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Wyder, U.

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Chapter 5

STRAIN DEPENDENCE; A TYPICAL FEATURE OF HEAVY-FERMION BEHAVIOUR

5.1 General Trends

As argued, one of the problems for heavy-fermion compounds is that there is an almost infinite list of striking properties to be considered. To select only one property to focus on, would not do full justice to the peculiarity of the heavy-fermion behaviour. The theoretical challenge is to draft a device for an interpretation of its whole complex of properties and not some limited subset. Each property on its own, although striking, is often not impossible to explain. It is its combination which presents the greater challenge.

Heavy-fermion compounds have chemically complex crystal structures and exotic elements are involved. This only further complicates matters.

But, from a pragmatic standpoint we have to start with some finite list of properties to focus on. Eventually, the understanding conceived must allow for an explanation of all the other properties as well. The situation is to some degree similar as discussing superconductivity by starting with a theory focussing on the Meissner state and the zero resistivity. At the end, the developed concepts must allow for also an understanding of the effects of paramagnetic inclusions, type I and II superconductivity, vortex arrangements, pinning centra, et cetera.

In the first chapters such a list is suggested. This list contains those properties which we believe to be the most salient for heavy-fermion behaviour. The items on the list, although justifiable, form a personal choice. Defining heavy-fermion behaviour from an experimental standpoint is complicated and not unambiguous.

The three items listed before are: the apparent heavy electron mass (e.g. [1]), the uncommon extremely small, but essentially non-zero, magnetic moment ($0.02 \mu_B$ in case of UPt_3) associated with some type of magnetic ordering (e.g. [2]) and, thirdly, the unusually strong molar volume dependence (e.g. [3] [4][5][6]) related to properties such as specific heat, susceptibility, resistivity, etc.. At low temperatures, where heavy-fermion behaviour is said to be present, the linear temperature coefficient of the specific heat is strongly enhanced with respect to the high-temperature behaviour where heavy-fermion behaviour turns out to be absent. This implies that, due to the formation of the heavy-fermion state, much more energy can be stored per kelvin (up

to a factor of hundred) as was to be expected in its absence. Clearly, the apparent high effective mass is what gave heavy-fermion behaviour its name. Also the molar volume dependence of this linear temperature coefficient, along with other properties such as resistivity, susceptibility, etc., is strongly enhanced. Additionally, the formation of the heavy-fermion state results in a dramatic change in molar volume. It is this molar-volume dependence of various properties that demonstrates the spatial extensiveness of the correlated behaviour present in heavy-fermion compounds. The same molar-volume dependence makes heavy-fermion behaviour so clearly observable in dilatation experiments, the technique used in our studies of the $U(Pt_{1-x}Pd_x)_3$ system.

The heavy-fermion behaviour is, generally, believed to be a consequence of the electronic, not the phononic, part of the system. On the other hand, a strong molar-volume dependence could suggest a strong electron-phonon coupling.

There are several methods open to externally vary the molar volume. One can apply external or chemical pressure. Let us focus on external pressure alone for the moment. It is an experimental fact that for properties such as the specific heat, susceptibility and resistivity, the pressure dependence is strongly enhanced once heavy-fermion behaviour sets in. At sufficiently high temperatures, where such compounds do not display heavy-fermion behaviour, the pressure dependence is normal. Of course, there is a difference between a pressure or stress and a volume or strain dependence. For this, the hydrostatic compressibility, κ , is defined as:

$$\kappa \equiv -\frac{1}{V} \times \left. \frac{\partial V}{\partial P} \right|_{\text{fixed } T, B}, \quad (5.1)$$

where P , V denote the pressure and volume, respectively. In general, the pressure dependence of any property X can be represented in terms of a volume dependence as $(1/V)(\partial X/\partial P) = -\kappa(\partial X/\partial V)$.

Yoshizawa et al. have measured the temperature dependence of the elastic constants from 1 K up to 600 K for UPt_3 ([4]). From this set of data, the temperature dependence of κ can be determined. At 1 K, a temperature at which heavy-fermion behaviour is well established, κ for UPt_3 turns out to be equal to 0.476 Mbar^{-1} , while at 300 K, a temperature where heavy-fermion behaviour is completely suppressed, $\kappa = 0.477 \text{ Mbar}^{-1}$. The dramatic and strongly enhanced pressure dependence of properties can, therefore, not be explained by a similar dramatic change in κ (a drastic softening of the elastic constants of the crystal). This does not imply that no anomalies, related to the creation of the heavy-fermion state, are observed in the elastic constants. The data of Yoshizawa et al clearly reveal low-temperature anomalies of order 0.03-1.1 %.

