Instabilities in heavy-fermion systems

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We review (i) an itinerant antiferromagnetic phase transition below 4 K in Ni-rich $Ce(Cu_{1-x}Ni_x)_2Ge_2$ systems, (ii) the coincidence at $T = 0.63$ K of both a structural lattice instability in "as-grown" (non-superconducting) $CeCu_2Si_2$ single crystals and bulk superconductivity in annealed ones as well as (iii) antiferromagnetic and superconducting transitions at $T_N = 4.6$ K and $T_c = 1$ K, respectively, in the heavy-fermion compound UNi_2Al_3.

1. Introduction

Heavy-fermion (HF) compounds are intermetallics of Ce, Yb, U and Np for which k_BT^*, the energy of the fundamental Kondo interaction, competes with the indirect Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction of energy k_BT_{RKKY} [1]. Whereas the first interaction tends to form a non-magnetic singlet state well below T^* (= several kelvins), the second one tends to arrest the Kondo reduction of the local f-derived magnetic moments. Since in HF compounds k_BT^* and k_BT_{RKKY} are of the same order of magnitude [2], a variety of ground-state properties is observed: for $T_{RKKY} > T^*$, local-moment magnetic ordering (LMM) develops below an ordering temperature $T_m < T_{RKKY}$. As first observed for the exemplary system $CeAl_2$, the ordered moments are reduced [3], while at the same time the electronic specific-heat coefficient γ (= 135 mJ/K^2 mole [4]) is substantially enhanced. For $T^* > T_{RKKY}$ a Pauli paramagnetic state is approached, which is characterized by very large values of γ and the Pauli spin susceptibility, χ_p, due to extremely-heavy-fermion quasiparticles. For example, $\gamma = 1.6$ J/K^2 mole was found for the exemplary system $CeAl_3$ [5], which corresponds to an effective carrier mass of $m^* \simeq 300 m_{el}$, m_{el} being the free-electron mass. A pronounced low-T decrease in the electrical resistivity, $\rho(T)$, indicates a freezing out of the incoherent scattering. Coherence among the heavy-fermion quasiparticles is established below $T_{coh} \ll T^*$, where $\rho(T) - \rho_0$ obeys an AT^2 dependence [5] (ρ_0 is the residual resistivity). For $CeAl_3$ (with $T^* \simeq 5$ K and $T_{coh} \simeq 0.4$ K [6]), $A = 35\ \mu\Omega$ cm K^{-2}. $\sqrt{A}$ scales with γ or m^*. Correspondingly small values are estimated for both the Fermi velocity, indicating a state of carrier motion that is dominated by the large intra-atomic correlation energies, and for the width of the 4f band ($\sim k_BT^*$), which forms below T_{coh} at the Fermi energy, E_F. At very low temperatures, the coherent heavy fermions contribute to the Fermi surface as was demonstrated by de-Haas–van-Alphen measurements, e.g., on $CeCu_6$ [7] and UPt_3 [8].

Residual interactions between the heavy quasiparticles of strength k_BT^* cause an inherent tendency of the heavy-Fermi-liquid phase to become unstable against either a superconducting [9] or a heavy-fermion-band magnetism (HFBM) [10] type of phase transition or both [11,12]. An increasing number of exciting phenomena has been discovered [2] for the four known HF superconductors (HFS) $CeCu_2Si_2$ [9], UBe_{13} [13], UPt_3 [14] and URu_2Si_2 [15], such as non-exponential temperature dependences of the specific heat and related thermal properties, multiphase diagrams [16,17] and the possible coexistence between superconductivity and HFBM, the latter being characterized by extremely small ordered moments, $\mu_s \simeq 10^{-2}\ \mu_B$ [11,12]. For both URu_2Si_2 [11] and UPt_3 [12] the Néel temperature $T_N \simeq 10T_c$. Apart from such similarities, several inconsistencies are found among HF superconductors. We mention as an example the pronounced phase-transition anomaly that occurs for URu_2Si_2 near $T_N = 17$ K [15] in spite of the tiny ordered moment. On the other hand, no one was able to resolve a specific-heat anomaly at $T_N \simeq 6$ K for UPt_3. These kinds of inconsistencies, as well as the limited number of HFS, have so far prevented a unified microscopic understanding, e.g., of the shape of $\Delta(\boldsymbol{k})$, the superconducting order parameter, and of the pairing mechanism [18,2].

