Mean-field expression for the characteristic Grüneisen parameter of the Kondo lattice

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In addition to the enhanced specific heat coefficient and susceptibility, heavy fermion compounds also exhibit a large characteristic Grüneisen parameter (Γ) for different properties. We clarify the relevant intrinsic energy scale in the presence of a magnetic field, and derive the analytic expression for Γ by use of the slave-boson mean-field results. Our results are *at variance with* the belief that Γ is proportional to the enhancement of the quasiparticle mass. We find instead that, besides the contribution from the sensitive volume dependence of the hybridization matrix element, Γ roughly depends on the *logarithm* of the mass enhancement.

I. INTRODUCTION

Experimentally, the Grüneisen parameter[1,2] Γ of the heavy-fermion compounds is about two orders of magnitude larger than in ordinary metals,[3] which is similar to the enhancement for the linear temperature coefficient γ of the specific heat at low temperatures and the zero-temperature spin susceptibility χ_0. In accordance with the scaling behavior[4-6] and a unique intrinsic energy scale[4,5] observed experimentally, Γ values obtained from different properties[5] are very nearly the same. Based on these observations, there have been many theoretical efforts, for example, the free-energy approach which includes the work by Takke *et al.*,[7] who separated the elastic part from that of the electron and electronic lattice coupling, and the scaling approach by Thalmeier and Fulde.[8] But the actual dependence of Γ on the anomalous density of states, due to the Kondo resonance, remains unclear in comparison to other thermodynamic quantities. It was conjectured by Jaccard and Flouquet[9] that Γ obeyed the same scaling law as γ and χ_0, i.e., Γ is proportional to the enhanced quasiparticle mass or the ratio of conduction bandwidth W and the Kondo temperature.

In this paper we derive an analytic expression for the Grüneisen parameter in the presence of external magnetic field at zero temperature. Special attention is paid to find out the contribution from the large density of states and compare with the aforementioned conjecture. Our analyses are based on the large-ground-state-degeneracy expansion of the slave-boson approach[10] at the mean-field level. There are already interesting new results at this level without considering lattice anisotropy, crystal field, and possible magnetic correlations in the compound (we emphasize that these effects[2] are crucial for a realistic Γ). Since the renormalized impurity-electron one-body energy E_f for the $\uparrow$-spin electrons is shifted differently by the magnetic field from that of the $\downarrow$-spin ones, the conventional definition of the Kondo temperature $T_K \equiv E_f - \mu$ (μ denotes the chemical potential) no longer seems to be a good energy scale. It is then tempting to use the seemingly more physical hybridization gap width $E_{\rm gap}$, which governs the interband charge excitations. This, however, will turn out later not to be the right energy scale for describing the density-of-states effect. We analyze in this paper what the relevant energy scale is and derive an analytic expression for the heavy-fermion Grüneisen parameter. Since the generalization of the slave-boson mean-field results to finite magnetic fields has been made in a previous paper,[11] some of the results will be quoted without further derivations. In accordance with the existence of crystal-field splitting in most compounds, we assume a doublet ground state. The total number of electrons per unit cell participating in the hybridization (n) is set to be slightly less than 2 so that the density of states at the chemical potential is enhanced[12] at zero field.

II. DEFINING THE CHARACTERISTIC ENERGY SCALE

The effect of a large Γ is of particular interest to recent studies of the metamagnetic-like transition in heavy-fermion compounds,[13,14] for example, in $CeRu_2Si_2$ there is an enormous 50% drop in the elastic constant c_{33} (Ref. 15) and a sharp peak in the magnetostriction which corresponds to an abrupt increase in the volume by 10^{-3} (Ref. 16). As mentioned above, Γ values obtained from different properties are similar in these compounds; e.g., if the entropy obeys the scaling law, then a related Grüneisen parameter can be defined[2] as

$$\Gamma \equiv \frac{3aV_m}{\kappa\gamma} = -\frac{\partial \ln E^*}{\partial \ln(\text{volume})} \quad \text{or} \quad \frac{\partial \ln E^*}{\partial \varepsilon}, \tag{1}$$

where a comes from the thermal expansion coefficient ($\approx 3aT$ at low temperatures T), V_m is the molar volume, κ is the isothermal compressibility, and E^* is the characteristic energy under strain, ε. It is expected from Eq. (1) that a should be enhanced more than γ. But detailed theoretical expressions for the thermal expansion coefficient of heavy-fermion compounds are not available, therefore we shall determine Γ from the characteristic energy.

