Recent Progress in Heavy Fermion/Valence Fluctuation Physics: Introduction

It has been five years since a discussion of theories of heavy electron systems appeared in these pages[1]; in the interim important new experimental and theoretical results have appeared. We feel that a new series of Comments on heavy fermion/valence fluctuation compounds is merited. As an introduction to such a series, in this article we review the understanding of these materials as of 1986, briefly summarize the newer results and conclude by outlining key problems raised by recent work.

As of 1986 the issues in heavy fermion physics were clearly identified. In valence fluctuation[2] and heavy fermion compounds,[3] a nearly localized f state associated with each rare earth ion is degenerate with the conduction band; the f level resides a small distance E_f below the Fermi level. The hybridization $\Gamma = v^2\rho$ of the f level with the band is small (0.1 eV) while the intrasite Coulomb correlation U is large (5–10 eV). Under these circumstances, localized spin magnetism might be expected; however, the heavy fermion ground state is paramagnetic. That is, the susceptibility approaches a finite value $\chi(0)$ as $T \to 0$, as for a Pauli paramagnet, and the specific heat is linear with temperature $C = \gamma T$. The very large values of γ that are observed (10 to 1000 times those of ordinary metals), coupled with the observation that in a Fermi liquid γ is proportional to the effective mass m^*, led to the appellation "heavy fermion."

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It is believed that the basic process responsible for the nature of the ground state is the same as is responsible for the nonmagnetic ground state of dilute alloys (of Ce, Fe, Mn, etc.), namely the Kondo effect.[4] In the Kondo/Anderson[5] theory of magnetic impurities, this occurs due to virtual excitations whereby an f electron is promoted to a band state at the Fermi level, and the f hole is filled by a conduction electron with spin of the opposite sign. Such virtual fluctuations in valence thus result in spin fluctuations which quench the magnetic moment at low temperatures.

Already in 1986 there were several theoretical solutions to the isolated Kondo impurity problem in hand (renormalization group, Bethe Ansatz and $1/N$ expansions, where N is the orbital degeneracy).[1] These solutions yielded detailed predictions[6] for basic thermodynamic measurements such as the magnetic susceptibility, specific heat, resistivity and thermopower as well as electronic and magnetic spectral densities (i.e., photoemission spectra and inelastic magnetic neutron scattering spectra, respectively). A key feature of the theory is *universality*, i.e., the temperature and energy dependences of the physical quantities vary as T/T_K or $\hbar\omega/kT_K$, where T_K is the Kondo temperature.

At that time it was appreciated that the high temperature properties of *periodic* cerium and ytterbium compounds which have f levels on each rare earth site were those predicted by theory[6] for a collection of non-interacting Kondo impurities. For example, in several of these compounds the resistivity decreases with temperature in an approximately logarithmic manner over an extensive temperature range; this $\log T$ variation of ρ is precisely the behavior which Kondo originally derived[4] in the 1960's from his perturbation theoretic treatment valid for temperatures above T_K. The susceptibility of certain cerium and ytterbium compounds agrees almost exactly with single ion Kondo theory: it approaches a finite value $\chi(0)$ at $T = 0$, has a broad maximum at a temperature T_{max}, and at higher temperature varies in Curie–Weiss fashion, $\chi(T) = C/(T + \theta)$. The quantities $C/\chi(0)$, T_{max} and θ vary proportionally from compound to compound and are all proportional to T_K in the theory. The inelastic neutron scattering lineshape is predicted to be of quasi-elastic form $\omega\omega_0/(\omega^2 + \omega_0^2)$ with $\hbar\omega_0 = kT_K$; this further implies a relationship between the linewidth and the static susceptibility.

