Phase diagram of heavy fermion systems

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Abstract

The Meccano of heavy fermion systems is shown on different cases going from anomalous monochalcogenides to cerium intermetallic compounds with special focus on the ideal case of the CeRu2Si2 series. Discussion is made in the frame of the interplay between valence, electronic structure (Fermi surface), and magnetism. The nice tools given by the temperature, the pressure, and the magnetic field allow to explore different ground states as well as the slow downhill “race” before reaching a Fermi liquid finish line at very low temperature. Experimentally, the Grüneisen parameter i.e. the ratio of the thermal expansion by the specific heat is a coloured magic number; its temperature, pressure, and magnetic field dependence is a deep disclosure of competing hierarchies and the conversion of this adaptive matter to external responses.

Key words: Kondo lattice, valence instability, magnetism, superconductivity
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Heavy fermion physics are approached by pedestrian looking of basic questions on the electronic occupancy n4f of the 4f shell and the magnetic properties. The monochalcogenide cases of Sm and Tm compounds are revisited with recent data obtained on SmS [1,2]. For the cerium intermetallic compounds, special attention is given close to the so called magnetic quantum criticality i.e. near the critical electronic density ρc or pressure Pc where drastic changes occur on the ground state. Pressure and magnetic field are elegant tool to modify the weight or even the sign of the magnetic interactions by comparison to the strong local fluctuations inherent to Kondo lattices. Emphasis is given on the results on the CeRu2Si2 family since the pure compound i.e. with vanishing disorder allows to scan through different temperature and field regimes [3].

1. Monochalcogenides of Sm and Tm: conduction, valence, and magnetism

In the monochalcogenides of anomalous rare earths (RE) like Sm or Tm the equilibrium between two valence states (Sm2+/Sm3+ or Tm2+/Tm3+) governs the release of a 5d electron [4]. Let us start with our new guided tour of the canonical example of SmS. The full line TB−G of the (T − P) phase diagram (see Fig.1) represents the first order isostructural transition between the black (B) insulating (I) Sm2+ phase and the so called gold (G) phase where the Sm ions jumps to an intermediate valence state v ≈ 2.7. In this gold phase, smoothly increasing the pressure must lead to recover a trivalent Sm3+: it is a Kramers ion, long range magnetic order must appear above this threshold P = Pc.

Furthermore a sound experimental fact is that up to PΔ = 20 kbar in the low pressure gold phase a many body insulating phase is smoothly formed
on cooling. Whatever the sample quality and the pressure conditions, $P_\Delta$ is a fixed pressure above which the sample is clearly metallic i.e. its resistivity $\rho$ decreases on cooling after reaching a maximum $\rho_{\text{max}}$ at $T_m$ [5,6,7,8]. The recent combination of macroscopic measurements by transport and ac specific heat and of the microscopic probe of the hyperfine field on the Sm nuclei by nuclear forward scattering (NFS) using ESRF facility demonstrates that long range antiferromagnetic (AF) order appears at $P_c \sim P_\Delta$. As the pressure variation of $T_m$ now identified as the Néel temperature $T_N$ is huge, $P_c$ is presumably a first order point associated with a lattice parameter discontinuity i.e. a tiny valence jump at $P_c = P_\epsilon$ towards the trivalent state.

By contrast to the Sm case where the valence fluctuations occur between the Sm$^{2+}$ state with a zero angular momentum ($J = 0$) and Sm$^{3+}$ with a $J = 5/2$ angular momentum, for the Tm ions the mixing is between two finite angular momentum states, respectively $J = 7/2$ (Tm$^{2+}$) and $J = 6$ (Tm$^{3+}$). Whatever the pressure i.e. the valence and even the electronic conduction, the ground state is magnetic. However, the similarity with SmS is a link between magnetic properties and $4f$ localisation. For TmTe as shown on Fig. 2, the $P$ sequence of ground states is AF/I up to $P_{BG}$, ferromagnetic (F) and metallic (M) up to $P_v$ and finally the entrance to a AF metallic state [9,10]; the rapid collapse of $T_{Curie}$ just below $P_v$ and the fast increase of $T_N$ just above $P_v$ suggests a first order transition. For TmSe, already in the gold phase at $P = 0$, the switch at $P_v$ occurs between an AF insulating phase $P < P_v - \epsilon$ and another AF metallic state above $P_v$ [11]. TmS itself appears already at $P = 0$ as a quiet quasitrivalent metallic state, in principle

