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LATTICE INSTABILITIES IN HEAVY FERMION SUPERCONDUCTORS

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INTRODUCTION

Heavy Fermion superconductors are a subclass of the socalled Heavy Fermion (HF) systems, a class of intermetallic compounds with rare earth or actinide component characterized by an enormous value of the electronic specific heat coefficient $\gamma(T) = C/(T)/T$ in the Helium temperature range and below, where it can become larger than 1 J/mole K^2. A somewhat arbitrary limit of $\gamma > 0.4$J/mole K^2 distinguishes these systems[1] from a much larger number of compounds with similar constituents whose specific heat is also still very large compared with ordinary metals like copper ($\gamma = 0.65$ mJ/mole K^2). For the following we shall call such compounds with say 0.4 J/mole $K^2 > \gamma > 0.04$ J/mole K^2 Bantam Fermion (BF) systems. The large γ is thought to be a measure of the inverse width w_f of an extremely narrow band of f states, which intersects the Fermi energy at T = 0. Interest in HF systems became intense after superconductivity was discovered in some of them[2,3,4], because contrary to all previous experience, according to which narrow f states at the Fermi level strongly suppress superconductivity, in the HF superconductors they seemed to cause it.

In the following we shall show that while in nonsuperconducting HF systems such as $CeCu_6$, $CeAl_3$ and stochiometric $CeCu_2Si_2$ the large γ is indeed due to a very narrow f band, in the three HF superconductors UBe_{13}, UPt_3 and nonstochiometric $CeCu_2Si_2$ it is not. The f band of these systems, as measured by their response to magnetic fields in three different ways, is much wider than suggested by the large γ. According to their actual f band width, the HF superconductors belong into the Bantam Fermion class. We then argue that most of the large γ of the HF superconductors is not of electronic origin and that it is instead caused by the precursor of a martensitic phasetransition of the lattice or by a crystallographic phase mixture, i.e. that it is due to the displacive degrees of freedom. This suggests that the superconductivity of all three HF superconductors is caused by some special, low energy phonons rather than by a narrow f band.

It requires a careful and thorough evaluation of the available data to arrive at the above conclusions, which is too voluminous for the space available here. We therefore will publish a full paper elsewhere[5] and give here only the main results. We shall first discuss the response to magnetic fields (susceptibility, field dependence of the specific heat, volume magnetostriction), which clearly distinguishes the HF superconductors from the

true HF systems $CeAl_3$, $CeCu_6$ and (ns) $CeCu_2Si_2$*. We then discuss the martensitic origin of γ in the HF superconductors, starting with the interplay of superconductivity with a well studied martensitic phase transition in Uranium metal. We argue that the driving mechanism for this martensitic phase transition, which extends over a temperature range of more than 60 K is the magnetoelastic interaction between the f induced quadrupoles on the Uranium atoms and that the same interaction must cause similar martensitic phenomena in UBe_{13} and UPt_3. We finally show that in $CeCu_2Si_2$ a pressure driven first order and hysteretic γ - α transition coincides with the large upward shift of the superconducting transition temperature and argue that surplus copper in $CeCu_2Si_2$ causes a corresponding superconducting crystallographic phase mixture of γ and α type $CeCu_2Si_2$ already at atmospheric pressure.

THE RESPONSE OF HF SUPERCONDUCTORS TO MAGNETIC FIELDS

Quite generally the specific heat coefficient γ_o is proportional to the density of energy eigenstates within kT around the groundstate. It may be written in units of states per Kelvin and molecule. If γ_o is exclusively due to a narrow band of electronic states with degeneracy g, the bandwidth then follows directly from

$$w_f = g / \gamma_o \quad \text{or} \quad w_f\,[K] = 8.3\ g\ (\gamma_o\,[J/\text{mole}\ K^2])^{-1}. \tag{1}$$

For a doublet band with $\gamma_o = 1$ J/mole K^2 the bandwidth is then 16.6 K and the Fermi temperature of the band at T = 0 is $T_{fo} = 8.3$ K , 10^4 times smaller than the Fermi temperature of copper.

When a magnetic field is applied to such an electronic band, its response is governed by the ratio of the Zeeman energy $\mu_z H$ to the occupied bandwidth $k_B T_{fo}$. For $\mu_z H / k_B T_{fo} \ll 1$, the susceptibility at T = 0 is proportional to this ratio and the change of the specific heat and of the length (magnetostriction) are proportional to its square. When $\mu_z H$ reaches $k_B T_{fo}$, which is possible in practice in true HF systems, the band begins to split into g separate components and the response changes in a characteristic fashion. If the magnetic moment μ_z is known, all three measurements can then be used to determine T_{fo} independently; they all can therefore test whether γ is indeed due to an electronic band of width w_f as suggested by equ. (1) or not.

