Heavy Fermions: Typical Phenomena and Recent Developments

F. Steglich, C. Geibel, K. Gloos, G. Olesch, C. Schank, C. Wassilew, A. Loidl* , A. Krimmel† and G.R. Stewart‡

Institut für Festkörperphysik, Fachgebiet Technische Physik, SFB 252, Technische Hochschule Darmstadt, D-64289 Darmstadt, Germany

**Institut für Festkörperphysik, Fachgebiet Experimentalphysik, SFB 252, Technische Hochschule Darmstadt, D-64289 Darmstadt, Germany*

†*Hahn-Meitner Institut, D-14109 Berlin-Wannsee, Germany*

‡*Institut für Physik, Universität Augsburg, D-86159 Augsburg, Germany, and Department of Physics, University of Florida, Gainesville, Fla. 32611, USA*

A survey is given of typical phenomena, new materials and recent developments in heavy-fermion physics. In particular, the following topics are addressed: (i) YbNiAl, *a new heavy-fermion local-moment antiferromagnet (LMM) with Néel temperature* $T_N = 3\,K$, *(ii) "non-Fermi-liquid" behavior at the magnetic instability in two heavy-fermion systems with intact f-ion sublattice, i.e. orthorhombic* $CePt(Si_{1-x}Ge_x)$ *and tetragonal* $U(Cu_{4+x}Al_{8-x})$, *(iii) the low-temperature properties of the anisotropic "Kondo insulator"* CeNiSn, *and (iv) some of the most unusual observations made on "low-carrier-density" rare-earth systems like* Sm_3Te_4 *and* Sm_3Se_4. *While the exotic symmetry-broken (superconducting and magnetic) ground states of heavy-fermion metals are discussed in several other contributions to this volume, we focus in the remainder of this paper on the relationship between LMM ordering and heavy-fermion superconductivity: Firstly, the LMM ordered compound* $CeCu_2Ge_2$ ($T_N = 4.1\,K$) *is addressed which was recently found to become a non-magnetic heavy-fermion superconductor under high hydrostatic pressure,* $p \geq 70\,kbar$ *(D. Jaccard et al., Phys. Lett.* A 163, 475 (1992)*). Point-contact spectroscopy is used to investigate in more detail the high-pressure superconducting phase of* $CeCu_2Ge_2$. *Secondly, we summarize high-pressure results on* UPd_2Al_3, *the first compound to show homogeneous coexistence between LMM ordering and heavy-fermion superconductivity.*

1. CLASSIFICATION OF HEAVY-FERMION SYSTEMS

In the field of strong electronic correlations in solids, several classes of materials are at the focus of present interest. Among them, and next to the cuprates, heavy-fermion (HF) metals have been studied most thoroughly. For about the last

15 years systems like $CeAl_3$, $CeCu_2Si_2$, YbCuAl, UBe_{13}, UPt_3 and $NpBe_{13}$ have been under investigation. HF metals are regular three-dimensional intermetallic compounds of certain lanthanides (notably Ce and Yb) and actinides (notably U, Pu and Np). They contain a lattice of f ions, embedded in a Fermi sea of (s,p,d) conduction electrons. Each of these materials is characterized by a temperature T^* (the "Kondo-lattice temperature"): Well above T^* the lanthanide/actinide ions carry local f-derived magnetic moments which are coupled only weakly to the conduction electrons ("weak-coupling" regime). Below T^*, however, this coupling becomes increasingly strong, eventually leading to a non-magnetic low-temperature state ("strong-coupling" regime).[1] The ground state of a rare-earth based HF metal depends critically on the competition between the magnetic inter-site interaction, i.e. the indirect RKKY exchange interaction, and the demagnetizing on-site Kondo interaction.[2] Using the dimensionless coupling constant for the exchange between the local 4f/5f spin and the conduction-electron spins, $g = N_F \mid \mathcal{J} \mid$ (N_F: conduction-band density of states at the Fermi energy, E_F; $\mathcal{J} < 0$: exchange constant), one can write for the respective RKKY and Kondo energies, $k_B T_{RKKY} \sim g^2$ and $k_B T^* \sim \exp(-1/g)$. $\mathcal{J}$ is connected with the parameters of the degenerate Anderson-impurity model (the on-site Coulomb repulsion, the f-electron valence excitation energy and the strength of the f-electron conduction-band hybridization) via the Schrieffer-Wolf transformation.[1] For the actinide-based HF compounds, with negligible direct 5f-wavefunction overlap, hybridization between 5f and ligand valence-electron states is usually stronger than for the more localized 4f electrons.[1] Therefore, two adjacent 5f configurations ($5f^2$ and $5f^3$) may be nearly degenerate and one single parameter (g) may not in every case be sufficient to classify the various ground states.[3]

Fig. 1 indicates[1] for exemplary Ce-based compounds that HF metals are found for $g < 1$, i.e. intermediate between the stable-moment regime of ordinary rare-earth magnetism ($g \ll 1$) and the intermediate-valence (IV) regime dominated by real charge fluctuations between the 4f/5f shell and the conduction band ($g > 1$). In most cases, IV compounds (like $CePd_3$) show a nonmagnetic Fermi-liquid ground state. For rare-earth based HF metals, valence fluctuations are usually ignored; an approximation which holds the better, the weaker the local exchange coupling. The latter gives rise to local spin fluctuations, which have essentially the same origin as in dilute Kondo alloys. Thus, HF metals characterize both the "magnetic limit" of the IV compounds and the "concentrated limit" of the Kondo alloys.

There exists a critical value of the local coupling parameter, g_c, at which the RKKY and Kondo interactions have the same strength.[1,2] For $g_c < g < 1$, the f-conduction-electron hybridization is sufficiently strong to fully compensate the local f-derived moments well below T^*. In a few cases like in $CeCu_6$, the thermodynamic and transport properties can be described within the framework of a heavy Fermi liquid. However, these Fermi liquids appear to be rather unstable against antiferromagnetic and/or superconducting phase transitions at $T_N/T_C \ll T^*$.

"HF superconductivity" was first observed in 1979 for $CeCu_2Si_2$,[5] whereas a clear-cut case of "HF band magnetism" has only recently been found in $Ce(Cu_{1-x}Ni_x)_2Ge_2$ alloys for $x \gtrsim 0.6$.[6] Heterogeneous forms of cooperative magnetism like in $CeAl_3$,[1] antiferromagnetic (AF) order with extremely small ordered moment ($10^{-2} - 10^{-3}\mu_B$) like in $CeRu_2Si_2$[7] and, in addition, finite magnetic cor-