In section 2 we wish to focus on the Ce-based system $Ce(Cu_{1-x}Ni_x)_2Ge_2$ for which HFBM has been established at $x \gtrsim 0.5$ [10]. Also, we shall briefly comment on the possibility of HFBM coexisting with HFS in $CeCu_2Si_2$ [19]. In section 3, evidence for a recently discovered [20] novel type of lattice instability will be presented. Subsequently, preliminary results on a new HFS, UNi_2Al_3 [21] will be shown in section 4 before the paper is completed by a short perspective section.

2. Heavy-fermion band magnetism in Ce compounds: $Ce(Cu_{1-x}Ni_x)_2Ge_2$

The ternary compound $CeCu_2Ge_2$ crystallizes in the tetragonal $ThCr_2Si_2$ structure. It is a local-moment type of antiferromagnet with a Néel temperature of $T_{N1} = 4.1$ K [22]. $T_{RKKY} \simeq 7$ K, the temperature at which short-range magnetic correlations develop, nearly coincides with $T^* \simeq 8$ K [23]. The isostructural compound $CeNi_2Ge_2$, with somewhat smaller lattice parameters a and c, $T^* \simeq 30$ K and $\gamma \simeq 0.4$ J/K^2 mole, is a nonmagnetic heavy-fermion system [24]. Intensive studies of the quasibinary solutions utilizing several bulk techniques [25] and neutron scattering [10] revealed the magnetic phase diagram of fig. 1, which shows the concentration dependences of the magnetic ordering temperatures T_{N1} and T_{N2}, and that of T^*. As expected [1], $T_{N1}(x)$ is strongly depressed by a small Ni concentration, implying that $T_{N1} \to 0$ for $x \to 0.2$. However, at higher Ni concentrations a second type of antiferromagnetic ordering below $T_{N2}(x)$ develops rather unexpectedly. In contrast to the strongly nonmonotic dependence of $T_{N2}(x)$ one finds a steady increase of $T^*(x)$. The latter is inferred, e.g., from the width of the quasielastic magnetic neutron line in the paramagnetic low-T phase, as displayed in fig. 2 for $CeCu_2Ge_2$, $CeNi_2Ge_2$ and two quasibinary alloys with $x = 0.28$ and 0.65.

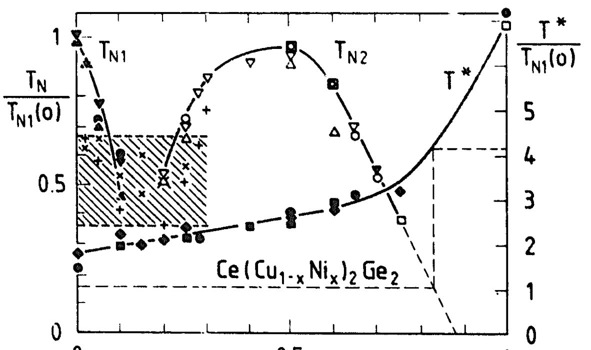

Fig. 1. Left-hand scale: T_N against x phase diagram for $Ce(Cu_{1-x}Ni_x)_2Ge_2$ as determined from specific heat (▼, ▽, +), thermal expansion (▲, △, ×), dc susceptibility (●, ○) and resistivity (□) measurements [25]. Right-hand scale: T^* against x as determined from the residual quasielastic neutron line width (●), thermal expansion (■) and resistivity (◆) peaks. Positions of the latter are scaled by factors of 1.5 and 1.9, respectively, ref. [10]. The hatched area indicates the (T, x) range of two subsequent antiferromagnetic transitions, see ref. [10]. Thin dashed lines illustrate the possibility of heavy-fermion-band magnetism in $CeCu_2Si_2$, see text.