The Pauli Sommerfeld ratio

The most popular and also the most problematic test is via the so-called Pauli Sommerfeld ratio (often also called the Wilson ratio)

$$R = (\pi^2 k_B^2 / 3 \mu_z^2) \cdot (\chi_o / \gamma_o) \tag{2}$$

Here χ_o and γ_o are the susceptibility and the specific heat coefficient, measured near T = 0. $\mu_z^2 = \mu_{eff}^2/3$ is measured preferably by neutron scattering or by the Curie Weiss constant taken in a temperature interval as close as possible to T = 0.

In Table I we have collected what we consider sufficiently reliable and complete data available for the R test on three nonsuperconducting HF systems with Ce and on the three HF superconductors. No such complete set of data is unfortunately available for any nonsuperconducting HF system with Uranium. We justify our choice of data in [6].

* There are two versions of $CeCu_2Si_2$ [6]; stochiometric $CeCu_2Si_2$ is not a superconductor, while nonstochiometric $CeCu_2Si_2$, with up to 10% surplus of Cu is. In the following we shall distinguish these two versions by the prefixes (ns) and (s).

Table I. The Pauli Sommerfeld (Wilson-) Ratio of Some HF Systems

System	χ_o [emu/mole]	γ [J/mole K^2]	μ_{eff} [μ_B]	R
$CeAl_3$ (ns)	0.030 [7] (0.5 K)	1.7 [7] (0.5 K)	1.29 [8]	2.0 - 2.9 [9] (0.5 - 0.01 K)
$CeCu_6$ (ns)	0.039 [10] (0.6 K)	1.53 [11]	1.60 [12]	2.16
$CeCu_2Si_2$ (ns)	0.0327 [13] (xtal C)	0.635 < γ < 0.89 [13]	1.65 [17]	4.26 - 3.04
	0.044 [14] (poly)	1.1 [15]	1.65 [17]	3.26
				$\bar{R}$ = 2.94
$CeCu_2Si_2$ (s)	0.0055 [16] (poly)	1.08 [16]	1.65 [17]	0.43 - 0.8 [9] (0.5 - 0.01 K)
	0.0086 [13] (xtal A)	0.7 [13]	1.65 [17]	1.0
	0.0074 [13] (xtal B)	1.1 [13]	1.65 [17]	0.55
				$\bar{R}$ = 0.7
UBe_{13} (s)	0.0151 [18]	0.7 [18]	3.5 [5]	0.38 (1.5 K)
	0.0151 [18]	1.1 [19]	3.5 [5]	0.24 (1.5 K)
				$\bar{R}$ = 0.31
UPt_3 (s)	0.0085 [20] (a axis)	0.415 [20]	2.4 [5] (a axis)	0.78

The table shows the R values of the (ns) HF systems with Ce to lie between 2 and 4, with an average $\bar{R}$ = 2.9(4), while those of the HF superconductors are all smaller than one. Comparison with (ns) $CeCu_2Si_2$ shows that the low R value of (s) $CeCu_2Si_2$ is caused by its small susceptibility.

The experimental problems with the R test are reflected directly in the scatter of the data. The theoretical problems may be collected in the statement that nobody can actually predict the R value of a true HF system with confidence at its time. The test is e.g. only sensible in a paramagnetic metal, for which ferro and antiferromagnetic spin correlations, which raise and lower R with respect to the ideal (paramagnetic) value, are negligible. There are also magnetoelastic interactions between f moments which in Ce systems are usually stronger than the spin interactions. Finally, the susceptibility is anisotropic in noncubic systems. Antiferromagnetic correlations were recently detected by neutron scattering in $CeCu_6$ [21]. They also are expected in all other systems listed in table I. Their strength may be estimated roughly from the magnetic ordering temperatures of certain reference compounds like $GdAl_3$ (T_o = 160 K), $GdCu_6$ (T_o = 29 K) and $GdCu_2Si_2$ (T_o = 12 K), via de Gennes scaling. Obviously for $CeCu_2Si_2$ the antiferromagnetic correlations are then expected to be weakest. Note, that indeed the R values of (ns) $CeCu_2Si_2$ are the largest (least

depressed by af correlations). This suggests that the ideal (paramagnetic) R value of the (ns) HF systems should be still larger than the average $\bar{R}$ = 2.9(4) in table I. A simple thermodynamic calculation, sketched in the following section, gives R = 4.75 for a paramagnetic doublet band, suggesting that the R value of (s) $CeCu_2Si_2$ is nearly seven times lower than the ideal value, or that the specific heat coefficient of its f band is only γ = 150 mJ/mole K^2.