Within the mean-field treatments,[10] the quasiparticle

dispersion relations for the Kondo lattice are

$$E_{\pm}(\varepsilon_k)=\tfrac{1}{2}[\varepsilon_k+E_f\pm\sqrt{(\varepsilon_k-E_f)^2+4V^2(1-n_f)}]\ , \quad (2)$$

where $E_+(E_-)$ is for the upper (lower) hybridization band, ε_k is the bare conduction-band energy, and V is the root-mean-square value of the hybridization matrix element averaged over the Fermi surface. In the presence of magnetic field H, it is easy to show from Eq. (2) that the hybridization gap width is roughly independent of H:

$$E_{\text{gap}}=\frac{V^2(1-n_f)}{W+E_f\pm H}+\frac{V^2(1-n_f)}{W-E_f\mp H}\approx\frac{2V^2(1-n_f)}{W}\ , \quad (3)$$

where the approximate sign is justified by the fact that W is much bigger than the magnitudes of E_f and H. The average number of impurity electrons per impurity site is denoted by n_f, and the $+(-)$ sign is for the $\downarrow$-($\uparrow$-) spin electrons. Note that we have set the product of the impurity-electron angular momentum J and its Lande g factor to unity for convenience (caution is required in calculating the magnetization, since the g values are different[11] for the conduction electron and the impurity electron).

Assuming a constant density of states $\mathcal{D}$ for the conduction band, the resulting density for the hybridization bands can be obtained from Eq. (2) as

$$\mathcal{D}=\frac{1}{W}\frac{\partial\varepsilon_k}{\partial E_{\pm}}=\frac{1}{W}\left[1+\frac{V^2(1-n_f)}{(E_f-E_{\pm})^2}\right]\ ,$$

where the quantity 1 in the last expression is negligible when $\mathcal{D}$ is large. This enhancement happens when the chemical potential lies close to the narrow Kondo resonance, which then equals, relative to the bare $\mathcal{D}$ of $1/W, V^2(1-n_f)/(E_f-\mu)^2$ or $W/|E_f-\mu|$ at zero magnetic field.[10] The latter expression shows that the Kondo temperature, defined as $|E_f-\mu|$, is a useful energy scale for the $\mathcal{D}$-related physical quantities at zero field. However, the validity of this energy scale is not clear in the presence of magnetic field because the hybridized bands are shifted differently for each spin. For small fields, μ remains in the lower $\uparrow$-band which we shall call region I (see Fig. 1), and we find the density of states $\mathcal{D}$ is given by

$$\mathcal{D}\approx\frac{1}{2}\left[\frac{1}{(E_f-H)-\mu}+\frac{1}{(E_f+H)-\mu}\right]=\frac{T_K(H)}{T_K^2(H)-H^2}\ . \quad (4)$$

But, when μ enters the $\uparrow$-spin gap (region II), there is no state for the $\uparrow$-spin electrons, and we obtain

$$\mathcal{D}\approx\frac{1}{2}\frac{1}{(E_f+H)-\mu}\ . \quad (5)$$

Finally, for large fields, μ moves into the upper $\uparrow$-band (region III). Note that the chemical potential remains in the lower $\downarrow$-spin band for all fields. For region III, μ is further away from the dense states accumulated at the lower $\downarrow$-spin band edge, and the density of states comes mainly from the $\uparrow$-spin electrons:

$$\mathcal{D}\approx\frac{V^2}{W(\mu-E_f+H)^2}\times\left[(2-n)-\frac{|E_o|}{W}+\frac{V^2}{2W^2}\ln\frac{W^3}{V^2T_K(H)}\right]\ , \quad (6)$$

where a simple expression as Eqs. (4) or (5), valid only for small fields, is not applicable.

It has been shown[11] that

$$\mu\approx W(n-n_f-1)+O\left[\frac{V^2(1-n_f)}{W}\right] \quad \text{for all fields}\ , \quad (7)$$

and for region I:

$$T_K(H)\approx\sqrt{T_K^2(0)+H^2}\ , \quad (8)$$

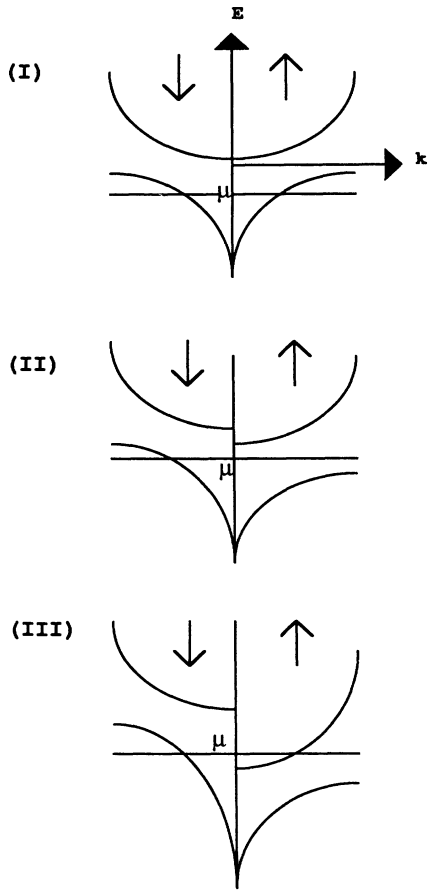

FIG. 1. Three regions are distinguished for the isotropic hybridization case according to the relative position of the chemical potential to the dispersion bands (the $\uparrow$-spin bands are on the right).