The difference in pressure dependence of several orders of magnitude due to the introduction of heavy-fermion behaviour at lower temperature must, therefore, be the result of an enhancement of the strain (volume) dependence of heavy-fermion properties, much more than an enhancement of the compressibility.

In some cases, mostly for Ce-based compounds, heavy-fermion compounds

have sister compounds with the same crystal structure but not displaying heavy-fermion behaviour. In the case of Ce-based compounds, these are compounds where Ce is replaced by La. From studies of these substituted compounds, estimates can be made concerning the phononic part in, for instance, the specific heat. From these studies the conclusion arises that heavy-fermion behaviour predominantly involves the electronic degrees of freedom of the system. The not-completely filled outer *f* shell of Ce (the major difference to La) clearly plays a role in the heavy-fermion behaviour. For UPt₃, however, such sister compounds with the same crystallographic structure and with normal behaviour do not exist. A different approach has to be applied here. One could, for instance, make use of the fact that phonons are hardly magnetic field dependent.

Let us introduce the Sommerfeld coefficient, γ , the coefficient of the linear term in the specific heat, $c_v(T)$, at low temperature:

$$\gamma \equiv \lim_{T \rightarrow 0} \frac{c_v(T)}{T}, \quad (5.2)$$

where T represents the temperature. In a Fermi-liquid approach, γ is proportional to the apparent effective mass, m^* , of the Fermionic quasi-particle excitations (the electronic part of the system). In the heavy-fermion state, the value of γ as well as its pressure dependence are strongly enhanced. This suggests not only a high effective mass or a high density of states at the Fermi level of the low-energy excitations, but also that these low-energy excitations must have a strong molar-volume dependence.

Alternatively, if one would use similar Fermi-liquid arguments as to relate γ to m^* to calculate the thermal expansion:

$$\beta_i \equiv \frac{1}{L_i} \times \frac{\partial L_i}{\partial T}, \quad (5.3)$$

where i indicates a specific crystallographic direction (i is either *a*-, *b*-, or *c*-axis) and where L_i represents the length of the sample along a specific direction, one would obtain (see section 5.3):

$$\beta_i = - \left(\kappa \gamma \left(\frac{1}{m^*} \frac{\partial m^*}{\partial L_i} \right) \right) T + \kappa \frac{S}{L_i} \quad (5.4)$$

where S represents the entropy. The low-temperature linear temperature coefficient of β_i is proportional to the relative strain dependence of the effective mass. At sufficiently low temperatures we obtain:

$$-\frac{1}{m^*} \frac{\partial m^*}{\partial L_i} = \lim_{T \rightarrow 0} \frac{\beta_i}{\kappa \gamma T}, \quad (5.5)$$

$$\text{or} \\ -\frac{\partial \ln(m^*)}{\partial \ln(L_i)} = \lim_{T \rightarrow 0} \frac{\beta_i L_i}{\kappa \gamma T}. \quad (5.6)$$

Notice the - sign in the left hand side of both expressions. The right hand side of this equation consists out of experimentally accessible parameters.

We note that $(1/m^*) (\partial m^*/\partial L_i)$ can be determined via two alternative routes: either by measuring the uni-axial pressure dependence of γ or by combining the thermal expansion and specific data using Eqn.5.6.

In normal metals, a value for $|(\partial \ln(m^*)/\partial \ln(L_i))|$ is obtained in the order of one. This holds as well for heavy-fermion compounds in the non-heavy-fermion regime (at temperatures well exceeding the characteristic temperature and/or magnetic fields well exceeding the characteristic field). However, once heavy-fermion behaviour sets in, this value is at least an order of magnitude larger.

A serious note of caution is needed here. If we assume the electronic part of the system to be strongly strain dependent in the heavy-fermion state, this could imply that a strong electron-phonon coupling exists. This coupling could be so strong that a clear separation between electronic and phononic parts of the system, as is possible in normal metals, can no longer be made.