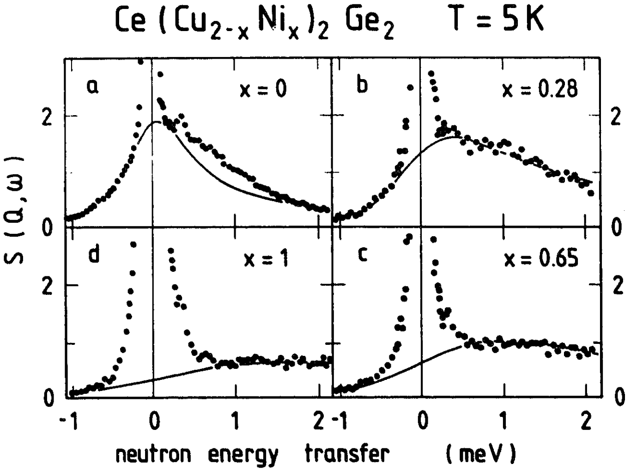

Fig. 2. Neutron scattering intensities against energy transfer for an average scattering angle $\theta = 19°$ as obtained in $Ce(Cu_{1-x}Ni_x)_2Ge_2$ for concentrations $x = 0$, 0.28, 0.65 and 1 at $T = 5$ K. The solid lines are the results of fits using a Lorentzian line shape [10].

Whereas for $x \geq 0.28$ all $Ce(Cu_{1-x}Ni_x)_2Ge_2$ systems exhibit quasielastic lineshapes of Lorentzian type, strong deviations from the latter have been found in the $x = 0$ spectrum (fig. 2a). They have been ascribed to intersite spin correlations. These apparent differences in the inelastic neutron-scattering spectra between low and high Ni concentrations have been supported by neutron powder diffraction results [10]. The latter reveal for the most probable magnetic configurations incommensurate spirals with substantially different ordering wave vectors q_0, e.g., $q_0 = (0.28, 0.28, 0.54)$ for $x = 0$ [23] and (0, 0, 0.14) for $x = 0.5$, given in units of ($2\pi/a$, $2\pi/a$, $2\pi/c$). In addition, the ordered Ce moment decreases continuously from 0.74 μ_B ($x = 0$) to 0.3 μ_B ($x = 0.5$) and further to less than 0.2 μ_B ($x = 0.65$). Whereas the larger ordering wave vectors, found for the LMM $CeCu_2Ge_2$ and for low Ni concentrations, are typically of the order of the Fermi surface diameters and, thus, indicative of RKKY interactions, the small value of q_0 for the $x = 0.5$ alloy characterizes a modulated spin structure that extends over almost ten unit cells. Along with the low ordered moment, this fully meets the theoretical prediction of HFBM in a Kondo lattice [26]. We conclude that

(i) at low Ni concentrations, (Kondo-reduced) local moments are coupled via RKKY processes, which also give rise to the short-range ordering effects visible in fig. 2a, and

(ii) at $x \geq 0.28$ an itinerant type of ordering develops out of a heavy-Fermi-liquid phase for which the magnetic neutron cross section is dominated by single-site relaxation effects (figs. 2b–d).