These predictions appear to be borne out at high temperatures in valence fluctuation compounds. The theory also predicts a large maximum in the thermopower, positive for cerium and negative for ytterbium, at a temperature comparable to T_{max}, and this is indeed observed experimentally. The theory predicts that for temperatures well below T_K the specific heat $C(T)$ is linear with temperature, with a coefficient γ which varies inversely with T_K; the large γ which results when T_K is small is the characteristic signature of a heavy fermion compound. A further prediction is that $C(T)$ should exhibit a maximum in the vicinity of T_K. Such behavior is indeed observed, and the Wilson ratio $R = \pi^2 N_A k_b \chi(0)/3C_{eff}\gamma$ (where $N_A k_b$ is the gas constant and C_{eff} is the ground state Curie constant) is indeed observed to be close to unity as predicted by theory, for large degeneracy. These results are modified when spin orbit splitting and crystal fields are present, most especially because the orbital degeneracy of the ground multiplet is different when these effects are present. In the absence of these effects the degeneracy is $N = 14$; when spin orbit splitting is present, $N = 6$ for cerium and 8 for ytterbium; when crystal fields are present, N can be 2 or 4. The theory is able to deal with these details, and predict their effects on the physical quantities.

One of the most compelling features of this approach is that it gives an explanation to the core problem of the relation between the large energy scales of the problem (E_f, Γ and U) and the very small scales implied by the universality of the thermodynamics. At least with the experimental resolution available five years ago, the valence band photoemission spectra of cerium compounds also appeared to agree more-or-less with the predictions of the theory.[6,7] In particular, in cerium compounds the main local $4f$ emission occurs at an energy $E_f = 2$ eV, there is a feature above the Fermi level at $E_f + U$ observed in inverse photoemission (BIS), and in some compounds a feature is observed at the Fermi level. Kondo theory predicts a "Kondo Resonance" located a distance kT_K above ϵ_F with total weight T_K/Γ. When T_K is large enough this can be observed directly in BIS, and the tail of the peak can be observed in photoemission. Crystal fields and spin orbit effects again introduce complications which were already fairly well understood in 1986. The theories also give good predictions for core level photoemission and L_{III} x-ray absorption. It was under-

stood on this basis, for example, that the valence of cerium is never very different from the value three; i.e., that for $z = 4 - n_f$, the f occupation n_f varies in the range 0.7–1.0, so that there are no tetravalent cerium intermetallic compounds.

As implied above, there is little or no distinction in the high temperature behavior between the various valence fluctuation compounds. However, the low temperature behavior and hence ground states can differ dramatically. The ground state can be paramagnetic, antiferromagnetic, superconducting or semiconducting.[2,3] Clearly, as temperature is lowered, single ion Kondo theory must break down. For example, if one regards each rare earth ion as a spin fluctuator uncorrelated with its neighbors, the resistivity would remain finite as T approaches 0, saturating at a value representing the unitarity scattering limit; whereas in real heavy fermion/valence fluctuation compounds (with the caveat that in a small number of cases the ground state is semiconducting) the resistivity always vanishes as $T \rightarrow 0$. In any periodic array of cerium atoms, the scattering potential will be periodic at $T = 0$ so the resistivity must vanish; this is Bloch's Law. Thus, as temperature is lowered, coherence will be established in the system, and it is this that drives the resistivity to zero. More fully, in the coherent ground state of a periodic cerium or ytterbium compound there will be interactions/correlations between the behavior on the different $4f$ sites. At the very least, RKKY interactions between the $4f$ moments will occur. The resulting ground state of the periodic, correlated system at temperatures $T << T_K$ will differ quantitatively from the picture provided by uncorrelated single ion theory.

Given that the single ion problem is solved, the central issue in the physics of heavy fermion compounds is the understanding of how the coherent ground state evolves from the well understood high temperature regime, as temperature is lowered. From our earlier remarks, very diverse ground states are realized in practice and currently we have no understanding of which ground state will be achieved in any particular instance, given knowledge of the high temperature state.

Experimentalists had already[2,3,8] identified several manifestations of coherence in 1986: for example, the resistivity was found to vary as T^2 at low temperature, with a coefficient that scales as γ. The temperature dependent linear coefficient of specific heat

$C(T)/T$ was known to have a low temperature maximum, contrary the predictions of single ion theory which are that it should be monotonically decreasing with increasing temperature. Anomalies in the Hall coefficient, thermal expansion and thermopower at temperatures smaller than the single-ion Kondo temperature were also known to exist. Most crucially, de Haas van Alphen measurements in certain cerium compounds had indicated that one-electron band theory gets many of the features of the Fermi surface correctly: the $4f$ states indeed form a band. This is a definitive manifestation of coherence.