Why is the ideal R value of HF systems at least 3 times larger than the Pauli Sommerfeld ratio? Because the simple free electron theory with a parabolic band, which has a lower, but no upper band edge, severely overestimates the specific heat of a band with lower and upper band edge, at least when the thermal energy k_BT approaches and surpasses k_BT_{fo}, the Fermi energy of the band at T = 0. This theory actually predicts an electronic Dulong Petit law, $C_e \to 3R$, for $T \gg T_{fo}$, while experiment shows $C_e \to 0$ and $S \to k_B \ln g$ in this situation[22]. In the Pauli Sommerfeld theory the electrons have both kinetic and magnetic degrees of freedom, while the kinetic energy of the local f electrons with respect to the lattice is zero. These electrons have only g magnetic degrees of freedom. Of course, there is kinetic energy with respect to the lattice in the narrow f - d hybrid band, but it comes exclusively with the almost negligible d amplitude of the band. Therefore, the Pauli Sommerfeld expression for the specific heat severely overestimates the specific heat of a narrow f band and then underestimates the R value. The experimental R values of all HF superconductors are then far too low to assign their large γ to a narrow f band.

The magnetic field dependence of the specific heat

More decisive than a quantitative R test, which is certainly problematic, is the test via the magnetic field dependence of the specific heat. It so happens that the values of γ_o and μ_z in table I together with equ (1) predict a precipitous drop of γ in fields between about 5 and 20 Tesla, which was indeed found in the (ns) HF systems, but not in the three HF superconductors.

Measurements of $\gamma(H)$ have been performed in fields up to 11 T and at temperatures ranging from small to large compared to k_BT_{fo} as calculated from γ_o via equ (1). In order to extract all the available information from these data, one needs an expression for γ as function of both, field and temperature. For reasons discussed above, the Pauli Sommerfeld C(H,T) is clearly inappropriate. An alternative model is that of the single Kondo impurity, which is of questionable applicability to concentrated systems[24], although in practice it does not do badly [25]. Here we shall use a simple thermodynamic approach, which has been quite successful in calculations of a wide variety of equilibrium properties of Heavy and Bantam Fermion systems in the past [26,27,28,36]. We make the following Ansatz for the free energy of an f band deriving from a crystal field doublet:

$$F_f(T,H) = -N_f k_B T^* \ln (2 \cosh \varepsilon) \qquad (3)$$

$$\varepsilon \equiv \mu_z H/k_B T^* \qquad T^* \equiv (T^2 + T_{fo}^2)^{1/2} \qquad T_{fo} \equiv w_{fo}/2k_B = \text{const.}$$

From equ (3) we derive the specific heat coefficient and the susceptibility via $\gamma = -\partial^2 F_f/\partial T^2|_{H,T_f}$ and $\chi = -\partial^2 F_f/\partial H^2|_{T,T_f}$. For $T \ll T_{fo}$ and H = 0 we find

$$\gamma_o = N_f k_B \ln 2/T_{fo} \quad \text{and} \quad \chi_o = N_f \mu_z^2/k_B T_{fo}. \qquad (4)$$

When inserting these expressions into equ (2), we find R = 4.75 rather than R = 1, because our γ_o is 4.75 times smaller than in the Pauli Sommerfeld theory. To test equ (4), we make use of a direct measurement of T_{fo},

which is e.g. available for $CeCu_6$ [12], if one accepts $\Gamma_o/2 = 5.7\ K = k_B T_{fo}$, where $\Gamma_o/2$ is the quasielastic neutron linewidth. With equ (4) this predicts $\gamma_o = 0.89$ J/mole K^2, 60% smaller than observed, and $\chi_o = 0.05$ emu/mole, 30% larger than observed (table I). Antiferromagnetic correlations [21] are expected to increase the specific heat and to decrease the susceptibility with respect to the ideal value. We see that our "ideal" expressions in equ (4) leave room for just such effects, i.e. R = 4.75 seems to be a quite reasonable number without antiferromagnetic correlations.

Fig. 1 shows $\gamma(T,H)$ as calculated from equ (3) for a HF system with T_{fo}= 3.9K (appropriate for $CeCu_6$ when ignoring antiferromagnetic correlations) and for a BF system with T_{fo} = 100 K (appropriate for (s) $CeCu_2Si_2$; this system shows its large f bandwidth not only by its small R value, but already directly by a paramagnetic Curie Weiss temperature of about - 100 K [16] in polycrystals; single crystals show Θ_p = - 80 K and - 130 K in c and a direction [13]). The difference between HF and BF systems is dramatic; for H < 20 Tesla the field dependence of γ is very strong and complicated for the HF system, but practically nonexistent for the BF system. In Fig. 1 we have also included the data for $\gamma(H,T)$, for $CeCu_6$ and $\gamma(H = 0,T)$ at higher T [29]. Similar data for $\gamma(H,T)$ exist for $CeAl_3$ [23]. These data confirm the basic features predicted for a true HF system, in particular the strong drop of $\gamma_o(H)$ and the crossover of $\gamma(H,T)$ at a temperature just below T_{fo}. The crossover and the maximum of $\gamma(H,T)$ predicted at higher fields may be viewed as due to a quasi Schottky anomaly, which develops, when the two magnetic states of the f band are split by a Zeeman energy, larger than the width of these states.