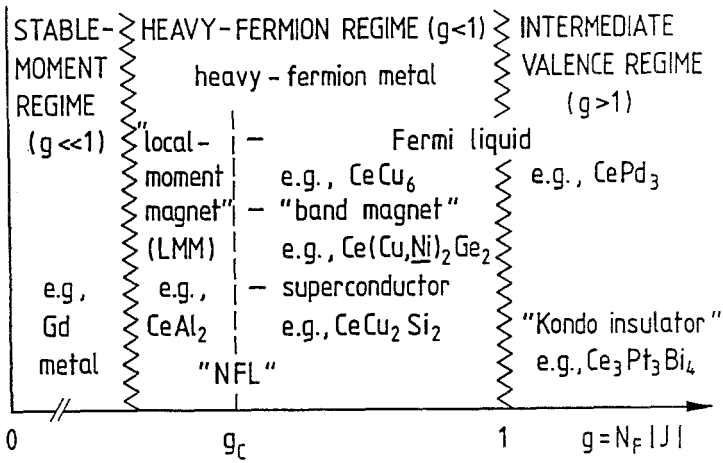

Fig. 1.
Schematic classification of heavy-fermion (HF) and intermediate-valence (IV) compounds using exemplary Ce intermetallics. Plotted on the abscissa is the dimensionless indirect local exchange-coupling constant $g = N_F \mid \mathcal{J} \mid$, roughly reflecting the degree of delocalization of 4f states.[1] HF compounds can adopt various ground states below the "Kondo-lattice temperature" T^*; HF "local-moment magnets" (LMM) and HF "band magnets" (with Néel temperatures T_N) are distinguished by $T_N/T^* \gtrsim 1$ and $T_N/T^* \ll 1$, respectively. LMM do not exist for $g > g_c$.[1] "Non-Fermi-liquid" (NFL) effects have been postulated[4] for systems with $g = g_c$. Note that all "Kondo insulators" known so far appear to be IV compounds ($g > 1$).

relation length like in URu_2Si_2[8] and UPt_3[9] have been discovered in the past few years. While already the nature of the magnetic phases with extremely small ordered moment is controversially discussed in the literature,[1,10,11] their coexistence with HF superconductivity in both URu_2Si_2[12] and UPt_3[13] holds even more challenges. A recent example of this coexistence between AF order of small moments and HF superconductivity well below T^* is UNi_2Al_3.[14] For the two "heaviest" HF superconductors, $CeCu_2Si_2$ and UBe_{13},[15] particularly complex phase diagrams are found upon application of a magnetic field in the former compound[16,17] and upon doping with Th in the latter.[18,19]

If the coupling constant $g < g_c$, $k_B T_{RKKY}$ exceeds $k_B T^*$ and the local f-derived moments are retained, though considerably reduced (to $\mu_s = 0.5 - 1\mu_B$) by the Kondo effect. Usually, a complex antiferromagnetically ordered state develops below $T_N < T_{RKKY}$ where $T_N \gtrsim T^*$. Most of the HF metals adopt this local-moment magnetically (LMM) ordered ground state, $CeAl_2$ being the archetypical example.[20]

This paper is organized as follows: In Sec. 2, we briefly discuss the characteristic properties of both heavy Fermi liquids and LMM ordered systems, emphasizing a new Yb compound: YbNiAl. Subsequently, we address new issues in HF physics: (i) the observation of "non-Fermi-liquid" (NFL) effects at $g = g_c$, i.e. at the magnetic

instability (Sec. 3), (ii) the properties of the so-called "Kondo-insulator", a novel ground state of HF/IV compounds (Sec. 4), and — in close connection with it — (iv) the very unusual class of "low-carrier-density" (LCD) rare-earth systems (Sec. 5). Several contributions to this volume are devoted to the exotic magnetic and superconducting properties of HF compounds like $CeCu_2Si_2$ and UPt_3. In order to avoid repetition, we wish to address in Sec. 6 only one particular aspect, i.e. the relationship between an LMM ordered ground state and HF superconductivity. The paper will be concluded in Sec. 7 by a short summary.

2. CHARACTERISTIC PROPERTIES OF HEAVY-FERMION METALS

2.1. Single-site vs inter-site effects

It is by now generally accepted that essential properties of HF systems are well described by the degenerate Anderson-impurity model.[1] In this model, a many-body (Kondo or Abrikosov-Suhl) resonance of width $k_B T_K$ and, in case of Ce, slightly above the Fermi level, is predicted to form below the single-ion Kondo temperature T_K. This has been verified recently by optical experiments, i.e. photo-emission spectroscopy (PES) and inverse photo-emission spectroscopy on $CeSi_2$ and $CePd_3$[21] as well as PES and X-ray absorption-edge spectroscopy on $YbAl_3$.[22] Since these latter systems belong to the class of IV compounds, one infers that the local spin fluctuations underlying the Kondo resonance persist in the presence of charge fluctuations.

In the HF intermetallic compounds interionic correlations and lattice-coherence phenomena can strongly modify the low-temperature properties when compared to those of the related Kondo alloy. Lattice-coherence phenomena are most convincingly found in the temperature dependence of the electrical resistivity: The f-ion increment, $\rho_m(T)$, deviates from the distinct Kondo-impurity behavior at $T \lesssim T^*$ and becomes very small at low T. Below $T_{coh} \simeq 0.1\,T^*$, $(\rho_m(T) - \rho_0)$ follows an AT^2 law, where ρ_0 is the usual residual resistivity. The gigantic coefficient A, which exceeds that of simple metals by several orders of magnitude, suggests that in the coherent heavy-Fermi-liquid phase extended Bloch states of very large effective mass (m^*) are scattered from one another: $\sqrt{A}$ scales universally[23] with the Sommerfeld coefficient, $\gamma_0 = C(T \to 0)/T \simeq C_m(T \to 0)/T$ which, for example, is about $1.5\,J/K^2(mole - Ce)$ for $CeCu_6$. Both γ_0 and the gigantic "Pauli-like" spin susceptibility χ_0 are proportional to m^*, which is estimated to exceed the free-electron mass by several hundred times: Despite these astonishing numbers, the Sommerfeld-Wilson ratio χ_0/γ_0 (properly normalized) is of order one as in simple metals.

The following picture has been deduced: Light conduction electrons ($m^* \lesssim 10 m_0$) are incoherently scattered from localized f electrons at high temperature. Upon cooling, the scattering rate strongly increases and the f electrons start to be weakly delocalized: A weakening of the f-derived moments (transition from Curie to Pauli behavior in $\chi(T)$) goes along with an increase in $\gamma(T) = C_m(T)/T$. Well below T^* the weakly delocalized f electrons become the eigenstates of the Kondo lattice, which form a very narrow 4f/5f band at E_F and, thus, dominate the

thermodynamic and transport properties. Their contribution to the low-T renormalized Fermi surface has been convincingly demonstrated by de Haas van Alphen and Shubnikov de Haas experiments.[24] The fact that the large m^* values develop only on lowering the temperature proves the inapplicability of one-electron theory: Rather a gradual removal of local Zeeman degeneracies is responsible for the formation of heavy fermions:

$$\int_0^{T \gg T^*} (C_m/T')\,dT' = \int_0^{T \gg T^*} \gamma(T')\,dT' = R \ln N$$

per mole f-ions, where, e.g., $N = 2$ for the low-lying crystal-field (CF) doublet of Ce^{3+} in $CeCu_6$. Obviously, the heavy masses originate in the Kondo-type magnetic fluctuations of the f-ions. (The definite proof that the huge linear specific heat is of electronic origin stems from the observation[5] that for $CeCu_2Si_2$ $\gamma(T \to 0) \simeq 1\,J/K^2$mole scales with superconducting properties like ΔC and $(-dB_{c2}/dT)_{T_c}$). Continentino[25] has recently provided arguments that the crossover from a "dense Kondo regime" into a heavy-Fermi-liquid regime below $T = T_{coh}$ shows universal behavior. This conclusion, drawn from analyzing the results of various techniques applied under external pressure to different HF metals, was ascribed to the vicinity of such compounds to the zero-temperature magnetic instability at $g = g_c$ (Fig. 1). In Sec. 3 we will discuss experimental evidence that magnetic fluctuations give rise to "non-Fermi-liquid" behavior if $g = g_c$ is chosen in suitable HF alloys. But, also for $g > g_c$ antiferromagnetic short-range correlations play an essential role in constituting the coherent heavy-Fermi-liquid phase.[26] This way Nozières' concern[27] that in a Kondo lattice there are not enough conduction electrons to screen all f moments is accounted for. Very roughly, one expects[28] the binding energy to form a many-body singlet state in the Kondo lattice, $k_B T^*$, to be smaller than $k_B T_K$, the corresponding energy gain of an isolated Kondo impurity, by the energy gain associated with these short-range correlations.