The volume or strain dependencies are generally expressed in terms of what are called Grüneisen parameters ([5]). These will be discussed in a separate chapter.

Already from the above argument it is clear that the low-temperature thermal expansion will be enhanced as a result of the presence of heavy-fermion behaviour. But, there is another way of looking to dilatation experiments, being so sensitive to heavy-fermion behaviour.

The total Helmholtz Free energy contains various terms, as there are: a term for the electronic system, another one for the phonon part, the interaction part, et cetera. The observed molar volume is the result of a balance between different contributions, minimizing the total free energy. A hypothetical change in molar volume will cause these different contributions to the free energy to change, some positive, others negative. The net effect is positive, since the molar volume observed must be the one for which the free energy is minimal. As now, by the creation of the heavy-fermion behaviour for one part of the free energy (related to the electronic part) the relative molar-volume dependence is strongly enhanced, the original molar volume forms no longer the molar volume for which the free energy is minimal. A new balance sets in to which a different molar volume corresponds. As $-(\partial \ln(m^*)/\partial \ln(V))$ for most heavy-fermion compounds is positive in sign, plotting the volume or lengths along specific crystallographic axes versus temperature or field will reveal the heavy-fermion behaviour as clearly visible valleys in those temperature-field regions. If $-(\partial \ln(m^*)/\partial \ln(V))$ is negative in sign, instead of valleys, mountains will be observed. But, as will be discussed, a positive value of $-(\partial \ln(m^*)/\partial \ln(V))$ is in agreement with some physical notions, although negative values are observed as well. A plot of the length versus temperature and/or field can be used to identify regions of temperature and field where heavy-fermion behaviour exists, even if such regions do not border zero temperature.

Both magnetostriction (measuring the change in length as function of field

for fixed temperature) and thermal-expansion measurements are ideal tools to study heavy-fermion behaviour, more than just tracking the phase boundary of the heavy-fermion state. Both experimental techniques reveal a strong correlation between the properties related to heavy-fermion behaviour and the molar volume. This goes two ways. Affecting the molar volume, externally, affects the properties of the heavy-fermion behaviour. And the other way around, the size of the molar volume depends heavily on the extent heavy-fermion behaviour is created.

We argued that, in terms of band structures, a hallmark of heavy-fermion behaviour is the formation of a narrow peak in the density of states at the chemical potential. It are the states within this peak which are held responsible for the heavy-fermion behaviour. As a large density of states at the Fermi energy is often unstable, Jahn-Teller type of arguments suggest that it is often favourable for the system to undergo a phase transition in order to lower the energy of occupied states. This can take many forms; crystallographic changes, magnetic ordering, the occurrence of spin- or charge-density waves and even superconductivity (see [7] and references therein). It is remarkable that several of the heavy-fermion systems do not undergo such a transition.

In the following sections, various elements of the above discussion will be focused on, while in the next chapter a detailed discussion about Grüneisen parameters and a single-energy scaling, which seems to hold for heavy-fermion behaviour, can be found.

5.2 The origin of the strong strain dependence of the heavy-fermion state

The heavy-fermion state is the result of a delicate energy balance of various contributions, each with its own strain dependence. Several parameters involved stick out of being suspected for having a strong molar-volume or strain dependence. All these parameters are crucially involved in the heavy-fermion behaviour. Some of them are listed below.

- The strongest effect results from the strain dependence of the ligand hybridization. As it is argued before, its strength can be estimated by calculating the degree of overlap between the *f* orbital of the magnetic ion and a ligand orbital. The *f* orbitals are non-spherical (*f* symmetry) and highly localized. The arrangement of atoms with respect to each other but also the orientation of the orbitals in space is of importance. Hence, the ligand-hybridization strength is expected to be strongly strain dependent. Both the Kondo- and RKKY-interaction parameters are dependent on this ligand-hybridization strength. Their actual functional dependencies are different: one is exponential the other one is quadratic. Both Kondo- and RKKY-interaction parameters are, therefore, expected to have a strong but different strain dependence.
- In terms of single orbitals, the presence of other atoms constitutes a screening charge for an *f* orbital from its nucleus. Such effects are generally included in

ϵ_f . But, due to the localized nature of the f orbitals, the degree of screening by ligand atom states is sensitive to the arrangements of these atoms and states with respect to the f orbital.

