \frac{\chi_s}{\gamma} \approx 2$ . Wilson (1976) found that this ratio is almost exactly equal to 2 in the numerical renormalization group treatment of the impurity Kondo model. The connection between this ratio and the local Fermi liquid theory was first identified by Nozières (1976), and Nozières and Blandin (1980). In real heavy-electron systems, the effect of spin-orbit coupling slightly modifies the precise numerical form for this ratio, nevertheless, the observation that  $W \sim 1$  over a wide range of materials in which the density of states vary by more than a factor of 100 is an indication of the incompressible and local character of heavy Fermi liquids (Figure 6).

A second consequence of locality appears in the transport properties. In a Landau–Fermi liquid, inelastic electron– electron scattering produces a quadratic temperature dependence in the resistivity

$$\rho(T) = \rho_0 + AT^2 \tag{15}$$



Figure 6. Plot of linear specific heat coefficient versus Pauli susceptibility to show approximate constancy of the Wilson ratio. (Reproduced from P.A. Lee, T.M. Rice, J.W. Serene, L.J. Sham, and J.W. Wilkins, *Comments Condens. Matt. Phys.* 9212, (1986) 99, with permission from Taylaor & Francis Ltd, www.informaworld.com.)

In conventional metals, resistivity is dominated by electronphonon scattering, and the 'A' coefficient is generally too small for the electron-electron contribution to the resistivity to be observed. In strongly interacting metals, the A coefficient becomes large, and, in a beautiful piece of phenomenology, Kadowaki and Woods (1986), observed that the ratio of A to the square of the specific heat coefficient  $\gamma^2$ 

$$\alpha_{\rm KW} = \frac{A}{\gamma^2} \approx (1 \times 10^{-5}) \mu \Omega \text{cm}(\text{mol } \text{K}^2 \text{mJ}^{-1}) \quad (16)$$

is approximately constant, over a range of A spanning four orders of magnitude. This can also be simply understood from the local Fermi-liquid theory, where the local scattering amplitudes give rise to an electron mean-free path given by

$$\frac{1}{k_{\rm F}l^*} \sim {\rm constant} + \frac{T^2}{(T^*)^2} \tag{17}$$

The 'A' coefficient in the electron resistivity that results from the second term satisfies  $A \propto \frac{1}{(T^*)^2} \propto \tilde{\gamma}^2$ . A more detailed calculation is able to account for the magnitude of the Kadowaki–Woods constant, and its weak residual dependence on the spin degeneracy N = 2J + 1 of the magnetic ions (see Figure 7). The approximate validity of the scaling relations

$$\frac{\chi}{\gamma} \approx \text{cons}, \qquad \frac{A}{\gamma^2} \approx \text{cons}$$
 (18)

for a wide range of heavy-electron compounds constitutes excellent support for the Fermi-liquid picture of heavy electrons.

A classic signature of heavy-fermion behavior is the dramatic change in transport properties that accompanies the development of a coherent heavy-fermion band structure (Figure 6). At high temperatures, heavy-fermion compounds exhibit a large saturated resistivity, induced by incoherent spin-flip scattering of the conduction electrons of the local f moments. This scattering grows as the temperature is lowered, but, at the same time, it becomes increasingly elastic at low temperatures. This leads to the development of phase coherence. the f-electron spins. In the case of heavyfermion metals, the development of coherence is marked by a rapid reduction in the resistivity, but in a remarkable class of heavy fermion or 'Kondo insulators', the development of coherence leads to a filled band with a tiny insulating gap of the order  $T_{\rm K}$ . In this case, coherence is marked by a sudden exponential rise in the resistivity and Hall constant.

The classic example of coherence is provided by metallic  $CeCu_6$ , which develops 'coherence' and a maximum in



**Figure 7.** Approximate constancy of the Kadowaki–Woods ratio, for a wide range of heavy electrons. (After Tsujji, Kontani and Yoshimora, 2005.) When spin-orbit effects are taken into account, the Kadowaki–Woods ratio depends on the effective degeneracy N = 2J + 1 of the magnetic ion, which when taken into account leads to a far more precise collapse of the data onto a single curve. (Reproduced from H. Tsujji, H. Kontani, and K. Yoshimora, *Phys. Rev. Lett* 94, 2005, copyright © 2005 by the American Physical Sdociety, with permisison of the APS.057201.)

its resistivity around T = 10 K. Coherent heavy-electron propagation is readily destroyed by substitutional impurities. In CeCu<sub>6</sub>, Ce<sup>3+</sup> ions can be continuously substituted with nonmagnetic La<sup>3+</sup> ions, producing a continuous crossover from coherent Kondo lattice to single impurity behavior (Figure 8).

One of the important principles of the Landau–Fermi liquid is the Fermi surface counting rule, or Luttinger's theorem (Luttinger, 1960). In noninteracting electron band theory, the volume of the Fermi surface counts the number of conduction electrons. For interacting systems, this rule survives (Martin, 1982; Oshikawa, 2000), with the unexpected corollary that



**Figure 8.** Development of coherence in  $Ce_{1-x}La_xCu_6$ . (Reproduced from Y. Onuki and T. Komatsubara, *J. Mag. Mat.* 63–64, 1987, 281, copyright © 1987, with permission of Elsevier.)

the spins of the screened local moments are also included in the sum

$$\frac{2V_{\rm FS}}{(2\pi)^3} = [n_e + n_{\rm spins}] \tag{19}$$

Remarkably, even though f electrons are localized as magnetic moments at high temperatures, in the heavy Fermi liquid, they contribute to the Fermi surface volume.