The theory of the coherent heavy fermion ground state is more limited. A key question is why the ground state can remain nonmagnetic in the presence of the interactions. After all, Fe impurities in simple metals give a Kondo effect, but when placed in a periodic array they order ferromagnetically. The basic notion is that the $4f$ ions must have their moment compensated (due to the Kondo effect) more rapidly as the temperature is lowered than they will magnetize as a consequence of the interactions. In this spirit, in certain theories,[1] intersite interactions are ignored entirely; all the coherence arises simply from the underlying periodicity of the otherwise non-interacting Kondo impurities. (A periodic array of ions all scattering with the same amplitude will give a vanishing resistivity and will lead to a Fermi surface.) By 1986 it was appreciated[1] that $1/N$ (where $N = 2J + 1$ is the f orbital degeneracy) provides an appropriate expansion parameter in the theory; at $N = \infty$ it was demonstrated that mean field theory is exact; to lowest order in $1/N$ the intersite interactions can be ignored. Using "slave boson," functional integral and other methods in the large N limit the Kondo Lattice reduces to an effective one-electron (band) Hamiltonian with renormalized hybridization V_{eff}, f energy $\tilde{E}_f$ and $U_{\text{eff}} = 0$.

The Kondo Lattice "Standard Model" that we have given so far starts from a localized description of the f electron, as seems appropriate for rare earth valence fluctuators such as cerium or ytterbium. This approach has the virtue that it readily includes the effects of the large intrasite Coulomb correlation U; however, one pays the price that it is then very difficult to describe the coherent, band-like ground state. The main alternative approach is the use of first principles one-electron band theories; this seems more ap-

propriate for uranium compounds, where the $5f$ orbital is large enough that band theory is often successful. For heavy fermion materials however, this approach has the opposite problem: it can describe the band-like coherence, but has great difficulty treating the effects of the large U. For example, such calculations correctly describe the topology of the Fermi surface observed in the dHvA experiments, because the topology is mainly determined by the crystal structure and the dynamics of the weakly correlated (non-f) electrons; however, they fail to predict the observed large mass enhancement. For cerium the band theoretic approach predicts a bandwidth (~1 eV) which is much too large, and in any case is unstable against formation of a magnetic state.

An alternative approach[1] is "Renormalized Band Theory." This mixes the ab initio approach (including materials specific properties) with the many-body approach by utilizing the single-ion phase shifts obtained from Kondo theory to construct the Fermi surface. This is an ad hoc procedure, but has the virtue that it automatically obtains both the correct topology and the large mass enhancements.

Yet another alternative is to construct a Fermi Liquid theory of the ground state which can successfully correlate different properties, but which essentially avoids the issue of how to correctly obtain the Fermi liquid parameters.

The observation of superconductivity in several heavy fermion compounds generated much of the excitement about these compounds. As of 1986 it was known[1,3] that the superconductivity arises from the same electrons that are responsible for the heavy fermion behavior: the ratio of the specific heat jump at T_c to the normal state linear coefficient of specific heat $\Delta C/\gamma T_c$ has the BCS value only when the large heavy fermion value of γ is utilized in the formula.

It was appreciated fully that this superconductivity is highly unusual. The main evidence for this came from the observation for $T < T_c$ of power law behavior (as opposed to the exponentially activated behavior expected for simple superconductors) in such quantities as the specific heat, the ultrasonic attenuation, the thermal conductivity and the NMR rate $1/T_1$. The interpretation was that the energy gap was not uniform over the fermi surface, as for simple s-wave superconductors, but had point nodes or lines of

nodes where it vanished. Such effects were argued to be manifestations of higher angular momentum components (p-wave, d-wave, etc.) of the order parameter. Group theory was used to classify the possible representations of the order parameter associated with the different crystal symmetries. These can be grouped into odd parity (giving zeros at points) or even parity (giving lines of zeros); furthermore, in some cases the order parameter can carry a magnetic moment. A key issue for theory is thus to identify the order parameter symmetry present in the real materials. The second key issue is to determine the origin of the pairing—whether it arises from exchange of spin fluctuations or from a lattice mediated interaction (where the "Kondo volume collapse" or sensitivity of the hybridization V to cell volume is a key ingredient). A third is to calculate T_c in a situation where the effective $4f$ band width ($\sim T_K$) is not much smaller than T_c.