![Fig. 1. Phase diagram of SmS with the first order line between the black and the gold phase. Insert: Zoom on the metallic gold phase and the discovery of magnetism by three different techniques: specific heat (C), transport ($\rho$) and nuclear forward scattering (NFS).](image1)

![Fig. 2. Pressure cascade of ground states in Tm chalcogenides: $\nu$ is the rare earth valence.](image2)

### 2. Cerium heavy fermion systems: valence and magnetism

As pointed out already, the cerium heavy fermion problem can be summarized by two major $(T, P)$ phase diagrams. The well-known $T_{\alpha,\gamma}$ first order transition of the cerium metal and the up to date magnetic phase diagram $T_N$ or $T_{Curie}$ versus pressure where the ordering temperature may collapse at $P_c$ [13]. For the cerium metal, the treatment of the magnetism can be crude as all characteristic temperatures $T_{\alpha,\gamma}$ are high by comparison to any hypothetical $T_N$ or any fine structure as the crystal field splitting $C_{CF}$ of the trivalent $\gamma$ phase. At $P = 0$, $T_{\alpha,\gamma}(0)$ is already positive, finite and near 100 K and the critical end points $T_{cr} = 700$ K, $P_{cr} = 22$ kbar are large. For typical cerium heavy fermion compounds $P_v$ is lower or comparable to $P_{cr}$ and of course $T_{\alpha,\gamma}(P = 0)$ and $T_{cr}(P_{cr})$ will be negative. However, the $4f$ electron will feel the distance from $P_{cr}$ and cause the crossing through a characteristic pressure $P_v$ where the local susceptibility loses the anisotropy given by its reaction to the crystal field (that corresponds to the well known condition $k_B T_K$ (Kondo energy) greater than $C_{CF}$). Above $P_v$, the $4f$ electron stays rigidly linked to the full degeneracy of the $J = 5/2$ angular momentum.

At $P_v$, the sensitivity of the $4f$ electron to the crystal field has vanished: $P_v$ is characteristic of a valence crossover. The relative location of $P_v$ and the hidden parameter $P_{\epsilon}$ is one of the key issue. The idea that singular properties is underpinned by a quantum critical point i.e. pressure is one of the trends of strongly correlated electronic sys-
systems (see references [14] for the hidden order of URu$_2$Si$_2$ or [15] for the metamagnetic quantum criticality in Sr$_3$Ru$_2$O$_7$ and [16] for the conversion of a Kondo gas to heavy electron Kondo liquid).

Recently special focus has been given on systems just on the paramagnetic verge of $P_c$, i.e. at $P_c + \epsilon$ [17]. The Non Fermi liquid (NFL) label refers to the difficulty to reach the standard Fermi liquid regime where usual laws are found, even for non-interacting Fermi gas (specific heat $C = \gamma T$ linear in temperature $T$, susceptibility in $T^2$, scattering rate proportional to $T^2$); the NFL label guarantee “vintage” describes a very large temperature crossover before reaching the Fermi liquid grail or a new state of matter.