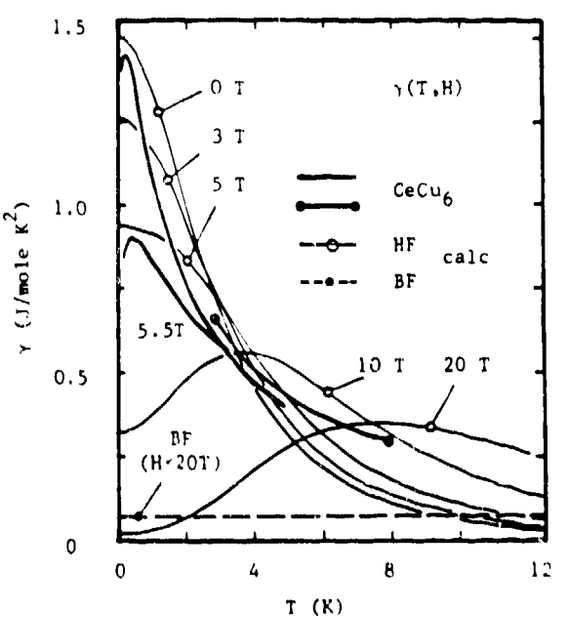

Fig. 1. The dependence of the linear specific heat coefficient γ on temperature and magnetic field for a true Heavy Fermion system (T_f = 3.9 K) with data for $CeCu_6$ [11] and for a Bantam Fermion system (T_f = 100 K).

Data taken on (ns) $CeCu_2Si_2$ by Stewart [1] in 0 and 11 T between 1 and 10 K show similar effects as $CeCu_6$, including a crossover at 3 K. However, the size of the effect is only about 25% of what is expected from the calculation for a HF system with T_{fo} = 5 K, suggesting that only 25% of the HF phase was present in this sample, the rest being of the BF type. Many other measurements [6, 13, 16, 30] also indicate that actual samples of $CeCu_2Si_2$ are mixtures of the HF and the BF version. The fact that the HF phase suppresses superconductivity completely, already when only present as a minority, indicates that the very narrow f band of the HF phase is just as poisonous to superconductivity as longstanding experience has shown in all other systems with concentrated and dilute slightly unstable Ce atoms.

Data taken on a sample of (s) $CeCu_2Si_2$ [16] with very little amount of the HF phase present show no field dependence of γ whatsoever, within the noise of the measurement, in spite of the fact that γ of this sample is of order 1 J/mole K^2 near 1 K and strongly decreasing with increasing temperature, i.e. in spite of the fact that $\gamma(T)$ looks very similar to the curve calculated for H = 0 in Fig. 1! The integrated $\gamma(T)$, i.e. the entropy S(T) of this sample is shown in Fig. 2, together with similar data for UBe_{13} which again shows a $\gamma(T)$ nearly as calculated for H = 0 in Fig. 1, but again shows almost no field dependence. The third HF superconductor, UPt_3, shows some field dependence of γ, which is however much less than we calculate from γ_o and μ_z (table I) in magnitude and has moreover the wrong sign! We shall discuss Fig. 2 further down.

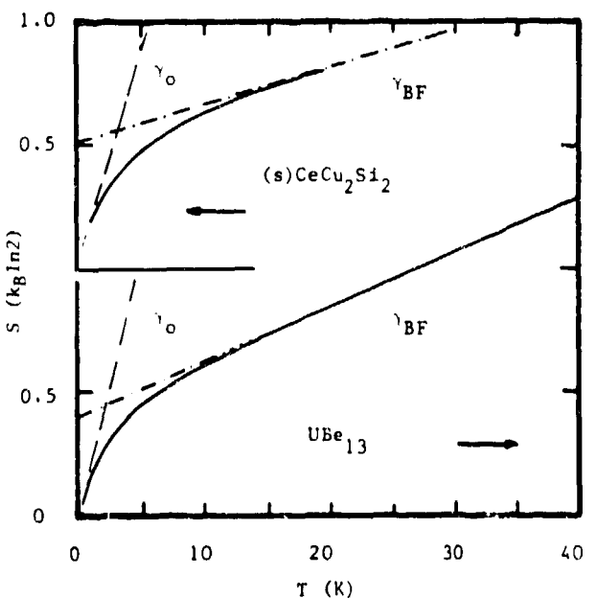

Fig. 2. The entropy of the specific heat anomalies of (s) $CeCu_2Si_2$ [16] and of UBe_{13} [31] as function of temperature. The high field slope is the γ of their Bantam Fermion f bandwidth. The low temperature anomaly with its steep initial rise and with total entropy $\Delta S < k_B \ln 2$ is independent of magnetic field and therefore not of electronic origin.