The magnetic phase diagram of fig. 1 suggests that HFBM is suppressed and the transition to the nonmagnetic heavy-Fermi-liquid ground state induced near $x = 0.75$. It can at present, however, not be ruled out that antiferromagnetic ordering with an extremely small μ_s value persists at even higher Ni concentrations: for example, as mentioned before, no phase transition anomalies can be resolved in the bulk properties near $T_N \simeq 6$ K of UPt_3 with $\mu_s \simeq 2 \times 10^{-2}$ μ_B/U [12]. If we *assume* that

(i) long-range ordering of this kind of HFBM exists in $Ce(Cu_{1-x}Ni_x)_2Ge_2$, say, up to $x \simeq 0.85$,

(ii) the characteristic energies in the CeM_2X_2 homologs (M: transition or noble metal; X: Si or Ge) are mainly determined by the volume, and

(iii) the (inverse of the) latter is satisfactorily simulated by the Ni-concentration x,

we deduce for $CeCu_2Si_2$ from $T^* = 15 \pm 2$ K the onset of HFBM below $T_{N2} = 0.6$–0.8 K (cf. fig. 1). In fact, different techniques [27–29] revealed anomalies in this temperature window that were tentatively ascribed to antiferromagnetic ordering [28–30].

3. Instabilities in the low-temperature phase of $CeCu_2Si_2$

In order to shed light on the possibility of the coexistence between superconductivity and HFBM in this compound, Lang et al. [20] have recently investigated new single crystals which, after an appropriate heat treatment [31], exhibit $T_c \simeq 0.63$ K and pronounced superconducting properties, as is demonstrated in figs. 3a and b. "As grown" crystals, on the other hand, do not show bulk superconductivity: in bulk measurements like specific heat and thermal expansion they can, therefore, serve as non-superconducting reference compounds, cf. figs. 4a and 4b.

We begin with a discussion of the results on the annealed crystals: a comparison of the specific-heat

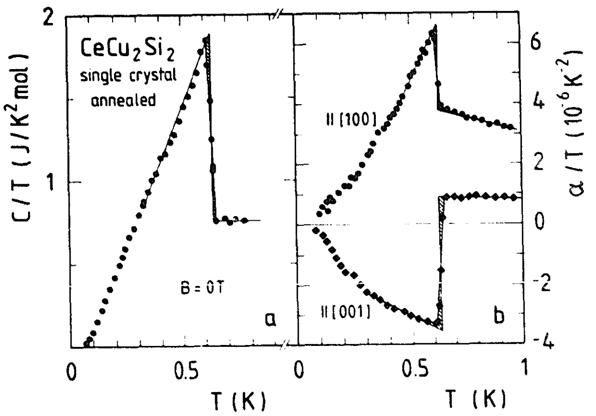

Fig. 3. (a) Specific heat of an annealed $CeCu_2Si_2$ single crystal as C/T against T. (b) Coefficient of linear thermal expansion as α/T against T for the same crystal measured along the [100] (●) and [001] (◆) directions [20].

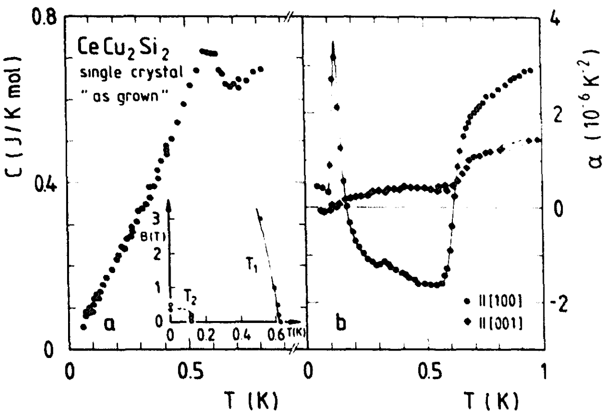

Fig. 4. (a) C against T for an "as grown" (non-bulk superconducting) $CeCu_2Si_2$ single crystal. (b) α against T for the same crystal measured along the [100] (●) and [001] (◆) directions. The inset in (a) shows the field dependences of the phase-transition anomalies as derived from α against T measurements along [100] at fixed B-fields [20].

and the linear thermal-expansion anomalies (measured along the a- and c-axes, respectively) via Ehrenfest's relation leads to the (hydrostatic) pressure derivative (as $p \to 0$) of T_c

$$T_c^{-1}(\partial T_c/\partial p)_{p=0} = V_{mol}(2\Delta\alpha_a + \Delta\alpha_c)/\Delta C$$
$$\simeq +3.5 \text{ mK/kbar},$$

in close agreement with the value previously obtained via pressure experiments [32]. Thus, the material is found to contract slightly stronger upon cooling in the superconducting than in the normal state. No phase transition anomalies, in addition to the superconducting ones, can be resolved for $B \leqslant 4$ T in the $C(T)$ and $\alpha(T)$ data, in contrast to the "step-like" transitions that show up in the T-dependences of certain elastic constants [33].