To clarify the complexity of this strongly correlated electronic system, an old fashioned approach via thermodynamic languages will be carried out [18,19,20,21]. In the same spirit as the Clapeyron and Ehrenfest relations on the $P, T$ feedback for first or second order transitions, the Grüniesen parameter

$$\Omega^*(T) = \frac{\alpha}{C} \frac{V_0}{\kappa}$$

(where $\alpha$, $V_0$ and $\kappa$ are respectively the volume thermal expansion, the molar volume and the isothermal compressibility) is a unique experimental gauge of interfering hierarchies. It will be reduced to a constant $\Omega^*(0)$ only if the free energy $F$ can be expressed by a unique parameter $T^*$ i.e.

$$F(T) = T \Phi\left(\frac{T}{T^*}\right) \quad \text{with} \quad \Omega^*(0) = -\frac{\partial \log T^*}{\partial \log V}$$

Figure 3 represents the temperature variation of the Grüniesen parameter of CeRu$_2$Si$_2$ at $P = 0$ i.e. roughly 3 kbar above the critical pressure $P_c = -3$ kbar. The two singular points are: (i) the huge extrapolated value of $\Omega^*(0) = +190$ and (ii) the slow entrance in a simple regime ($T \approx 1$ K) where $\alpha$ and $C$ reach their proportionality [22,23]. The pressure dependence of $\Omega^*_P$ is shown in the insert of fig.3. At low pressure close to $P_c$, $\Omega^*(0)$ is weakly pressure dependent changing from 190 to 220 for a negative shift of $P = 2$ kbar [22] while $\Omega^*_P$ drops to 80 at $P_c$ [23]. Other values of $\Omega^*_P(0)$ can be listed crudely for other heavy fermion system. In a double logarithmic representation of the volume dependence of the $A$ coefficient of the well known $AT^2$ Fermi liquid resistivity assuming the usual Kadowaki-Woods rule $A \propto \gamma^2$, $\Omega^*(0)$ is directly linked to the slope of the curve [24].

3. Magnetic field switch from AF correlation to F interactions

The compound CeRu$_2$Si$_2$ is a quasi-ideal Kondo lattice with a nice ordered tetragonal lattice, a robust Ising character of the local susceptibility, the realization of a clean limit condition i.e. a mean free path higher than 1000 Å far larger than an hypothetical superconducting coherence length with temperature $T_s = 200$ mK and good enough to obtain the complete determination of the Fermi surface (FS) at least above $P_c$ (see references in [3]).

The application of a magnetic field $H$ along the easy $c$ axis leads to a switch through a drastic continuous crossover at $H = H_m$ from a low field paramagnetic phase (Pa) dominated by AF correlations at a finite wavevector $k_0$ to a highly polarized state (PP) dominated by the low wavevector $q$ excitation. The microscopic vision of CeRu$_2$Si$_2$ was nicely given by inelastic neutron scattering experiments, (i) with at $H = 0$, the balance between the local response and the intersite coupling, (ii) with, under magnetic field, the continuous spreading of the AF response with the same characteristic gluonic energy $\omega_{AF} \sim 1.6$ meV up to $H_m$ [25] and the observation just in the vicinity of $H_m$ of an inelastic ferromagnetic signal at far lower energy transfer $\omega_F \sim 0.4$ meV than $\omega_{AF}$ (see Fig.4) [26,27].

A skillful mechanism characteristic of the Kondo lattice CeRu$_2$Si$_2$ controles the “ping-pong” between the magnetic interactions. Quite remarkably, the field and temperature response is well reproduced by a simple form of the thermodynamic as the entropy.

$$S = S\left(\frac{T}{T^*}, \frac{H}{H_m}\right)$$

with equal Grüniesen parameters $\Omega_{T^*} = \Omega_{H_m} = -190$. With this hypothesis one can predict the field variation of $\gamma_H$ knowing the field variation of
4. To be or not to be? Speculations on superconductivity

After a lecture describing the “beauty” CeRu$_2$Si$_2$ to quantum criticality, the first attack is to produce the proofs that CeRu$_2$Si$_2$ is close to a magnetic instability. Looking back to the primitive results one decade ago on the CeRu$_2$Si$_2$ series either sweeping electronic density (doping or pressure) or magnetic field, a NFL increase of $C/T$ on cooling in a given temperature window justifies the proximity to $P_c$ [31]. Furthermore, this variation is not drastically different from that popularized in the canonical example of CeCu$_{5.9}$Au$_{0.1}$ [32] after a rescaling of the temperature by some phenomenological parameter describing the proximity to $P_c$ and also differences in physical ingredients. As on approaching $P_c$, no drastic pressure dependence of $\Omega^*(0)$ occurs. Collapsing to $P_c$ on the paramagnetic side does not lead to an “earthquake” even if of course $T^*$ will collapse when $T \to 0$. The deviation from any singular scaling law of the imaginary part of the dynamical susceptibility $\chi''T^n \propto \Phi(\frac{P}{P_c})$ becomes also quite difficult to point out. The yet unanswered dilemma is if a new state of matter occurs right at $P_c$.