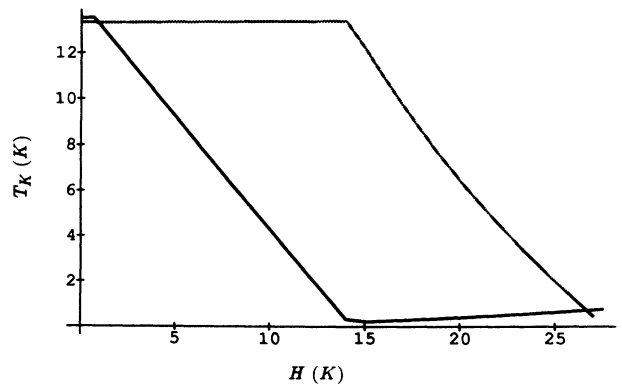

FIG. 2. Field dependence of $T_K(H) \equiv E_f - \mu$ (solid line) and $E_{\rm gap}/2$ (grey line). We set $N=2$, $n=1.95$, $W=50\,000$ K, $V^2/W=1000$ K, and $E_o=-10\,000$ K, which give $T_K(0)\approx 13.5$ K. The crossovers between regions are at 0.7 and 14 K.

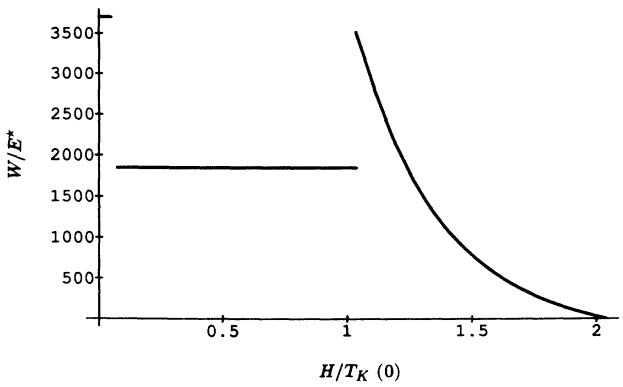

FIG. 3. Field dependence of W/E^*, which equals the enhancement of the density of states at μ (for the same parameters as in Fig. 2).

$$E_{\rm gap} \approx \frac{2T_K^2(0)}{T_K(H)} \approx 2T_K(0) \ . \tag{9}$$

This last approximation in Eq. (9) is made because the crossover field at which μ enters region II is

$$H_{\rm I,II} \approx (2-n)T_K(0) \ . \tag{10}$$

While the factor $2-n$, being small compared to unity for heavy-fermion compounds,[17] the term $T_K^2(0)$ in Eq. (8) is much bigger than $H_{\rm I,II}^2$, and $T_K(H) \approx T_K(0)$ in region I. From Eq. (4), the characteristic energy is defined as

$$E^* \equiv \frac{T_K^2(0)}{T_K(H)} \approx T_K(0) \ . \tag{11}$$

Note that the Kondo temperature

$$T_K(0) \approx W \exp\left[-\frac{W(\mu + |E_o|)}{V^2} \right] \tag{12}$$

is roughly independent of H because the H-dependent chemical potential is much smaller than the magnitude of the bare impurity-electron one-body energy, E_o.

Similarly for region II:

$$T_K(H) \approx T_K(0) - H \ , \tag{13}$$

$$E_{\rm gap} \approx 2T_K(0) \ , \tag{14}$$

and, from Eq. (5):

$$E^* \equiv 2T_K(0) \ . \tag{15}$$

The reason why $T_K(H)$ in Eq. (8) appears to be discontinuous at the boundary with the result of Eq. (13) is that we have neglected terms of order $H_{\rm I,II}$. The critical field at which μ goes into region III equals

$$H_{\rm II,III} \approx \frac{V^2}{W} \frac{1-n_f}{n-1} \approx \frac{T_K(0)}{n-1} \ , \tag{16}$$

which is roughly half of the gap energy.