With this as a summary of the situation as of 1986, we now return to the present. In the intervening years there have been several important developments.[8-10] Perhaps the most significant has been the discovery of the importance of magnetic correlations in the ground state of heavy fermion systems. These are observed most directly by inelastic neutron scattering; antiferromagnetic correlations are manifest in the Q dependence of the inelastic scattering. (Ferromagnetic correlations are also observed in certain systems, a typical manifestation being a large Wilson Ratio, i.e., large enhancement of the susceptibility relative to the specific heat). The antiferromagnetic correlations are sometimes related to magnetically ordered phases which are close to the ground state in total energy. In 1986 several compounds were known to have modulated moment structures (i.e., static spin density waves) which in some cases are incommensurate with the lattice. One of the big surprises of the last five years has been the discovery of magnetic ordering with extremely small ordered moments ($0.001-0.1\ \mu_B$) in systems previously believed to be nonmagnetic. Indeed, such small moments now appear to be the rule and not the exception.

Another manifestation of coherence is the observation of low temperature neutron scattering lineshapes which differ from the high temperature single-ion form. Low temperature anomalies in the static magnetic form factor (viz. the onset of a $5d$ component adding to the $4f$ component) have been known for some time[2];

more recently it has been appreciated that these are reflected in a low temperature feature in the d.c. susceptibility.[8] Low temperature modifications of the quasi-elastic lineshape in inelastic neutron scattering have also been observed recently[8]; the low temperature shape is closer to being inelastic. To some extent this is already expected in single-ion theory, but in certain cases additional spectral weight appears at low temperature which cannot be so explained.

There has been a substantial increase in the number of systems whose Fermi surface has been studied by de Haas van Alphen experiments[9]; the conclusion stated above that one-electron band theory can correctly derive the topology of the Fermi surface, but not the large mass renormalizations, appears to be reinforced. The Renormalized Band scheme has been very successful in describing these results. In addition, several groups have pursued[10] the difficult task of measuring the optical conductivity in the very far infrared (the energy scales relevant to heavy fermions being 0.0001 to 0.1 eV). Although the results are somewhat controversial, the onset of renormalization of the effective mass as the temperature is lowered appears to have been observed. The temperature scale for this onset may differ from the single-ion Kondo temperature.

This raises a more general point concerning the applicability of single-ion theory. It is becoming increasingly clear that there can be several temperature scales for the low temperature phenomena: those of rapid decrease in the resistivity, of rapid increase in the specific heat coefficient $C(T)/T$, and of the growth of magnetic correlations, as well as other temperature scales such as the position of the maxima in $C(T)/T$ or features in the Hall effect or thermal expansion. The T dependence of $C(T)/T$ and the (Wilson) ratio of its magnitude to the susceptibility sometimes appear to be that of single-ion theory, but this can occur in a temperature range where the magnetic correlations are *known* to be present, and where the resistivity is rapidly decreasing with temperature. For this situation it is not clear whether it is meaningful to talk of a "single ion" regime; i.e., the heavy mass sets in when coherence is already present. This situation occurs already in the heaviest cerium compounds (where typically the heavy fermion behavior occurs within a crystal field doublet), but more especially in the

uranium compounds. Since the $5f$ uranium electrons are closer to the band limit, this is perhaps not surprising.

This brings us back to the issue of whether the appropriate starting point for theory is the local moment or the band limit. One of the main controversies around this issue has concerned the photoemission spectra. As mentioned above, one school[6,7] has maintained that the spectra are adequately described by Kondo impurity theory, appropriately extended to include spin-orbit and crystal field effects, as well as more realistic one-electron hybridization effects. The most recent work of this school is devoted to the interesting question of how to derive the parameters of the Anderson model from first principles.[11] Other groups[12] have emphasized the importance of screening interactions, i.e., Coulomb scattering (as opposed to hybridization) between a $4f$ hole and $5d$ conduction electrons. Similar interactions are responsible for the satellites observed in transition metal photoemission spectra. Recent studies of uranium based heavy fermion compounds have been interpreted[8] in this fashion: a $5f$ band at the Fermi surface and a satellite at a few eV binding energy are observed, but nothing on a low energy scale (i.e., a "Kondo Resonance") is resolved. Furthermore, dispersion of the $5f$ band has been observed.[10] The question is whether cerium photoemission might be described in similar fashion. Experimental resolution has improved sufficiently in the last few years that the predictions of Kondo impurity theory (which has become quite detailed) should soon be testable. At present the issue is undecided: certain recent work[13] seems to indicate the validity of Kondo theory, but other work[14] suggests that the impurity theory does not correctly describe either the temperature dependence or the relative weight of the peaks near the Fermi surface in cerium compounds.