Magnetostriction of HF systems

Magnetostriction is another quantity, which is extremely sensitive to the f bandwidth, similar to the specific heat coefficient, and more easily measurable. In table II we give data for the volume magnetostriction (VMS) of $CeAl_3$, $CeCu_6$ and of (s) and (ns) $CeCu_2Si_2$ at 1 Tesla and 4.2 K [30]. The VMS, as measured between 1.5 and 40 K, shows strong temperature and field dependence, which can be fitted well with an expression derived again from simple phenomenological thermodynamics [26, 27, 30]

$$\frac{\Delta V}{V} = \frac{\Delta V_o}{V} \frac{\nu(1-\nu)}{2} \left(\frac{\mu_z H}{k_B (T+T_f)} \right)^2 \qquad (5)$$

Here ΔV_o is the volume difference between the tri- and tetravalent unit cell of the Ce compound and ν is the fractional occupation of the tetravalent state. Note the similar magnitudes of the VMS of the (ns) HF systems and the very much smaller value of (s) $CeCu_2Si_2$ III, which is comparable to the BF system $CeBe_{13}$. $CeCu_2Si_2$ II has the same temperature and field dependence of the VMS as (ns) $CeCu_2Si_2$ I, but a much smaller absolute value; apparently this sample is a mixture of minority HF and majority BF $CeCu_2Si_2$, the latters VMS being practically zero. For a difference of T_f of the two phases by a factor seven, equ (5) predicts a difference of the VMS by a factor 33 at 4.2 K (at T = 0, the VMS is proportional to T_{fo}^{-2}!) In short, the VMS says again that the f bandwidth of (s) $CeCu_2Si_2$ is about an order of magnitude larger than that of the other three HF Ce systems, in spite of the fact that all γ are comparable.

Table II The Volume Magnetostriction of Some Heavy and Bantam Fermion Systems with Ce at H = 1 Tesla and T = 4.2 K.

System	$\Delta V/V$	Remarks
$CeAl_3$	$1.4 \cdot 10^{-6}$	
$CeCu_6$	$1.8 \cdot 10^{-6}$	
$CeCu_2Si_2$ I	$6.1 \cdot 10^{-7}$	(ns)
$CeCu_2Si_2$ II	$1.1 \cdot 10^{-7}$	(s) (ns) mixture
$CeCu_2Si_2$ III	$< 5 \cdot 10^{-8}$	(s)
$CeBe_{13}$	$4.5 \cdot 10^{-8}$	

THE NATURE OF γ IN THE HF SUPERCONDUCTORS

In the previous section we have seen that the f bandwidth in the HF superconductors is much larger than suggested by their large low temperature specific heat coefficients. Since the effects of the f band are actually seen in these materials, e.g. in the susceptibility via the Curie Weiss behavior, and since it is inconceivable that there be another electronic

band with a width as small as suggested by γ, but without response to a magnetic field, the large γ of these systems cannot be of electronic origin. The only possibility left is that it is caused by the displacive (vibrational) degrees of freedom in the solid, whose sensitivity to a magnetic field should be negligible, in first order. However, normal phonons are out of the question too, since they are essentially frozen out at Helium temperatures. We therefore suggest that the large γ is associated with the specific heat anomaly around a martensitic phase transition, which occurs in the Helium temperature range or even at a slightly negative temperature, in which case the specific heat near $T = 0$ would be enhanced by "paradisplaceons"[33], the dynamic precursors of a martensitic phase transition (in analogy to paramagnons, the dynamic precursors of a magnetic phase transition, which enhance γ_o in certain, barely paramagnetic metals like Pd). This enhancement of γ should decrease with increasing temperature (the farther T is away from the "slightly negative" critical temperature), just as observed in the HF superconductors.

We suggest two driving mechanisms for these martensitic phase transitions

a) Electric quadrupole-quadrupole interactions between neighboring atoms with open f shells with $L \neq 0$

b) Transitions between two fractional valence states

The first mechanism seems dominant in UPt_3 and UBe_{13} and the second in $CeCu_2Si_2$ (γ - α transition).