Fully unexpected, clear mean-field-type phase-transition anomalies are found at $T_1 = 625$ mK in both $C(T)$ and $\alpha(T)$ of "as-grown" crystals, i.e. in the absence of bulk superconductivity (figs. 4a and b). An additional phase transition at $T_2 = 115$ mK is seen in the thermal-expansion data only (fig. 4b). The B–T phase diagram in the inset of fig. 4a suggests an antiferromagnetic origin of the latter. The upper transition is very likely not a magnetic one, since susceptibility measurements have revealed only a very minor signal when passing through $T = T_1$ [33]. The Ehrenfest relation, which yields a gigantic negative (hydrostatic) pressure derivative $(\partial T_1/\partial p)_{p0=} \simeq -200$ mK/kbar, shows that already a few kbar will be sufficient to suppress this transition. Lang et al. [20] ascribed their finding to a lattice instability inherent to the heavy-Fermi-liquid phase. The pronounced *volume-expansion*, which occurs upon cooling the crystal from above to below

$T = T_1$, stabilizes the magnetic 4f configuration and, in this way, may induce antiferromagnetic ordering at $T_2 < T_1$. No explanation is at present to hand for the microscopic origin of the lattice instability at T_1. The most surprising discovery, i.e. that this transition temperature coincides with the highest T_c value which can be achieved in the same crystals upon optimal heat treatment, indicates very clearly an intimate relationship between the HF superconductivity and the new lattice instability. Recalling the above discussion of a possible HFBM state in the superconducting samples and also taking into account the development of pronounced "dynamical magnetic correlations" at $T \geq T_c$ as derived from recent Cu NQR and NMR measurements [34], one is faced with a rather complex scenario. It remains a challenging task to unravel the low-T phase diagram of $CeCu_2Si_2$ and, hopefully, the microscopic origin of its superconductivity.

4. Coexistence of antiferromagnetism and superconductivity in U-based heavy-fermion compounds

Whereas URu_2Si_2 [11] and UPt_3 [12] show long-range antiferromagnetism with a low ordered moment below $T_N \simeq 10T_c$ and the coexistence with HF superconductivity below T_c, a recent proposal [35] of a similar kind of magnetic ordering to develop at $T_N = 8.8$ K in UBe_{13} has yet to be confirmed as an intrinsic property of this compound. In order to enlarge the material basis for HF superconductivity, we have recently initiated a systematic search for new examples. As a result, Geibel et al. [21] discovered antiferromagnetism below $T_N = 4.6$ K and superconductivity below $T_c \simeq 1$ K in the hexagonal compound UNi_2Al_3. Fig. 5 displays the temperature dependence of its specific heat in a plot of C/T against T. As expected for an antiferromagnetic phase transition, the ordering temperature is only weakly depressed by an applied B-field

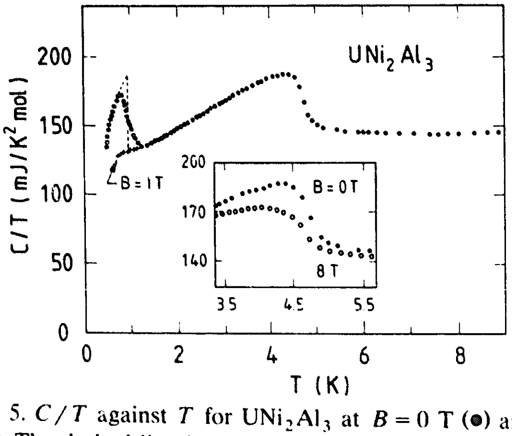

Fig. 5. C/T against T for UNi_2Al_3 at $B = 0$ T (●) and 1 T (+). The dashed line indicates an idealized jump at T_c: inset shows antiferromagnetic phase transition for $B = 0$ and 8 T (○), respectively [21].