2.2. Local-moment antiferromagnetism

The majority of HF compounds is found on the magnetic side ($g < g_c$) of the $T = 0\,K$ instability. These LMM ordered systems undergo a magnetic phase transition before both the heavy masses and coherence among the electronic quasiparticles can fully develop. As was first shown[20] for the prototype LMM ordered system $CeAl_2$, the Kondo reduction of μ_s is accompanied by a substantial enhancement of the electronic specific heat, $\gamma_0 T$, in the AF ordered state. Many Ce-, U- and Np-based HF compounds like CeB_6, $CeCu_2Ge_2$, UCd_{11}, U_2Zn_{17} and $NpBe_{13}$ have been shown to belong to this class of HF metals.[1]

Yb^{3+} ($4f^{13}$) with one 4f hole is the analogue to Ce^{3+} with one 4f electron. Since the Kondo interaction should be symmetric between electrons and holes, one should be able to find Yb-based examples for the various kinds of HF systems displayed in Fig. 1. However, there is a surprising shortage of Yb-based HF compounds[29] — one of the many open questions in this field. For example: The Yb monopnictides[30] exhibit large electronic specific heats along with AF order below $T = 1\,K$, but none of them shows a negative temperature coefficient of the electrical resistivity at

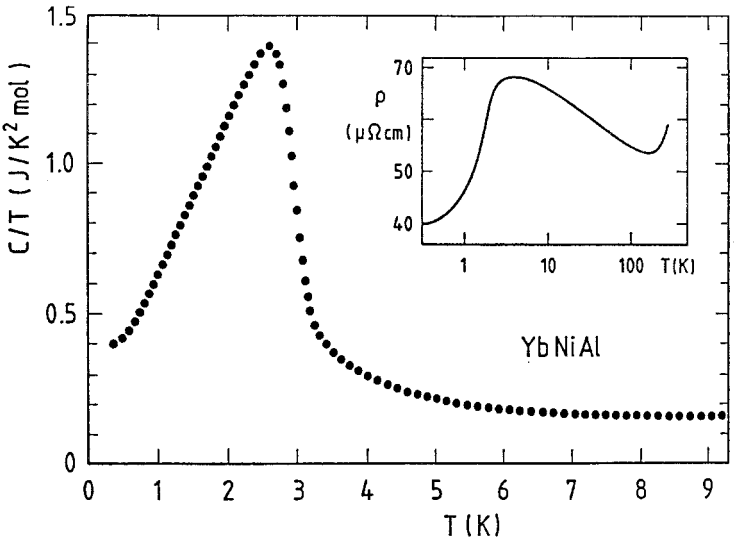

Fig. 2.
$C(T)/T$ (main part) and $\rho(T)$ (inset) for YbNiAl, a new HF compound with local-moment antiferromagnetism ($T_N \simeq 3\,K$).

elevated temperature, typical of incoherent Kondo scattering. Similar observations were made by Wohlleben's group[31] who compared the resistivities of the Ce and Yb members of several families of intermetallic compounds.

Fig. 2 comprises preliminary results on the new compound YbNiAl, one of the rare Yb-analogues to $CeAl_2$: Both the electrical resistivity, $\rho(T)$, and the specific-heat ratio, $C(T)/T$, indicate the onset of AF order below $T_N \simeq 3\,K$. This is also inferred from measurements of the magnetic susceptibility, $\chi(T)$ (not shown). For $T > T_N$, $\chi(T)$ follows a Curie-Weiss law indicative of a CF-split Yb^{3+} configuration. Above $T = 8\,K$, $\rho(T)$ decreases nearly logarithmically over one decade in temperature, before the population of excited CF levels causes an increase of $\rho(T)$ above 150K. A CF splitting $\Delta \gg k_B \cdot 10\,K$ and a low-lying doublet is concluded from the small molar entropy at T_N of $0.45\ln 2$, a typical number for LMM ordered systems.[1] Well below T_N, the resistivity is dominated by a quadradatic term, $\rho - \rho_0 = AT^2$, while a large linear term, $\gamma_0 T$, adds to a magnon-derived βT^3 term in the specific heat. The coefficients A and γ_0 are found to scale as in other HF compounds.[23] These enhanced AT^2 and $\gamma_0 T$ terms indicate itinerant, strongly correlated electronic states (of 4f symmetry) coexisting with AF order.

Ce- as well as U-based LMM materials are known to be sensitive to volume compression, which may eventually cause a collapse of AF order. In order to discuss the occurrence of "non-Fermi-liquid" (NFL) effects we address in the subsequent section two HF systems which exhibit such a magnetic-to-nonmagnetic transition.

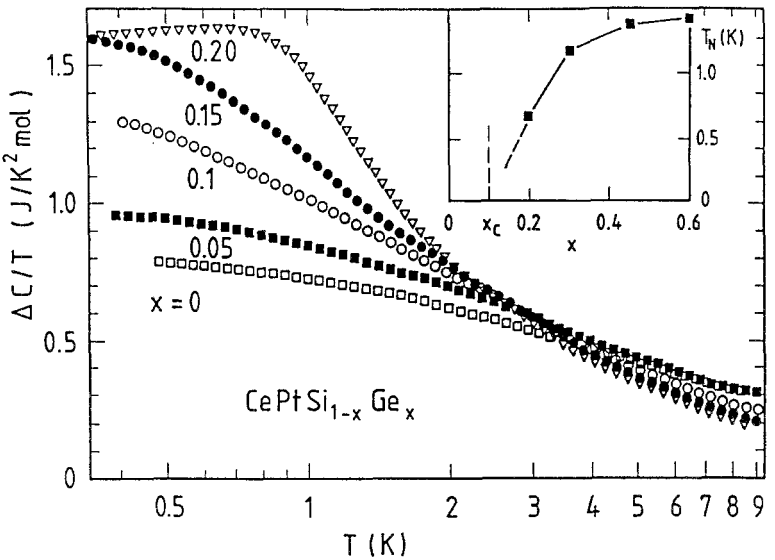

Fig. 3.
Ce increment, ΔC, to the specific heat of various $CePt(Si_{1-x}Ge_x)$ alloys, divided by T, as a function of temperature T (on a logarithmic scale).[44] Inset shows T_N vs x,[45] suggesting a complete suppression of LMM ordering at $x_c \simeq 0.1$.