THE QUADRUPOLE DRIVEN MARTENSITIC PHASE TRANSITION IN URANIUM METALS

Uranium metal is a striking example for the interplay of superconductivity with a martensitic phase transition. Fig. 3 shows the superconducting transition temperature T_c of Uranium and the temperatures T_{Mi} of three consecutive phase transitions of its lattice as function of pressure [34]. At $p = 0$, T_c of Uranium is below 0.15 K, but it increases very steeply to a maximum above 2 K near 12 kbar. It then drops again, much more slowly,

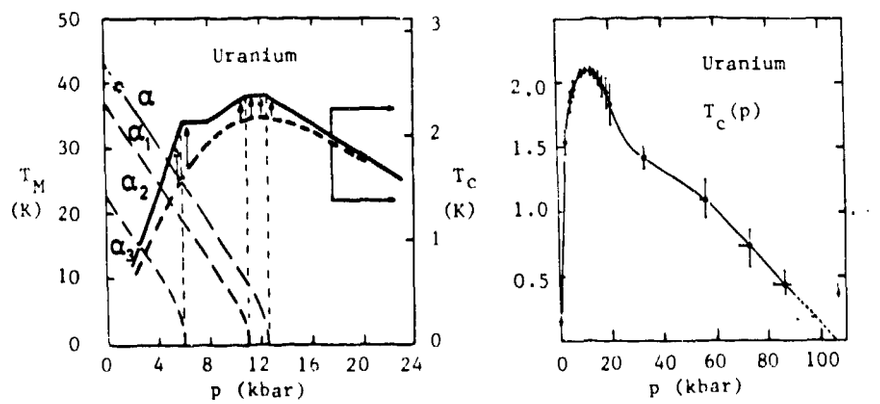

Fig. 3. The superconducting transition temperature T_c and the three temperatures T_{Mi} of the martensitic transitions in Uranium metal as functions of pressure [34].

to vanish below 0.3 K near 90 kbar. On the other hand the critical temperatures of the martensitic phase transitions, which lie at 43, 38 and 22 K at p = 0, drop precipitously with increasing pressure to cross zero near 6, 10 and 12 kbar, precisely at the pressures, where T_c goes through a series of kinks on its way through the maximum. It appears, as if the superconductivity were caused by the zero crossing of the martensitic phase transition and that it still lives fairly well on its dynamic precursors up to 90 kbar!

Neutron scattering has established [35] that at p = 0 the order parameter of this complicated series of transitions increases monotonously, starting at 70 K (i.e. far above the first singularity!) and finally saturating at 10 K. The entire transition, which is quite subtle, i.e. very difficult to detect in nearly all macroscopic measurements, is spread over 60 K! The temperature dependence of the order parameter is linear, with three abrupt changes of slope at the three T_{Mi} [35]. The linear temperature dependence is inconsistent with mean field behavior, but consistent with a thermodynamically stable crystallographic phase mixture, i.e. a mixture of two lattice types, whose relative weight is a linear function of temperature. In order to have such a mixture in thermal equilibrium, the grains of both phases must be very small (of order a few 100 Å), such that the interface energy can play a significant role [33]. Since the T_{Mi} are close to zero between 6 and 12 kbar, one may expect very slow fluctuations from one lattice type to the other in this pressure range near T = 0, i.e. very slow motion of the U atoms, which will contribute significantly to the low temperature specific heat and should be beneficial for superconductivity. Judging from the large temperature range of the precursor at p = 0 (from 70 to 43 K) at p > 12 kbar ($T_{Mi} < 0$), one expects the precursor to be felt over a large pressure interval.

The entropy change associated with the series of martensitic transitions was found to be $\Delta S = 0.06\ k_B \ln 2$ per U atom at p = 0 [36]. The order parameter is a nearly volume conserving distortion of the α-U structure, which goes from zero to about 1.8% of the lattice constant between 70 and 10 K [35].

The driving mechanism of this martensitic transition in U metal has never been discussed in the literature, to our knowledge. We suggest here that it is a magnetoelastic interaction between the U atoms through a small, aspherical, in first order quadrupolar distortion of the charge distribution of the U atoms, which is tied axially to the instantaneous vector of the f angular momentum $\underline{J}$. This quadrupole Q is detectable via magnetostriction in all metals containing atoms with open f shell with $L \neq 0$ [37,38,39]. It should be considered as a constant of the motion, similar to the f magnetic moment μ. The magnitude of Q depends on the solid. It ranges in practice from about 0.2% in compounds to about 2% in the f elements.