(cf. inset of fig. 5). The idealized specific-heat jump ΔC at T_c is smaller than $C_n(T_c)$, the normal-state specific heat at T_c, and rather sample dependent. In the best case, $\Delta C/C_n(T_c) \simeq 0.5$ was found [21]. This has to be considered a lower bound of $\Delta C/C_{el}(T_c)$, because $C_n(T_c)$ contains a spin-wave-derived contribution and, thus, is an upper limit of the electronic contribution, $C_{el}(T_c)$. However, from the fact that ΔC and $C_{el}(T_c)$ are of the same order of magnitude, we conclude that the new compound is a bulk superconductor. In addition, UNi_2Al_3 appears to be phenomenologically related to the HF superconductor URu_2Si_2. In particular, their Sommerfeld coefficients extrapolated from the paramagnetic phase to $T = 0$ are rather similar (150–200 mJ/K^2 mole), and their T_c values are nearly identical. On the other hand, the value of $T_N = 4.6$ K of the new compound is much lower than $T_N = 17$ K in URu_2Si_2. This disproves universality of the empirical "10% rule" ($T_c \simeq 0.1T_N$) as extracted from the previously known U-based HS superconductors.

From the experimental value of the upper-critical-field slope at T_c, $B'_{c2} = 1.4$ T/K, one estimates [36] for the effective carrier mass in UNi_2Al_3 $m^* \simeq 50m_{el}$. Other microscopic parameters (as $T \to 0$) are ξ (BCS coherence length) $\simeq 240$ Å, λ (magnetic penetration depth) $\simeq 3300$ Å and κ (Ginzburg–Landau parameter) $\simeq 14$. Since the elastic mean free path is estimated from the $\rho(T)$ data to be $l \simeq 450 \simeq 2\xi$, this compound is another candidate, besides UPt_3, for a superconductor with "non-conventional" order parameter, whose symmetry is lower than that of the Fermi surface [18,2].

The molar entropy released at the Néel temperature amounts to only $0.13R \ln 2$, which points to a relatively small μ_s value as characteristic of HFBM. No additional phase transition anomaly is found between the lowest accessible temperature of $T = 0.4$ K and T_c. This suggests coexistence between HF superconductivity and HFBM, at least in this temperature regime. Very recently, the homologous compound UPd_2Al_3 has been found to show even more exciting properties, e.g., $T_c = 2$ K and $T_N = 14$ K [37].

5. Perspective

Three kinds of instabilities have been discovered in the heavy-Fermi-liquid phases that form in $CeCu_2Si_2$ and its homologous Ce-based partners: heavy-fermion superconductivity, heavy-fermion band magnetism and a lattice instability. The latter, though as yet unexplained, was assigned as inherent to the heavy-fermion system. To what extent the development of superconductivity in $CeCu_2Si_2$ relies on these other two cooperative phenomena remains to be unraveled by future work. Like for URu_2Si_2 and UPt_3, the new heavy-fermion superconductors UNi_2Al_3 and UPd_2Al_3 exhibit an antiferromagnetic phase transition well above T_c. It should be noted, however, that the large and commensurate ordering wave vectors in the former two compounds [11,12] are at variance with the theoretical prediction of HFBM in Kondo lattices [26]. Another open question concerns the valence state of U in the HF superconductors [2]. In the case of a (non-Kramers) tetravalent $5f^2$ configuration, a quadrupolar, rather than the usual magnetic, Kondo effect might be operating to bring about the observed heavy-Fermi-liquid phase and its instabilities [38].

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