- We will introduce an effective parameter which has the dimensions of a charge-transfer parameter. It will be argued that for a correlated state to be created, each f site/state should be slightly less than integer occupied. For the correlated state to be formed, room must be created in the phase space. For this, charge has to be moved from f to c states. Not completely filled f sites correspond to not-completely filled f bands, which must be located near the Fermi level. Originally ϵ_f was situated far below the chemical potential, μ . Hence, the transfer of charge must be linked to an excess energy, the charge-transfer energy. This charge-transfer energy must be a function of the amount of charge transferred. Linearizing this function (with a Taylor expression), its linear coefficient is called the charge transfer parameter. We treated this charge-transfer parameter simply as the charge-transfer parameter found in the Miedema model. In the Miedema model, a capacitive charging effect occurs when charge is moved from one type of atom to another. The Miedema charge-transfer parameter is expected to be strongly strain dependent. We expect the same for our charge-transfer parameter.

The above list is not meant to be complete. In summary, it is the highly localized and non-spherical nature of the f orbitals which is the key feature for the strain dependence.

5.3 The linear term of the electronic thermal expansion

In terms of the Helmholtz free energy, F , the thermal expansion can be expressed as:

$$\beta_i \equiv \frac{1}{L_i} \frac{\partial L_i}{\partial T} = -\kappa_i \frac{\partial^2 F}{\partial T \partial L_i} \quad (5.7)$$

where i numbers the different crystallographic directions and in which κ_i are the corresponding components of the compressibility tensor. The Einstein summation convention is used. Repeating indices implies a summation.

On the other hand, as $F = E - TS$, where E and S represent the energy and entropy, respectively, we can write:

$$\begin{aligned} -\frac{1}{\kappa_i} \beta &= \frac{\partial^2 F}{\partial T \partial L_i} = \frac{\partial^2 E}{\partial L_i \partial T} - \frac{\partial}{\partial T} \left(\frac{\partial}{\partial L_i} (T \times S) \right), \\ &= \frac{\partial^2 E}{\partial L_i \partial T} - T \frac{\partial^2 S}{\partial T \partial L} - \frac{\partial S}{\partial L}. \end{aligned} \quad (5.8)$$

The laws of thermodynamics enforce $\lim_{T \rightarrow 0} (\partial S) / (\partial L_i) = 0$. This implies:

$$\lim_{T \rightarrow 0} \frac{\partial^2 F}{\partial L_i \partial T} = \lim_{T \rightarrow 0} \frac{\partial^2 E}{\partial L_i \partial T} \quad (5.9)$$

For finite temperatures, the deviations from the above expression can be determined from a more statistical mechanical approach. Of course, such an approach leads to the same equality at zero temperature, but that approach can be more readily extended to finite temperatures.

In terms of statistical mechanics, the Helmholtz free energy for the electronic part of the system reads as:

$$F_e = -k_B T \ln(Z) = k_B T \ln \left(\sum_{\{i\}} e^{-\beta E_i} \right). \quad (5.10)$$

The subscript "e" is added to indicate that we only consider the electronic part of the system. $\beta = 1/(k_B T)$, where k_B stands for the Boltzman's constant. Within the framework of Fermi-liquid theory, it is possible to describe Z as a sum over states in the grand-canonical ensemble:

$$Z = \sum_{\{i\}} e^{-\beta E_i} = \prod_{E_i} \sum_{\{n_i\}} e^{-\beta n_i (E_i - \mu)}. \quad (5.11)$$

Here, n_i is the occupation number for a certain excitation labelled by the index i and $\{n_i\}$ represents the collection of all possible occupation numbers. In the case of Fermionic excitations $(n_i) \in [0, 1]$. μ is the chemical potential, introduced to assure that the total density of particles remains fixed. Hence:

$$F_e = -k_B T \sum_{E_i} \ln (e^{-\beta(E_i - \mu)} + 1). \quad (5.12)$$

Interchanging the index i by the quasi-momentum vector, \mathbf{k} , and approximating the sum by an integration over \mathbf{k} we can write:

$$F_e = -k_B T 4\pi \int_0^\infty dk k^2 \ln (e^{-\beta((\mathbf{k}) - \mu)} + 1) \Omega(V), \quad (5.13)$$

where $\Omega(V)$ represents the density of states in k -space. $\Omega(V)$ is proportional to the (molar) volume. Notice that only $\Omega(V)$, $E(\mathbf{k})$, and μ are molar volume dependent. Now taking the derivative of F_e with respect to L_i leads to:

$$\frac{\partial F_e}{\partial L_i} = -k_B T \left[\int_0^\infty dk k^2 \frac{-\beta \frac{\partial}{\partial L_i} (E(\mathbf{k}) - \mu)}{(e^{-\beta((\mathbf{k}) - \mu)} + 1)} \right] \Omega(V) + \frac{F_e}{L_i}. \quad (5.14)$$