3. NON-FERMI-LIQUID EFFECTS AT THE MAGNETIC INSTABILITY

Nozières and Blandin[32] were the first to study the "overscreening" problem which arises when the impurity spin S on a Kondo ion interacts with conduction-electron channels for which $N > 2S$. This problem, in particular the special case of $S = 1/2$, $N = 2$ ("two-channel Kondo model"), has attracted much interest in the 1980s when theorists have calculated its thermodynamic properties.[33] Instead of the local Fermi-liquid that is theoretically predicted and experimentally observed well below T_K in the ordinary one-channel Kondo model, logarithmic divergencies are found both for the magnetic susceptibility and the ratio C_m/T, i.e. $\chi \sim C_m/T \sim (-\ln T/T_K)$ ($B_{ext} = 0$). Such T dependencies are expected for a local marginal Fermi liquid (LMFL).[33] So far, one dilute magnetic alloy, (Th,U)Ru_2Si_2, is known to show the afore-mentioned logarithmic divergencies in both $\chi(T)$ and $C_m(T)/T$.[34] However, the corresponding[33] LMFL law of the electrical resistivity, $\rho - \rho_0 = -aT^{1/2}$, has not been observed in (Th,U)Ru_2Si_2.[34]

In a more general sense, multi-channel Kondo models can also imply orbital degrees of freedom of the Kondo impurity. This possibility was first discussed by Fulde and Loewenhaupt[35] and subsequently applied by Cox[36,37] to U- and Ce-based HF compounds. Moderately diluted $(Y_{1-x}U_x)Pd_3$ is the prime candidate[38,39] of the so-called quadrupolar Kondo-impurity effect, and the $(Y_{1-x}Pr_x)Cu_2Si_2$ system ($0.05 \leq x \leq 0.4$) seems to be a further example.[40] Alternatively, NFL effects found in $(Y_{1-x}U_x)Pd_3$ have been attributed to magnetic U-U correlations above a second-

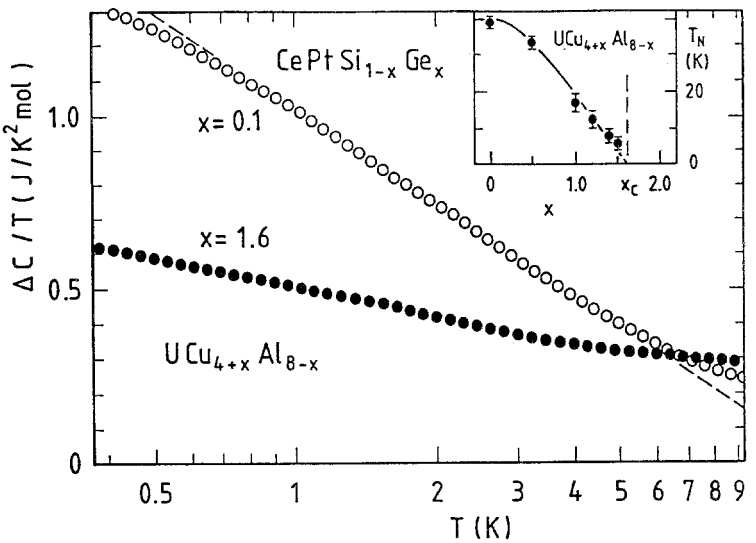

Fig. 4.
Ce/U increment, ΔC, to the specific heat of $CePt(Si_{0.9}Ge_{0.1})$ and $U(Cu_{5.6}Al_{6.4})$, divided by T, as a function of T (on a logarithmic scale). Inset: T_N vs x for $U(Cu_{4+x}Al_{8-x})$,[46] suggesting $T_N \to 0K$ at $x_c \simeq 1.6$.

order phase transition at $T = 0\,K$.[41] Starting from this interpretation of their observations on $(Y_{1-x}U_x)Pd_3$, Andraka[42] and Kim et al.[4] have successfully searched for NFL phenomena in the vicinity of the magnetic instability of several (more or less concentrated) HF systems, e.g. $UCu_{5-x}Pd_x$ and $U_{1-x}M_xNi_2Al_3$ (M=Th, Pr). Similar observations on $Ce(Cu_{1-x}Au_x)_6$ single crystals were communicated during this conference.[43]

In order to enlarge the material basis for NFL behavior, we have recently initiated an investigation of two HF systems in which the f-ion sublattice is kept intact while a magnetic instability can be induced either by controlled alloying or by controlled changes of the stoichiometry: Orthorhombic $CePt(Si_{1-x}Ge_x)$ is antiferromagnetic for $x \geq 0.2$,[45] and its Néel temperature vanishes at $x_c \simeq 0.1$, see inset of Fig. 3. For the tetragonal compound $U(Cu_{4+x}Al_{8-x})$ a wide homogeneity range and a steady decrease of T_N upon increasing Cu content was reported.[46] Antiferromagnetism, being completely suppressed at $x_c \simeq 1.6$ (inset of Fig. 4), is replaced in the Cu-rich systems by strong local HF effects.[46] In the main panels of Figs. 3 and 4 we show preliminary results on the specific heat near $x = x_c$ for these two very different systems. In fact, $CePt(Si_{0.9}Ge_{0.1})$ and $U(Cu_{5.6}Al_{6.4})$ exhibit a straight-line dependence if $\Delta C_m/T$ is plotted against a logarithmic temperature scale. (Here ΔC_m is obtained by subtracting from the raw data those of the respective La- and Th homologues). In both systems, this distinct behavior is found over about one decade in temperature. The molar entropy of the Ce- and U-based system between

0.4 K and 6 K changes by, respectively, 0.9 Rln2 and 0.55 Rln2 and, thus, points to a lowest-lying CF doublet in either case. Experiments on the magnetic susceptibility and the electrical resistivity are in preparation to support the NFL behavior inferred from the $\Delta C_m(T)/T$ data presented in Figs. 3 and 4. Since the Ce^{3+} ions in $CePt(Si_{1-x}Ge_x)$ experience an orthorhombic CF, the two-channel Kondo model is, due to selection-rule arguments,[37] not applicable. Furthermore, the single-impurity model is unlikely to explain the low-T properties of an intact f-ion lattice. We, therefore, conclude that the two systems displayed in Figs. 3 and 4 are further examples[4,42,43] for NFL behavior as a consequence of a $T = 0$ K quantum phase transition.

4. KONDO INSULATORS

The idea of a gap or pseudogap in the HF density of states at E_F arising from the hybridization of the renormalized f band with ordinary conduction bands has been developed already more than a decade ago.[47] The existence of a weak pseudo gap was previously proposed to explain a maximum (near $T = 0.5$K) in $\gamma(T) = C(T)/T$ for both $CeAl_3$ and normal(n)-state $CeCu_2Si_2$.[48] However, for these compounds, a complex renormalized band structure, heterogeneous cooperative magnetism[49] and/or phase transitions of unknown origin[17] render this explanation ambiguous. On the other hand, in the case of a sufficiently simple band structure (i.e. if only one half-filled conduction band can hybridize with the HF band) and in the absence of strong magnetic interactions, a hybridization gap of this kind may develop. In fact, there is increasing evidence[50] that several mostly cubic IV compounds (notably of Ce) which behave as disordered metals at high temperatures become semiconducting below T^*. Typically, their homologues are ordinary metals /ordinary band-gap semiconductors when Ce is replaced by a trivalent/tetravalent non-f ion. A prototype system is $Ce_3Pt_3Bi_4$[51] with $T^* \simeq 300$K and a transport gap Δ of order $T_g = \Delta/k_B \simeq 100$ K. Along with the charge gap, a spin gap seems to open below $T \simeq T_g$, which indicates that the lower hybridized subband is fully occupied.[50] Excitations across the gap induced by an external magnetic field manifest themselves in a large negative magnetoresistivity. In contrast to simple semiconductors where pressure is known to always reduce the gap, Δ of $Ce_3Pt_3Bi_4$ is found to increase under external pressure (reflecting the increase of the Kondo lattice temperature T^*).[51] Two further very striking observations with such systems should be mentioned:

(i) The optical weight removed from the gap in FeSi (another potential candidate for Kondo insulator) is not recovered just above the gap edge as it should for a simple band-gap insulator; rather, one has to go to energies of a few eV to meet the balance in optical weight.[52] This was ascribed to strong on-site correlations and to some extent resembles the observation that the BIS spectra of Ce-based IV compounds show, even at several eV, a remarkable temperature dependence below $T = 300$ K.[21] (ii) Though strong antiferromagnetic correlations are observed in the dynamic susceptibility of both $Ce_3Pt_3Bi_4$[53] and CeNiSn,[54] they appear to be absent in the static bulk susceptibility. This constitutes a remarkable difference of the Kondo insulators to the HF metals:[50] While no static magnetic correlations seem to exist in the former, these are essential for the latter,[26] as was mentioned before.

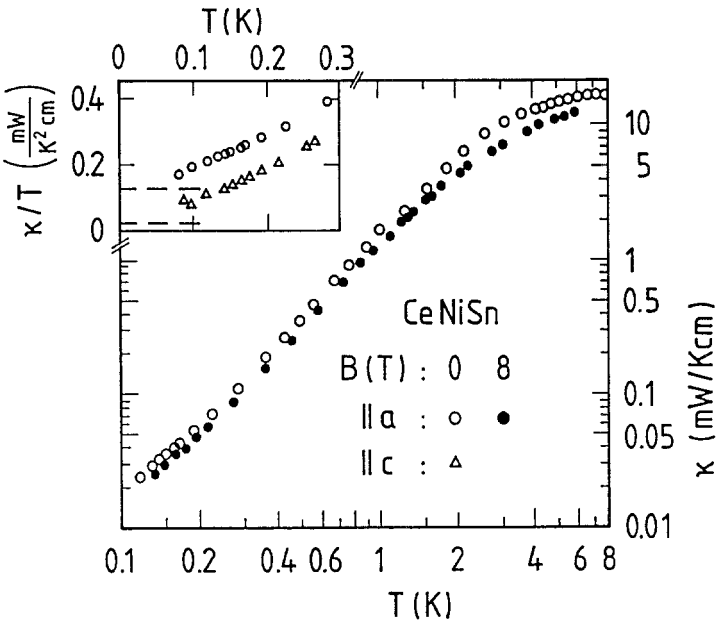

Fig. 5.
Double-logarithmic plot of the thermal conductivity κ *vs* T for a CeNiSn single crystal with heat flow along a axis at $B = 0T$ and $8T$. Inset shows κ/T *vs* T for $B = 0$ T results taken along a and c axis, respectively.[58] Dashed lines mark κ_{el}/T as calculated from the electrical residual resistivity ρ_0 via the Wiedemann-Franz law.

In the following, we discuss low-temperature results on CeNiSn, the first known (and only non-cubic) example of a Ce-based Kondo insulator.[55] CeNiSn crystallizes in an orthorhombic structure and is characterized by $T^* \simeq 100$ K. Takabatake et al.[55] have found a rather small gap corresponding to $T_g \simeq 7$ K, which shows a strongly anisotropic response to the application of an external magnetic field $\vec{B}$. For $\vec{B} \parallel \vec{a}$ (the easy axis), the gap is efficiently suppressed (and disappears at $B \simeq 20T$), while it is rather insensitive against B fields applied along the b or c axes. Previous resistivity and thermopower measurements indicate a metallic ground state of CeNiSn with low "residual" carrier concentration.[56] From the fact that the large low-T linear specific heat, γ_0T with $\gamma_0 \simeq 50\text{mJ/K}^2 mole$, shows a magnetic-field-induced increase ($B \leq 12$T) only if $\vec{B} \parallel \vec{a}$, the residual carriers inferred from the transport properties are found to be of a large effective mass.[57] This interpretation is supported by recent experiments of the thermopower and heat conductivity performed to $T < 0.1$K on CeNiSn single crystals:[58] Itinerant electronic states contribute to the heat transport which is dominated by the phonons:[59]

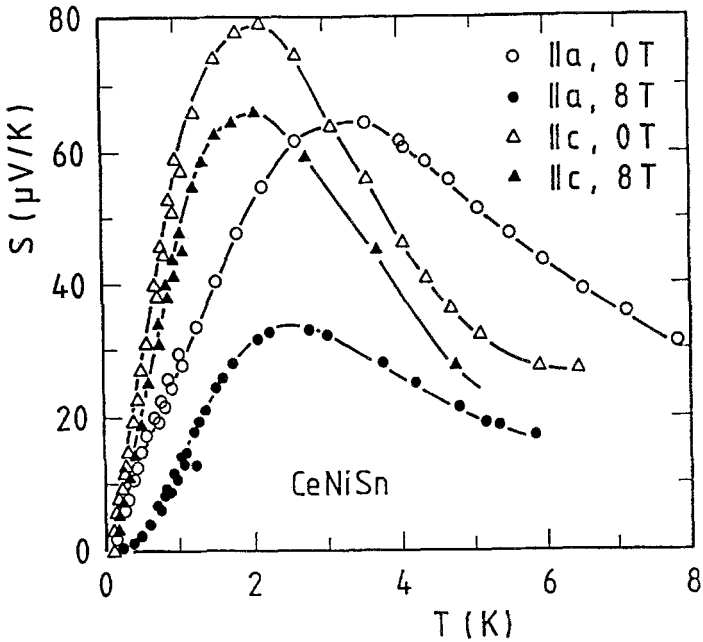

Fig. 6.
Thermopower S *vs* T for CeNiSn single crystals measured along a and c axes as well as at $B = 0\,\mathrm{T}$ and 8 T, respectively.[58]

$\kappa = \kappa_{\mathrm{el}} + \kappa_{\mathrm{ph}}$. As shown in the inset of Fig. 5, $\kappa_{\mathrm{el}} = \alpha T$ $(T \to 0\,\mathrm{K})$ is in accordance with the measured electrical resistivity ρ_0 (as $T \to 0\,\mathrm{K}$),[56] if validity of the Wiedemann-Franz law, $\alpha \cdot \rho_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$, is assumed.

The same carriers are held responsible for the linear T-dependence of the low-T thermopower S(T), its somewhat anisotropic record slope of $55\mu\mathrm{V/K}^2$ (Fig. 6) being suggestive of a strong energy dependence of their relaxation rate. These carriers act as the main scatterers of the propagating phonons: A strong reduction of the phonon conductivity as observed in a field of 8T only if B is applied along the a-axis (Fig. 5, main part) supports an efficient closing of the electronic gap in this direction as concluded from other experiments.[56,57] No surprise, the T-dependence of the thermopower is qualitatively changed in $B = 8\,\mathrm{T}$ only, if $\vec{B} \parallel \vec{a}$ (Fig. 6). We note that our results are in conflict with a "two-phase model" which predicts[60] the low-T thermopower to depend only very weakly on a magnetic field of this magnitude.