We estimate the interaction energy in elements and compounds by

$$\Delta E_Q = (c/2)\ Q^2\ (d_o/d)^6. \qquad (6)$$

Here c is the smallest (shear) elastic constant measured in the solid above T_M, Q is the quadrupole of the unit cell of the element and d_o and d are the distances between the f atoms in the element and in the solid in question. In table III we give ΔE_Q as calculated [5] for U, UPt_3 and UBe_{13}, using Q = 0.018 (i.e. the maximum distortion of the α-U unit cell at p = 0, T = 0) and measured elastic constants. For UBe_{13} there are two values of ΔE_Q, corresponding to two different values for the same elastic constant in the literature [40, 41].

For U metal $\Delta E_Q = 48$ K is only slightly above the first martensitic transition temperature. For UPt_3, $\Delta E_Q = 6.9$ K is slightly above the well

documented quadrupolar driven phase transition of the closely related compound UPd_3 [44] and close to the phase transition triggered in UPt_3 by Th and Pd impurities [45, 46]. For UBe_{13} the higher value of ΔE_Q is at the temperature, where the specific heat shows a maximum [31] and the lower value is close to the temperature of the transition triggered by Th impurities below T_c [47]. All this shows clearly that martensitic phenomena caused by the Uranium quadrupole at Helium temperatures and below must be discussed seriously in the two HF superconductors UPt_3 and UBe_{13}.

Since the specific heat anomalies of UPt_3 and UBe_{13} show no singularities as function of temperature, they must be due to the precursors of the martensitic transition. Judging from U metal, the entropy under the precursors may be a significant fraction of the entropy of the full transition. For UBe_{13} Fig. 2 allows to estimate this entropy. The high temperature slope of S(T) corresponds to the γ of the actual (Bantam) f band and its intercept with the ordinate at T = 0 gives the entropy of the precursor. We find $\Delta S = 0.45\ k_B \ln 2$ per molecule of UBe_{13} or $\Delta S = 0.032\ k_B \ln 2$ per atom (clearly, in a displacive transition all atoms of the molecule move). This is half of the entropy found in the full transition in U metal per atom, and therefore supports our picture.

In a cubic system like UBe_{13} the quadrupolar distortion can go into three directions and therefore will cause distortional domains below T_M at zero external magnetic and zero strain field. In this context it is interesting to note that the resistivity of UBe_{13}, one property, which does depend strongly on a magnetic field, decreases as a universal function of H/T, but saturates at high field at almost exactly 1/3 of the zero field value [48]! This suggests that the magnetic field is able to remove the directional degeneracy of the cubic lattice distortions, i.e. the domains, leaving a distortion with only one axis. Accordingly the resistivity anomaly of UBe_{13} seems to be caused entirely by scattering on slowly moving quadrupolar lattice distortions rather than by f spin scattering!

How an the U quadrupoles move slowly enough to almost lock into a statically ordered state at Helium temperatures, while their coaxial magnetic moments still flip as fast as suggested by the Bantam Fermion f bandwidth at the same temperatures ($T_f \cong 75$ K in UBe_{13})? The obvious answer is that $+J_z$ and $-J_z$ have the same Q_z, i.e. fluctuations between $\pm J_z$ do not cause fluctuations of Q_z directly. However, for $J > 3/2$ there are intermediate states through which J_z and Q_z can couple, and therefore J_z fluctuations are communicated to Q_z weakly. This explains, why pressure, which increases

Table III. Comparison of the calculated quadrupolar ordering energies ΔE_Q (equ 6) with the observed martensitic temperatures $T_M(Q=0.018)$

System	c_{min} [10^{12} erg cm^{-3}]	d [Å]	ΔE_Q [K]	T_M [K]	Remarks
α-U	2.0 [40]	3.13	48	43,28,22	
UPt_3	0.93 [41]	4.08	6.9	6 - 7	$U(Pt_{1-x}Th_x)_3$, UPd_3
UBe_{13}	1.6-3.0 [42]	5.13	2.7-5.2	2.9	max of C(T)
UBe_{13}	0.07±0.22 [43]	5.13	0.12-0.38	0.4	$U_{1-x}Th_xBe_{13}$

the f bandwidth in all Ce and U systems, simultaneously increases the Q_z fluctuations, i.e. decreases ΔE_Q and T_M.

MARTENSITIC EFFECTS ASSOCIATED WITH THE γ - α VALENCE TRANSITION OF $CeCu_2Si_2$

Quadrupolar distortions, which are a general property of all metals with open f shell with $I \neq 0$, are also observed clearly in all Ce systems with sufficiently weak f instability (see e.g. [30]). ΔE_Q is of order a few K in many Ce compounds, which is actually as a rule larger than the spin spin interaction energy extrapolated from the Gd reference. ΔE_Q is probably at the root of the anomalies, which are observed in many samples of (ns) $CeCu_2Si_2$ near 3 K [9]. However, when moving from HF to BF $CeCu_2Si_2$, these effects are weakened by the residual coupling between Q_z and J_z discussed above; at the same time a different and even stronger mechanism capable of driving a martensitic phase transition appears, namely the γ - α valence transition.