The first term is caused by the molar volume dependence of $E(\mathbf{k})$ and μ , while the second term is the result of the molar-volume dependence of $\Omega(V)$.

For the total energy we obtain:

$$E \equiv \frac{\partial}{\partial \beta} (\beta F_e) = 4\pi \int_0^\infty dk k^2 \frac{(E(k) - \mu) e^{-\beta(E(k) - \mu)}}{e^{-\beta(E(k) - \mu)} + 1} \Omega(V), \quad (5.15)$$

so that:

$$\begin{aligned} \frac{\partial E}{\partial L_i} &= 4\pi \int_0^\infty dk k^2 \left[\frac{\partial}{\partial L_i} (E(k) - \mu) \right] \times \\ &\quad \frac{1}{e^{\beta(E(k) - \mu)} + 1} \Omega(V) \\ &\quad + \int_0^\infty dk k^2 (E(k) - \mu) \frac{\partial (E(k) - \mu)}{\partial L_i} \times \\ &\quad \left[\frac{\partial}{\partial (E(k) - \mu)} \left(\frac{1}{e^{\beta(E(k) - \mu)} + 1} \right) \right] \end{aligned} \quad (5.16)$$

for T approaching to zero this turn into a δ function $\rightarrow \delta(E(k) - \mu)$

+

$$\frac{E}{L_i}$$

caused by the volume dependence of Ω

For temperatures approaching zero ($\beta = 1/k_B T$ approaching infinity):

$$\lim_{\beta \rightarrow \infty} \left[\frac{\partial}{\partial x} \left(\frac{1}{e^{\beta x} + 1} \right) \right] = \delta(x), \quad (5.17)$$

in which $\delta(x)$, denotes the Kronecker delta. Hence:

$$\lim_{T \rightarrow 0} \frac{\partial E}{\partial L_i} = 4\pi \int_0^\infty dk k^2 \left[\frac{\partial}{\partial L_i} (E(k) - \mu) \right] \times \frac{\Omega(V)}{e^{\beta(E(k) - \mu)} + 1} + \frac{E}{L_i}. \quad (5.18)$$

In such terms we recognize the first integral term in the expression for $(\partial F / \partial L_i)$.

$$\frac{\partial^2 F}{\partial L_i \partial T} = \frac{\partial^2 E}{\partial L_i \partial T} + \frac{1}{L_i} \frac{\partial}{\partial T} \left\{ \frac{F - E}{TS} \right\}. \quad (5.19)$$

$$= \frac{\partial^2 E}{\partial L_i \partial T} - T \frac{\partial S}{L_i \partial T} - \frac{S}{L_i} \quad (5.20)$$

Again for low enough temperatures:

$$\frac{\partial^2 F}{\partial L_i \partial T} \approx \frac{\partial^2 E}{\partial L_i \partial T} \quad (5.21)$$

The discrepancy between Eqs 5.19 and 5.8 is lifted as we realize that we defined all energy levels with respect to the chemical potential and that:

$$\delta S = T \frac{\delta q}{T} = \frac{c_v(T) \delta T}{T} = (c_v(T) = \gamma T) = V \gamma \delta T \quad (5.22)$$

where δq stands for a change in heat and where we used $c_V(T) = \gamma T$. As $S = V\gamma T$, we find that:

$$\frac{\delta S}{\delta L_i} = \frac{S}{L_i}. \quad (5.23)$$

With the help of this observation, the discrepancy between the two results is lifted. The results of the statistical mechanical approach can be readily extended to finite temperatures and explicit expressions for S at finite temperatures can be generated.