The most direct evidence for the large heavy f-Fermi surfaces derives from de Haas van Alphen and Shubnikov de Haas experiments that measure the oscillatory diamagnetism or and resistivity produced by coherent quasiparticle orbits (Figure 9). These experiments provide a direct measure of the heavy-electron mass, the Fermi surface geometry, and volume. Since the pioneering measurements on CeCu<sub>6</sub> and UPt<sub>3</sub> by Reinders and Springford, Taillefer, and Lonzarich in the mid-1980s (Reinders *et al.*, 1986; Taillefer and Lonzarich, 1988; Taillefer *et al.*, 1987), an extensive number of such measurements have been carried out (Onuki and Komatsubara, 1987; Julian, Teunissen and Wiegers, 1992; Kimura *et al.*, 1998; McCollam *et al.*, 2005). Two key features are observed:

- A Fermi surface volume which counts the f electrons as itinerant quasiparticles.
- Effective masses often in excess of 100 free electron masses. Higher mass quasiparticle orbits, though inferred from thermodynamics, cannot be observed with current measurement techniques.
- Often, but not always, the Fermi surface geometry is in accord with band theory, despite the huge renormalizations of the electron mass.

Additional confirmation of the itinerant nature of the f quasiparticles comes from the observation of a Drude peak in



**Figure 9.** (a) Fermi surface of UPt<sub>3</sub> calculated from band theory assuming itinerant 5f electrons (Oguchi and Freeman, 1985; Wang *et al.*, 1987; Norman, Oguchi and Freeman, 1988), showing three orbits ( $\sigma$ ,  $\omega$  and  $\tau$ ) that are identified by dHvA measurements. (After Kimura *et al.*, 1998.) (b) Fourier transform of dHvA oscillations identifying  $\sigma$ ,  $\omega$ , and  $\tau$  orbits shown in (a). (Kimura *et al.*, 1998.)

the optical conductivity. At low temperatures, in the coherent regime, an extremely narrow Drude peak can be observed in the optical conductivity of heavy-fermion metals. The weight under the Drude peak is a measure of the plasma frequency: the diamagnetic response of the heavy-fermion metal. This is found to be extremely small, depressed by the large mass enhancement of the quasiparticles (Millis and Lee, 1987a; Degiorgi, 1999).

$$\int_{|\omega| \leq T_{\rm K}} \frac{{\rm d}\omega}{\pi} \sigma_{qp}(\omega) = \frac{ne^2}{m^*}$$
(20)

Both the optical and dHvA experiments indicate that the presence of f spins depresses both the spin and diamagnetic response of the electron gas down to low temperatures.

# 2 LOCAL MOMENTS AND THE KONDO LATTICE 2.1 Local moment formation

#### 2.1.1 The Anderson model

We begin with a discussion of how magnetic moments form at high temperatures, and how they are screened again at low temperatures to form a Fermi liquid. The basic model for local moment formation is the Anderson model (Anderson, 1961)

$$H = \sum_{k,\sigma} \epsilon_k n_k \sigma + \sum_{k,\sigma} V(k) \left[ c_{k\sigma}^{\dagger} f_{\sigma} + f_{\sigma}^{\dagger} c_{k\sigma} \right]$$
  
+ 
$$E_{lnl} + Un_{ll} n_{ll}$$
  
$$H_{himms}$$
(21)

greue for and *Pressure*, describes the hyprorization of localized f electrons in the ion with the Bloch waves of conduction sea. For pedagogical reasons, our discussion ially focuses on the case where the f state is a Kramer's blet. There are two key elements to the Anderson model:

*muc limit:* The atomic physics of an isolated ion with ingle *(* state, described by the model

$$H_{\text{atomic}} = E_{\ell} n_{\ell} + U n_{\ell\uparrow} n_{\ell\downarrow}$$
(22)

Here  $E_f$  is the energy of the f state and U is the Coulomb energy associated with two electrons in the same orbital. The atomic physics contains the basic mechanism for local moment formation, valid for f electrons, but also seen in a variety of other contexts, such as transition-metal atoms and quantum dots. The four quantum states of the atomic model are

$$\begin{bmatrix} f^2 \\ f \end{pmatrix} = \mathcal{E}(f^2) = 2\mathcal{E}_f + \mathcal{U} \\ f \mathcal{U} \end{bmatrix} \text{ nonmagnetic}$$

$$\begin{aligned} & (\mathcal{U}) = 0 \end{aligned}$$
(23)

In a magnetic ground state, the cost of inducing a 'valence fluctuation' by removing or adding an electron to the f<sup>1</sup> state is positive, that is,

removing: 
$$E(f^0) - E(f^1)$$
  
 $= -E_f > 0 \Rightarrow \frac{U}{2} > E_f + \frac{U}{2}$  (24)  
adding:  $E(f^2) - E(f^1)$   
 $= E_f + U > 0 \Rightarrow E_f + \frac{U}{2} > -\frac{U}{2}$  (25)