In summary, we have found that a small number of strongly correlated carriers dominates the transport properties of CeNiSn well below $T_g \simeq 7\,\mathrm{K}$. It remains, presently, unclear whether these states are due either to an intrinsic pseudogap

in the HF density of states or to extrinsic "Kondo-holes" states, as predicted by Doniach et al.[61]

5. RARE-EARTH COMPOUNDS WITH LOW CARRIER DENSITY

It is interesting to note that the description of systems like $Ce_3Pt_3Bi_4$ and CeNiSn in terms of hybridization-gap formation involving a coherent HF band is not unambiguous: For example, Kasaya[62] argues that in either of these two compounds Ce is tetravalent with the gap being an ordinary band gap, though modified by 4f valence-band mixing. Similar ambiguity is found in the literature when the properties of other "gap materials", like pressurized SmS, SmB_6 and YbB_{12}, are discussed.[50,62] Alternatively to the (hybridization-) gap models involving coherent f-electron states, a local origin of the charge/spin gap in SmB_6 and YbB_{12} has been proposed.[63] According to Kasuya,[63] these materials are related to the so-called low-carrier-density (LCD) rare-earth systems. Here, the non-f reference compounds are either narrow-gap semiconductors or semimetals, with very weak overlap between the tails of the respective valence and conduction bands. At the outset, the carrier concentration in the IV counterparts is then very low. Poorly screened long-range Coulomb forces among the carriers may eventually result in a charge ordering or some related state ("Wigner-liquid formation").[30] The prototypical examples of LCD rare-earth systems are the Ce monopnictides which order antiferromagnetically at low T and whose La homologs are, in fact, semimetals. Kasuya's original motivation[30] to study LCD rare-earth systems is provided by Nozières' concern[27] that in a metallic Kondo lattice, only a minute fraction of the conduction electrons ($T^*/T_F \simeq 10^{-3}$) is available to "screen" one local f spin. Deeper insight into this problem is expected for a lattice of f spins embedded in a carrier system whose concentration, n_e, is much lower than in the metallic Kondo lattice. Very surprising observations have been made in LCD rare-earth systems, e.g.:

(i) The Kondo temperature estimated for CeSb ($n_e \simeq 10^{-2}$/Ce) on the basis of an effective Anderson-impurity model is $T_K \simeq 10^{-10}$ K.[30] However, instead of stable f moments, Kondo-lattice effects with $T^* \simeq 100$ K, in addition to AF order below $T_N = 16$ K, are observed.

(ii) The compound Yb_4As_3 (crystallizing in the "anti-Th_3P_4" structure) is so far the only LCD rare-earth system lacking long-range magnetic order. It shows metallic conductivity above a structural transformation at $T_s \simeq 300$ K. In its low-T phase, a $\rho(T)$ curve is found which strongly resembles that of a typical Kondo-lattice system, although Hall-effect measurements yield a carrier concentration as small as 10^{-3}/Yb.[64] The coefficient A of the T^2 term in $(\rho(T) - \rho_0)$ scales with the large Sommerfeld coefficient, $\gamma \simeq 0.2\,J/K^2 mole$, in the same universal way[23] as for the HF metals with large carrier concentration.

(iii) In Sm_3X_4 (X: Se,[65] Te;[66] crystallizing in the Th_3P_4 structure) the carrier concentration $n_e = 0$, in accord with an optical band gap of several eV[67] and a transport gap of $\simeq 0.15$ eV.[68] Charge neutrality requires one non-magnetic Sm^{2+} and two magnetic Sm^{3+} ions per formula unit, but so far no indication of charge ordering could be observed. Valence fluctuations were found[68] to be thermally driven above 30 K, but to occur in a less T-dependent manner at lower temperature.[69]

Fig. 7 shows the low-T specific heat of Sm_3Te_4[66] which displays complex anti-

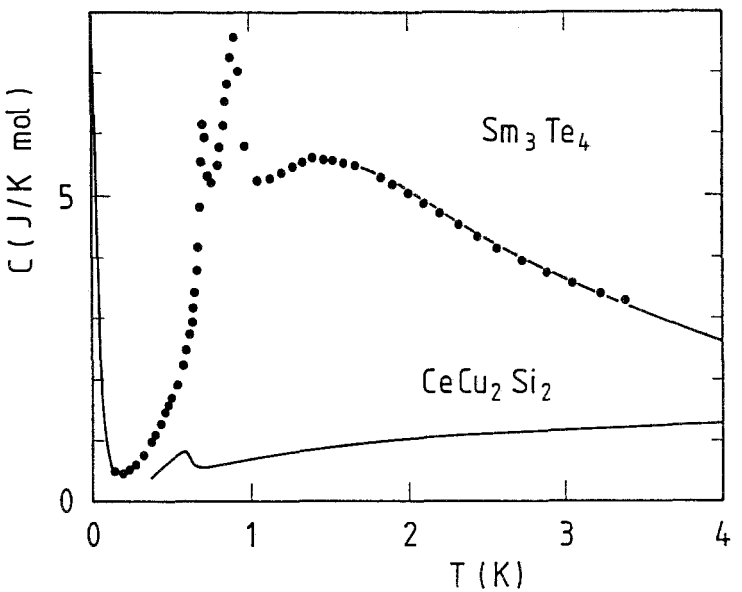

Fig. 7.
C *vs* T for Sm_3Te_4 at $B = 0\,T$.[66] Solid line corresponds to a fit of (i) a resonance-level model (RLM) to the data for $T > 1\,K$ and (ii) the same RLM plus the sum of a magnon term βT^3 and a nuclear term α/T^2 to the data below $T = 0.3\,K$, see text. For comparison, C *vs* T for the typical HF intermetallic $CeCu_2Si_2$ is also shown.

ferromagnetic order below 0.7 K. A broad maximum in C(T) occurs around 1.5K, associated with an entropy (at T $\simeq$ 4 K) of $\simeq$ Rln2/(*mole* − Sm_3Te_4). As indicated in the figure, the C(T) values measured for Sm_3Te_4 exceed the ones of the prototypical HF metal $CeCu_2Si_2$ considerably. Most surprisingly, C(T) can be well fit by the $S = 1/2$ Kondo-impurity model.[66] The fit parameters used for a simple resonance-level model (RLM) are $S = 1/2$, $T_K = 0.8\,K$ and a Zeeman splitting of the doublet (due to $Sm^{3+} - Sm^{3+}$ interactions) $E_Z = k_B \cdot 3.2\,K$. The asymptotic low-T behavior of this RLM curve yields $C = \gamma T$ with $\gamma = 1.2\,mJ/K^2(mole - Sm_3Te_4)$, or $\gamma = 0.6\,J/K^2(mole - Sm^{3+})$. Taken together with a nuclear term, αT^{-2}, and a magnon term, βT^3, this "HF-like" specific heat provides a very good fit of the measured low-T data. A similar γT term, $\gamma = 0.79\,J/K^2(mole - Sm^{3+})$, is found in Sm_3Se_4.[65] The nature of the low-energy excitations underlying the giant γT contributions and, more generally, of the "screening mechanism", which causes the observed gradual removal of most of the local Zeeman entropy and which replaces the ordinary Kondo effect in these insulators, remain to be unravelled.