For the lowest temperatures, one can assume that the electronic thermal expansion is due to states with energies within an energy window of $k_B T$ at the Fermi energy. Take the temperature window so small that only one effective mass can be ascribed to all the states within this window. Furthermore, presume that the length dependence of each individual state within this temperature window can be treated as originating solely from the length dependence of its effective mass. In zero-order approximation, all effective masses at sufficiently low temperatures are taken temperature independent (the band structure is assumed to be temperature independent). In terms of a Fermi-liquid approach, the changes in occupation densities with respect to zero temperature are sufficiently small so that the quasi-particle interactions and their effect on the energy levels can be discarded. One can show that in this limit:

$$\frac{\partial^2 F}{\partial L_i \partial T} \approx \frac{\partial^2 E}{\partial L_i \partial T} \approx \underbrace{\frac{\partial E}{\partial T}}_{c_V(T)} \left\langle \frac{-1}{m^*} \frac{\partial m^*}{\partial L_i} \right\rangle. \quad (5.24)$$

where m^* represents the effective mass, and where $\langle \rangle$ indicates an average over all the states with an energy within the temperature window of $k_B T$ at the Fermi energy. This implies that the thermal expansion at sufficiently low temperatures in the specific direction i is given by:

$$\beta_i = - \left(\kappa_i \frac{1}{m^*} \frac{\partial m^*}{\partial L_i} \right) c_V(T) = - \left(\gamma \kappa_i \frac{1}{m^*} \frac{\partial m^*}{\partial L_i} \right) \times T \quad (5.25)$$

For the expressions obtained we note that: $\beta(T=0) = 0$, as it should be.

$$\beta_i = -\kappa_i \frac{\partial^2 F}{\partial L_i \partial T} = \kappa_i \frac{\partial S}{\partial L_i}, \quad (5.26)$$

The low-temperature electronic thermal expansion is proportional to the temperature. Its proportionality constant contains information about the relative strain dependence of the apparent effective mass of the excitations close to the Fermi level, while the proportionality constant of the specific heat contains information about the effective mass itself. From the expression presented above, the relative length dependence of the effective mass can be expressed in terms of all measurable quantities ; i.e.:

$$-\frac{\partial \ln(m^*)}{\partial \ln(L_i)} = \frac{\beta_i L_i}{\kappa_i c_V(T)}. \quad (5.27)$$

It will turn out that this expression has a strong similarity with that for the anisotropic Grüneisen parameter, to be discussed in the next chapter.

5.4 The possible existence of a characteristic molar volume

In this section we will not treat the volume as an observable but as a parameter. We will discuss the effects a change in volume can have on the heavy-fermion state. The concept of a characteristic molar volume will be introduced and we shall extensively use it in our discussion of the effects of Pd-doping on UPt_3 .

It is the combination of the itinerant nature of the f states with the strong on-site repulsion which makes the heavy-fermion state energetically favourable. On the other hand, for the ability of the system to form a heavy-fermion ground state, each f shell must be slightly depopulated (with respect to one f site and shell).

For increasing molar volume, not only the ability to form a heavy-fermion state (e.g. the charge transfer decreases) but also the necessity to form the heavy-fermion state decreases (the itinerant nature of the f states decreases). For increasing volumes, the heavy-fermion state at some characteristic volume can no longer be formed but is also no longer energetically favourable.

Another effect of the decreasing ligand-hybridization strength is the increase of the effective mass. A decreasing hybridization strength also implies that the energy width of the peak at the Fermi level decreases. Related to this is a decreasing characteristic temperature for the heavy-fermion state. It is, therefore, to be expected that for increasing molar volumes, primarily the effective mass should increase. Simultaneously to the increasing mass, the characteristic temperature of the heavy-fermion state should decrease. Since there is a simple energy scaling relation between characteristic fields and temperatures for the heavy-fermion state, also the characteristic field decreases for increasing molar volumes. This process continues until a characteristic molar volume is reached at which the heavy-fermion state is no longer energetically favourable. Further increase of the molar volume smoothly destroys the heavy fermion state. The fact that also the charge transfer decreases should cause the occupation density per f site and shell to increase towards one. In terms of band structures, this implies that the peak in the density of states should shift downwards with respect to the Fermi level. The situation of each f shell being precisely once occupied is directly associated with this peak in the density of states being completely below Fermi energy. The destruction of the heavy-fermion state can be pictured as the peak in the density of states slowly sinking below the Fermi level.

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