Some of the most exciting recent work has been the delineation of the phase diagrams of the heavy fermion superconductors.[8-10] In all cases it appears that the superconductivity coexists with a small-moment antiferromagnetic phase of the type mentioned above. In UPt_3,[15] the observation of two heat capacity peaks, as well as kinks in the lower critical field and features in ultrasound experiments,[16] show that there are at least three superconducting phases in the HT plane. In $U_{1-x}Th_xBe_{13}$, for a limited range of x, a second transition occurs to a state which is now known to carry a magnetic

moment.[8] Various group theoretic treatments[15] have been given for these results, a key concept being that different representations of the complex order parameter occur in different phases. Interactions with the antiferromagnetism may remove the degeneracy of these representations.

In addition to the paramagnetic, antiferromagnetic and superconducting heavy fermion phases, another phase is possible, namely that of a small gap semiconductor. In the past,[2] the only known examples of this were in Sm compounds; more recently examples of cerium and ytterbium compounds with small (1–5 meV) activation energies have been discovered.[9] It is believed that this behavior reflects a hybridization gap which arises from the hybridization of the local 4*f* level with the conduction band; the gap is far too small, however, for this to be a simple one-electron effect. Many of the same issues as discussed above for the metals are relevant here; i.e., the nature of the crossover from a high temperature single-ion regime to a low temperature coherent semiconducting regime. Recent work has shown, for example, that single-ion theory fails to describe the low temperature susceptibility and thermal expansion of these semiconductors.[17]

An important issue for the valence fluctuation problem concerns the background chemical physics of the generalized phase diagrams of these materials, that is, the circumstances under which the various phase (paramagnetic, magnetic, superconducting or semiconducting) are observed. There has been steady growth of empirical and thermodynamic understanding in this area. A related issue concerns the existence of isomorphic valence transitions,[2] i.e., phase transitions where the valence and cell volume change discontinuously without change in crystal symmetry. These are believed to be driven by lattice mediated interactions, which arise because the hybridization increases as the cell volume decreases. This leads to the general question of the elastic properties of these compounds, i.e., the observed anomalous thermal expansion, compressibility, magnetostriction and ultrasonic behavior which is often observed.

There have been several interesting advances in theory as well. New work[18] on the two-impurity Kondo problem (which includes a magnetic coupling between impurities) has uncovered an unstable fixed point between nonmagnetic and antiferromagnetic phases of the impurities. In a Renormalization Group treatment the specific heat was shown to diverge at this fixed point—which suggests part of the heavy mass might be due to the divergence. However, a mean-field treatment showed no such divergence. Large N methods for the Kondo Lattice have demonstrated the existence of antiferromagnetic correlations, which are shown not to be soft. In a variational treatment a new class of excitations of the ($N = \infty$) Kondo Lattice have been proposed: "unbinding" excitations where a coherent state is locally replaced by a localized moment.[19] Perturbation theory in the Coulomb correlation U has been shown to have a simple $d \rightarrow \infty$ limit, allowing for reasonable treatment for finite dimension as well.[20] Finally, one of the most exciting developments[21] has been the solution for the spectral densities and transport behavior of the Anderson impurity model using quantum Monte Carlo. Hopefully this work can be extended to the Kondo/Anderson Lattice in the future.

Given these developments we plan a new series of Comments on heavy fermion/valence fluctuations. These Comments will discuss such topics as magnetic correlations and other manifestations of coherence, the photoemission spectra, the superconducting phase diagrams, small gap semiconductors, chemical physics, elastic properties and advances in theory.

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Note: In the interest of reducing the number of references, we have, wherever possible, cited review articles or conference proceedings which survey the relevant literature.

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