The obsessive focus just at $P_c$ or on the paramagnetic (Pa) side ($P > P_c$) leads to neglect the disappearance of long range magnetism. As many tunings were realized by doping i.e. at the cost of an increase of disorder, $P_c$ appears as a second order quantum phase transition. Comparison with the previous chalcogenide cases, recent NMR experiments on CeIn$_3$ close to $P_c - \epsilon$ with evidence of AF and Pa magnetic phase separation [33] as well as drastic Fermi surface changes at $P_c$ in CeRh$_2$Si$_2$ [34] point out that at the limit of a pure lattice at $P_c$ the transition may be first order. Today one key question is to determine precisely the Fermi surface on both sides of $P_c$ knowing the two limit conditions of a localized 4$f$ picture at low pressure ($P \ll P_c$) and an itinerant 4$f$ picture at high pressure ($P \gg P_c$). Progress will imply a deep interdisciplinary collaboration between experimentalists and theoreticians eager to track carefully the $P$ and $H$ variations including the modification of the Brillouin zone and the differentiation between spin up and spin down effective mass carriers.

For unconventional superconductivity, the nature of the phase transition at $P_c$ is not critical as proved by the occurrence of superconductivity in CeIn$_3$ and CeRh$_2$Si$_2$. There are examples like CePd$_2$Si$_2$, CeIn$_3$ and CeRh$_2$Si$_2$ where the superconducting pocket is stocked to $P_c \sim P_c'$; there

the linear thermal expansion $\alpha_c = a_H T$. A satisfactory agreement is found between this scaling derivation of $\gamma_H$ and the bare determination either by specific heat or by magnetization [22,28]. Physically, the adaptive formation of the many body Kondo lattice bands is characterized by a pseudogap. The Ising spin character of the bare local magnetic ion plays a capital role in the sharpness of this electronic substructure and correlatively for the pseudo-metamagnetism [29]. The pseudogap ingredient is a key input in any theory which needs to respect the scaling behavior [30]. Reminiscent of the $\alpha - \gamma$ collapse of the cerium metal, the associated spectacular lattice softening ($\approx 30\%$) is again in agreement with the push pull between magnetic, electronic and lattice instabilities [3] and the underpinned vicinity of a quantum critical end point.

Fig. 4. (a) Field variation of the inelastic response at the energy transfer $E = 0.8$ meV measured at the AF wave vector $(0.69, 1, 0)$; the AF contribution vanishes at $H_m$ while the local one survives. (b) Appearance of low energy ferromagnetic fluctuation $(E = 0.4$ meV) on crossing $H_m$. 

\[a) \quad Q = (0.69 \, 1 \, 0) \quad E = 0.8 \text{ meV} \quad T = 2 \text{ K}\]

\[b) \quad Q = (0.9 \, 1 \, 0) \quad E = 0.4 \text{ meV} \quad T = 170 \text{ mK}\]
are cases like CeCu$_2$Si$_2$ [35], CeCu$_2$Ge$_2$ [36] and CeNi$_2$Ge$_2$ [37] where two superconducting domains are centered on distinct pressures $P_c$ and $P_v$. We will test soon if superconductivity appears on the verge of $P_v \approx 20$ kbar in CeRu$_2$Si$_2$; near $P_c = -3$ kbar, the Ising character of the spin allows only longitudinal magnetic fluctuations which does not favor the observation of $d$ wave pairing [38,39] while near $P_v$ this superconductivity can be promoted by the emergence of transverse magnetic modes as well as valence fluctuations [40,41].