6. RELATIONSHIP BETWEEN LOCAL-MOMENT ORDERING AND HEAVY-FERMION SUPERCONDUCTIVITY

We now return to the HF metals and discuss recent results concerning the relationship between local-moment antiferromagnetic (LMM) ordering and HF superconductivity. A paradigm in HF physics, these ground-state properties were considered as excluding each other, as is illustrated in the first subsection of this section with the interesting case of $CeCu_2Ge_2$. However, homogeneous coexistence of LMM ordering and HF superconductivity was recently concluded from specific-heat measurements under hydrostatic pressure on UPd_2Al_3. This unprecedented coexistence will be addressed in subsection 6.2.

6.1. Competition: $CeCu_2Ge_2$

The Kondo-lattice system $CeCu_2Ge_2$ exhibits $T^* \simeq 8\,K$ and $T_{RKKY} \simeq 7\,K$, exceeding the AF ordering temperature $T_N \simeq 4\,K$.[70] These numbers place $CeCu_2Ge_2$ among those LMM ordered systems very close to the magnetic instability ($g \lesssim g_c$), cf. Fig. 1. Compared to its Si-homolog ($V_c \simeq 167\,\mathring{A}^3$), $CeCu_2Ge_2$ has a bigger unit-cell volume of $V_c \simeq 177\,\mathring{A}^3$. Employing the bulk modulus of the former compound, $C_B \simeq 1200$kbar,[71] one estimates that a hydrostatic pressure $p \simeq 70\,$kbar will be sufficient to compress the volume of $CeCu_2Ge_2$ such as to adopt that of $CeCu_2Si_2$ (at $p = 0\,$kbar). Jaccard et al.[72] have recently performed resistivity experiments on $CeCu_2Ge_2$ under hydrostatic pressures up to 100 kbar and observed, in fact, that for $p \gtrsim 30\,$kbar, $T_N(p)$ starts to decrease and that AF order is replaced by superconductivity if a pressure of $\gtrsim 70\,$kbar is applied. Not only the value of $T_c = 0.64\,K$, but also its small positive pressure derivative, dT_c/dp, and the upper critical field (as $T \to 0\,K$), highlights[72] superconductivity in the high-pressure phase of $CeCu_2Ge_2$ to be very similar to that of $CeCu_2Si_2$ at ambient pressure. In particular, the gigantic $B_{c2}(T)$ slope at $T_c(-11T/K)$ proves that Cooper pairs are formed by slowly propagating ("heavy") quasiparticles.[73] An important conclusion from Jaccard et al.'s discovery is that the ground-state properties in $CeCu_2X_2$ (X: Ge, Si) are governed by the unit-cell volume.

In the following, we describe preliminary results of point-contact spectroscopy on a $CeCu_2Ge_2$ single crystal. This technique can give valuable information on the properties of HF compounds.[74,75] In pressure-type microcontacts the local pressure at the contact can approach the plastic-flow limit of the electrodes. Choosing the right material one can achieve pressures as high as 100kbar. For our experiments we used tungsten wires cut sharply and pressed onto the $CeCu_2Ge_2$ sample. The onset of AF order below $T = T_N$ is manifested in the point-contact spectra by the formation of a broad minimum in dU/dI *vs* U, centered around zero-bias voltage and being 2 to $3meV$ wide (Fig. 8). The Néel temperature determined this way varies from contact to contact between 3.3 K and 0.66 K. We assume that a local-pressure effect gives rise to the observed depression[72] of T_N as compared to its $p = 0\,$kbar value of 4.1K. A number of these contacts showed additional anomalies at low temperatures with a reduced differential resistance around zero bias voltage.[76] Some, but not all, of those anomalies can be well described by the theory of Blonder, Tinkham and Klapwijk (BTK)[77] for Andreev scattering in the presence of ordinary quasiparticle scattering at a superconductor-normal conductor interface (Fig. 8).

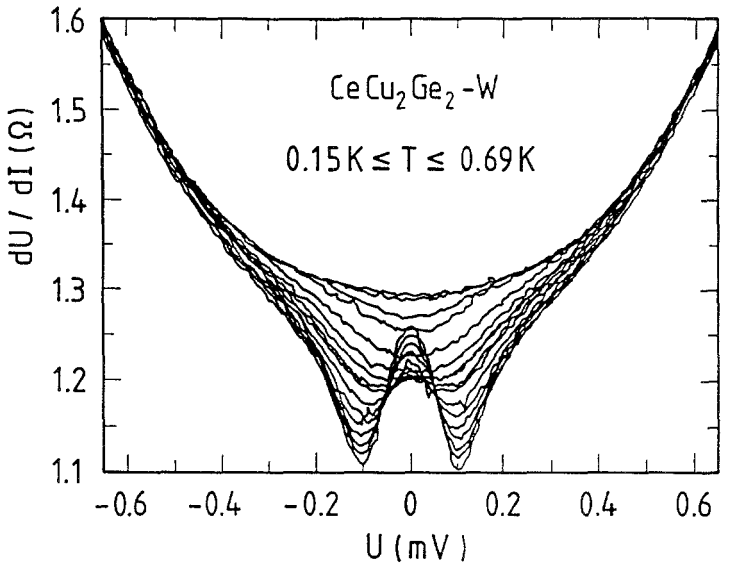

Fig. 8.
Differential resistance dU/dI as a function of bias voltage U for a metallic point contact between a $CeCu_2Ge_2$ single crystal ($I \perp c$) and a tungsten tip at differing temperatures between $T = 0.69\,K$ (upper-most curve) and $0.15\,K$ (lowest curve). The broad minimum indicates antiferromagnetic order below $T_N \simeq 3\,K$. An excess current and a two-well structure at temperatures below 0.69K is ascribed to local high-pressure superconductivity (see text).

With T_c being $0.68\,K$, the superconducting gap (as $T \rightarrow 0\,K$) amounts to $2\Delta = 0.23meV$, in good agreement with the BCS theory. Meanwhile, we have investigated those contacts in a magnetic field and find $B_{c2}(T \rightarrow 0\,K) \simeq 2$Tesla and a very large critical-field slope at T_c, in agreement with Jaccard et al.[72] We note that the data of Fig. 8 clearly show simultaneously the signatures of AF order ($T_N \simeq 3\,K$) and of HF superconductivity. This suggests that the point contact consists of an inner non-magnetic region of very high local pressure ($p \gtrsim 70\,kbar$) surrounded by an AF ordered region of intermediate pressure ($p = 40 - 60\,kbar$).[72] Similar observations, involving different superconducting high-pressure phases, have been made for certain organic charge-transfer salts.[78]

6.2. Coexistence: UPd_2Al_3

This hexagonal compound orders antiferromagnetically below $T_N \simeq 14\,K$.[79] Its magnetic properties appear phenomenologically closely related to the type-II AF ordered state of $CeAl_2$:[80,20] Surprisingly large ordered moments of $\mu_s = 0.85\,\mu_B$/U are ferromagnetically aligned within the basal planes and antiferromagnetically ali-