$CeCu_2Si_2$ is one of the very few Ce compounds with a discontinous γ - α transition (as in elemental Ce). This transition was recently found by L_{III} x - ray absorption at 38 kbar, with a very large hysteresis [49]. The singular pressure coincides with the pressure, at which the superconducting transition temperature of (s) $CeCu_2Si_2$ is known to jump from 0.9 to more than 2 K [50], very similar to the jump of T_c from 0.04 K to 2 K in the α - α' transition of Ce metal near 50 kbar [51], and also similar to the jump of T_c of U metal between 0 and 10 kbar Fig. 3.).

Fig. 4. shows a calculation of the Gibbs free energy of $CeCu_2Si_2$ as function of valence ($v = 3 + \nu$) [52]. Near $p = 0$, $G(\nu)$ shows only one minimum, near $\nu = 0.06$, but <u>two</u> local minima of $G(\nu)$ coexist between about 25 and 50 kbar, which are energetically degenerate near 35 kbar, almost exactly at the pressure, where the first order γ - α transition is observed [49]. Obviously, the calculation predicts a first order phase transition with large hysteresis, as observed. Significantly, however, the predicted valence shift is about 18%, while experimentally a shift of only 4% was observed [49]. Our calculation does not include a possible interface energy between small

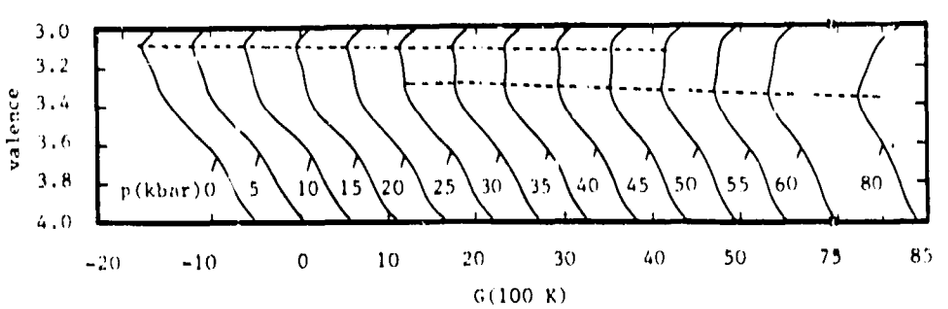

Fig. 4. The Gibbs free energy of $CeCu_2Si_2$ as function of valence ($v = 3 + \nu$) and pressure at 300 K [52]. Two local minima (dashed lines) coexist for 25 kbar < p < 50 kbar, consistent with the first order valence transition observed at 38 kbar [49]. (The figure is best viewed from the left)

grains of the two phases with fractional valence differing by 18%, i.e. it cannot predict a possible thermodynamically stable phase mixture.It seems likely that the observed valence shift is much smaller than predicted, because it starts from one phase mixture of the two fractional valence states and ends in another! This idea is quite consistent with the observed nonlinear behavior of $\nu(p)$ in the neighborhood of 38 kbar [49]. It therefore appears that in (s) $CeCu_2Si_2$ two phases with fractional valence differing by about 18% coexist over a wide pressure and temperature range, in thermal equilibrium!

As far as the lattice is concerned, the two phases are primarily distinguished by their volume , which decreases with increasing ν. The lattice displacements are therefore of different symmetry than in the quadrupolar Uranium martensites and of larger magnitude. Indeed, the entropy change extracted for the martensitic precursor in (s) $CeCu_2Si_2$ (Fig. 2.) is $\Delta S = 0.12\ k_B \ln 2$ per atom, considerably larger than in UBe_{13}!

The superconducting transition temperature of (s) $CeCu_2Si_2$ drops sharply again at pressures larger than 50 kbar [50], the pressure above which our calculation of G (ν) shows only one local minimum, i.e. a stable α type phase alone (Fig. 4.). This suggests that the pure α phase of $CeCu_2Si_2$ is not a superconductor either, just as the pure γ phase, (ns) HF $CeCu_2Si_2$), is not. If this is true, the superconductivity of $CeCu_2Si_2$ lives exclusively on a crystallographic phase mixture. It goes now almost without saying that from several points of view the addition of copper to stochiometric $CeCu_2Si_2$ strongly favors the envisioned phase mixture, i.e. it drives the compound into this peculiar state of a superconducting phase mixture already at atmospheric pressure.

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