It is time to concentrate on the complete bundle of curves on each side of $P_c$ in CeRu$_2$Si$_2$ as well as in the other cerium tetragonal lattices and Yb homologues following our Dresden colleagues [42].

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References

[1] Y. Haga et al. to be published.
[2] A. Barla et al. to be published.
[3] J. Flouquet et al. Physica B 319 (2002) 251.
[4] P. Wachter, Handbook of Physics and Chemistry of Rare Earths Vol. 19, p. 177, edited by K. A. Gschneidner, L. Eyring, G. H. Lander, and G. R. Choppin (North Holland-Amsterdam, 1994).
[5] F. Holtzberg and J. Wittig, Solid State Commun. 40 (1981) 315.
[6] F. Lapierre et al., Solid State Commun. 40 (1981) 317.
[7] H. Konzukowski et al. Solid State Commun. 40 (1981) 517.
[8] M. Ohashi et al., Rev. High Pressure Sci. Technology 7 (1998) 611.
[9] P. Link et al., Phys. Rev. Lett. 80 (1997) 173.
[10] J. M. Mignot et al., J. Magn. Magn. Mater. 211 (2001) 226.
[11] M. Ribault et al., Phys. Rev. Lett. 45 (1980) 1295.
[12] F. Holtzberg et al., J. Appl. Phys. 57 (1985) 3067.
[13] S. Kambe et al., J. Phys. Soc. Jpn. 69 (2000) 41.
[14] F. Bourdarot et al., to be published.
[15] M. Chiao et al., cond-mat/0207657.
[16] S. Nakatsuiji et al., cond-mat/0305427.
[17] A. Schröder et al., Nature (London) 407 (2000) 351.
[18] A. Benoit et al., Conference on Valence Fluctuations in Solids, p. 283, edited by L. M. Falicov, W. Hanke, M. B. Maple (Santa Barbara, 1981).
[19] J. Flouquet et al., J. Appl. Phys. 53 (1982) 2127.
[20] S. Kambe et al., J. Phys.: Condens. Matter 9 (1997) 4917.
[21] L. Zhu et al., to be published. cond-mat/0212335
[22] A. Lacerda, Thesis, University of Grenoble, 1990, unpublished, and A. Lacerda et al., Phys. Rev. B 40 (1989) 8759.
[23] S. Holtmeier, Thesis, University of Grenoble, 1993, unpublished, and K. Payer et al., Physica B 186-188 (1993) 503.
[24] J. Flouquet, to be published in: Progress Low Temperature Physics
[25] S. Raymond et al., Physica B 259-261 (1999) 48.
[26] M. Sato et al., J. Phys. Soc. Jpn. 70 (2001) Suppl. A, 118.
[27] S. Raymond et al. to be published.
[28] C. Paulsen et al., J. Low Temp. Phys. 81 (1999) 317.
[29] Y. Aoki et al., J. Magn. Magn. Mater. 177-181 (1998) 271.
[30] F. Ohkawa, Phys. Rev. B 57 (1998) 5891.
[31] R. A. Fisher et al., J. Low Temp. Phys. 84 (1991) 49.
[32] H. v. Löhneysen et al., Phys. Rev. Lett. 72 (1994) 3262.
[33] S. Kawasaki et al., private communication.
[34] S. Araki et al., Phys. Rev. B 64 (2001) 224417.
[35] B. Bellarbi et al., Phys. Rev. B 30 (1984) 779.
[36] D. Jaccard et al., Phys. Lett. A 163 (1992) 475.
[37] See D. Braithwaite et al., J. Phys.: Condens. Matter 12 (2000) 1339.
[38] See P. Monthoux and G. G. Lonzarich, Phys. Rev. B 66 (2002) 224504.
[39] G. G. Lonzarich, this conference.
[40] Y. Onishi and K. Miyake, J. Phys. Soc. Jpn. 69 (2000) 3955.
[41] A. Holmes et al., cond-mat/0306054.
[42] See S. Paschen et al., this conference.