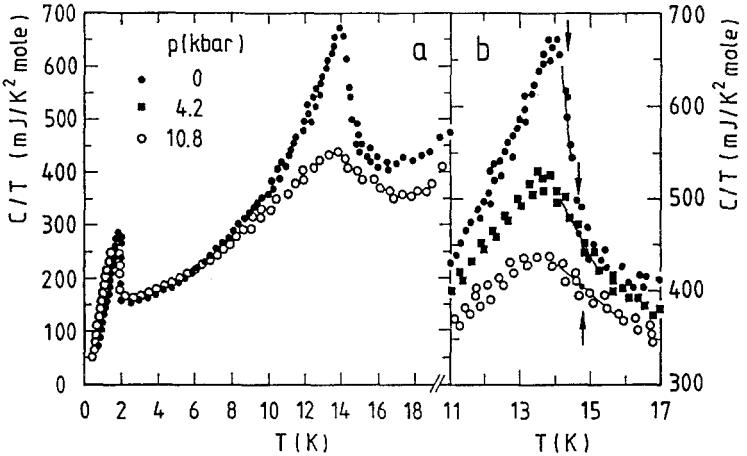

Fig. 9.
C/T *vs* T at differing pressures and $B = 0\,\mathrm{T}$ for UPd_2Al_3 for $T \leq 20\,\mathrm{K}$ (a) and $11 \leq T \leq 17\,\mathrm{K}$ (b).[85] Arrows in (b) mark Néel temperatures $T_N(p)$.

gned along the perpendicular (c) direction.[81] Pronounced CF-splitting effects have been inferred from susceptibility[82] and specific-heat[83] results. Inelastic neutron-scattering techniques have been used to determine the CF-level scheme.[84] The raw spectra reveal weak but well defined peaks indicating CF transitions above a broad quasielastic line. Even after the subtraction of the phonon spectrum of the non-magnetic reference compound $ThPd_2Al_3$ well defined CF excitations are derived. However, a more detailed analysis is necessary to identify both, the peak-like structures and the broad quasielastic line, as originating from the 5f electrons.

The n-state specific heat well below T_N can be decomposed[85] as $C_n(T) = \gamma_0 T + \beta T^3$ (cf. Fig. 9a), where the cubic term primarily is due to the spin-wave contribution. In this same temperature regime one finds that $\rho(T) - \rho_0 = AT^2 + BT^5$ provides a very good fit to the resistivity data.[85] Apart from the spin-wave-derived T^5 term, the low-T resistivity is dominated by the AT^2 contribution. For this compound, too, one finds that the coefficient A and the enhanced Sommerfeld coefficient $\gamma_0 = 0.14\,J/K^2 mole$ (being nearly identical to that of $CeAl_2$[20]) scale in the same universal way[23] as for other non-magnetic and AF ordered HF metals. These $\gamma_0 T$ and AT^2 terms in $C_n(T)$ and $\rho(T)$ manifest the presence of strongly correlated 5f states, coexisting with AF order. Similar to what was found[86] for the type-II AF phase of $CeAl_2$, the Néel temperature of UPd_2Al_3 is shifted slightly towards higher temperatures (Fig. 9). In contrast to $CeAl_2$, however, UPd_2Al_3 turns superconducting below the record-high T_c of 2 K out of this LMM ordered state.[79] Since the specific-heat jump ΔC at T_c is comparable to the enhanced value of $\gamma_0 T_c$, superconductivity in UPd_2Al_3 is clearly of the HF type. This is corroborated by the large $B_{c2}(T)$ slope at T_c, being $-4.3\,\mathrm{T/K}$.[87] Neutron-diffraction[81] as well as

μSR[87] measurements prove that HF superconductivity and AF (LMM) order, both phenomena essentially involving the same 5f electrons, coexist homogeneously below T_c. This is the more surprising since in the well-known "magnetic superconductors" (e.g. certain Chevrel phases) AF ordering and superconductivity are associated with different species of electrons, i.e. Mo-d derived 4d and rare-earth-derived 4f electrons, respectively.[88]

A possible resolution of the unexpected coexistence between LMM ordering and HF superconductivity was provided by recent specific-heat experiments under hydrostatic pressure, p.[85] Here, one finds that application of p $\simeq$ 11 kbar results in (i) a strong depression[89] of the specific-heat anomaly at the magnetic phase transition (Fig. 9), (ii) an increase of γ_0 which is unusual in view of the increase in T_N(p) (Fig. 9b), (iii) a rather weak[90] depression of both T_c and ΔC and (iv) nearly the same increase in the "residual" ($T \rightarrow 0$ K) specific-heat term,[91] γ_r, as stated for γ_0. This most surprising observation that the p-induced increase of γ_0 (for $T > T_c$) is the same as that of γ_r (for $T \ll T_c$) has led[85] to the suggestion of a n-state specific heat, $\gamma_0(p)T$, being decomposable into a pressure-independent term, $\gamma_1 T$, and a pressure-dependent one, $\gamma_r(p)T$. Caspary et al.[85] proposed to relate the p-dependent part $\gamma_r(p)T$ to one subset of "more localized" 5f quasiparticles, characterized by $T^*_{low} \lesssim T_N = 14$ K, and responsible for magnetic ordering. On the other hand, the p-independent term $\gamma_1 T$ was ascribed to another subset of "less localized" 5f quasiparticles (with $T^*_{high} \geq 25$ K), responsible for superconductivity. These two subsets, which represent the $CeAl_2$- and UPt_3-types of HF compounds on either side of the magnetic instability (Fig. 1) and which coexist in k-space, appear to be only weakly coupled to each other. This poses an interesting analogy to the Chevrel-phase superconductors, in which the superconducting and magnetic electrons are also only weakly coupled to each other, i.e. in r-space. Earlier measurements of the upper critical field[87] and of the Knight shift[92] have clearly indicated that UPd_2Al_3 is a clean, even-parity superconductor. The T^3 asymptotic low-T ($T \leq 0.6$ K) dependence of both the thermal expansion[93] and the specific heat[85] appears compatible with an axial order parameter, e.g. of octagonal d-wave symmetry.[94]

7. SUMMARY

HF metals have been classified according to the degree of localization of their 4f/5f electrons. Several ground states are found in these lanthanide/actinide compounds. The localization of the f-electron state can be weakened (in the case of Ce and U) by volume compression. This requires the application of external or internal pressure, the latter being introduced by either controlled alloying or controlled changes of the stoichiometry. In this way, a "Mott-transition" in the f-electron subsystem, associated with a $T = 0$ K transition between a cooperative magnetic into a non-magnetic heavy-Fermi-liquid state can sometimes be induced. The LMM ordered ground state on the "localized side" of this transition is phenomenologically described by the coexistence of local f-derived ordered moments μ_s (which are substantially reduced by the Kondo effect) on the one hand, and strongly renormalized Bloch states of dominant f character on the other. On the "delocalized side" one finds coherent heavy Fermi liquids, as well as exotic forms of HF superconductivity

and HF magnetism. The complex phase diagrams as well as the mutual dependencies between superconducting and magnetic order parameters are in the focus of current HF research as documented by several contributions to this volume. In this article we have commented on the following new developments: (a) the homogeneous coexistence between HF superconductivity and LMM ordering in UPd_2Al_3, a HF compound with surprisingly large values of both T_c and μ_s; (b) the occurrence of non-Fermi-liquid effects right at the magnetic instability, i.e. for concentrated periodic HF systems showing a $T = 0\,K$ quantum phase transition; (c) the formation of a true hybridization gap (or at least a pseudo gap) in certain IV compounds, frequently labeled "Kondo insulators"; (d) the existence of both gigantic Kondo-impurity-type phenomena in certain Sm-based band-gap insulators and gigantic "Kondo-lattice" effects in certain Ce- and Yb-based intermetallic compounds with extremely low carrier concentration.

These recent developments together with new discoveries[95,96] not mentioned in the present paper show that HF materials and the physics of strong electronic correlations continue to puzzle and fascinate solid-state researchers.

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