Finally, for region III, we obtain

$$\begin{aligned} T_K(H) &= \tfrac{1}{2}\{ -V^2/W + [(V^2/W)^2 + 4H^2]^{1/2} \} \ , \\ E_{\rm gap} &\approx \frac{2V^2}{W} \left[(2-n) - \frac{|E_o|}{W} + \frac{V^2}{2W^2} \ln \frac{W^3}{V^2 T_K(H)} \right] \ , \end{aligned} \tag{17}$$

and, from Eq. (6)

$$E^* \equiv \frac{W[H - T_K(H)]^2}{V^2\{(2-n) - |E_o|/W + (V^2/2W^2)\ln[W^3/V^2 T_K(H)]\}} \ . \tag{18}$$

From the diminished role of $T_K(0)$ in the expressions for region III, we expect the Kondo effect to have been largely disrupted. Therefore, this region is not of interest to us, where a single energy scale and the scaling law are expected not to be observed.

Numerical results for the field dependence of $T_K(H)$ and $E_{\rm gap}/2$ are plotted in Fig. 2. Figure 3 shows the field dependence of W/E^*, which equals the enhancement of the density of states at the chemical potential. The sharp contrast between region II and the other two regions is expected to be rounded off when lattice anisotropy,[11] fluctuations beyond the mean field, or finite-temperature effect are considered.

III. DERIVING THE HEAVY-FERMION GRÜNEISEN PARAMETER

By use of Eqs. (9), (14), and (3), the chemical potential in Eq. (7) can be rewritten as

$$\mu \approx W(n-2) + T_K(0)W^2/V^2$$

for regions I and II. The Kondo temperature, being the characteristic energy scale in both regions, and its derivative with respect to the strain can be obtained from Eq. (12) as

$$\frac{\partial T_K(0)}{\partial \varepsilon} = T_K(0)\left[\frac{2W(|E_o|+\mu)}{V^2}\lambda - \frac{W^3}{V^4}\frac{\partial T_K(0)}{\partial \varepsilon}\right]$$

$$= \frac{T_K(0)\,2W(|E_o|+\mu)\lambda}{V^2[1+T_K(0)W^3/V^4]}\ , \tag{19}$$

where $\lambda \equiv (\partial \ln V/\partial \varepsilon)$ is estimated to be of order 10. According to our previous definition in Eq. (1), the Grüneisen parameter for regions I and II is then of the same value:

$$\Gamma = \frac{\partial \ln T_K(0)}{\partial \varepsilon} = \frac{2\lambda \ln[W/T_K(0)]}{1+T_K(0)W^3/V^4}\ . \tag{20}$$

In general, the two terms in the denominator of Eq. (20) are comparable, and the expression in Eq. (20) *cannot* be reduced to the form suggested by Jaccard and Flouquet[9]: $\Gamma \propto 1/T_K(0)$.

In comparison, for the Kondo-impurity case when only one impurity electron is hybridizing with all the conduction electrons, valence fluctuations in n_f can hardly affect the energy level of the chemical potential. Therefore, we do not have the second term in Eq. (19) which comes from differentiating the chemical potential, and the resulting expression for the Grüneisen parameter is

$$\Gamma = 2\lambda \ln\frac{W}{T_K(0)}\ . \tag{21}$$

Both expressions, Eqs. (20) and (21), indicate that the anomalous Grüneisen parameter for the heavy-fermion compounds does not derive solely from the large density of states at the chemical potential, but the sensitive volume dependence of the hybridization matrix element is equally important in enhancing Γ.

Roughly speaking, since the thermal fluctuations tend to disrupt the Kondo coherence, we expect a lower chemical potential at small nonzero temperatures [due to the increase of n_f in Eq. (7) toward unity] which increases the Kondo temperature because of Eq. (12). Therefore, according to the expression in Eqs. (20) and (1), the Grüneisen parameter decreases at low temperatures. This is in line with most experimental data, e.g., for $CeSn_3$ (Ref. 7), $CeCu_6$ and $CeCu_2Si_2$ (Ref. 6), and $CeRu_2Si_2$, UPt_3, and UBe_{13} (Ref. 2). However, it is difficult from the low-temperature variation to distinguish whether the dependence of the Grüneisen parameter on T_K is linear or logarithmic.

Assuming that the Kondo temperature is the only energy scale at low temperatures,[18] the scaling law observed experimentally can be derived from the Grüneisen parameter.[5] We notice that Zieglowski *et al.*[6] have deduced the same T_K dependence for Γ as conjectured by Jaccard and Flouquet.[9] They combined the prediction in Ref. 7 with the observed scaling law[6] to obtain

$$\Gamma \propto \frac{1}{\chi}\frac{1}{(T+\theta)^2}\ ,$$

where θ is a constant chosen to fit the scaling law. Assuming θ to be the same as the T_f appearing in the high-temperature susceptibility, $\chi \sim (T+T_f)^{-1}$, the $\Gamma \sim (T+T_f)^{-1}$ conclusion is thus reached. There are two problems with this deduction: firstly, from their data[6] θ is noticeably different from T_f for $CeCu_6$ ($\theta = 12$ K while $T_f = 6$ K); secondly, the susceptibility is known to exhibit Fermi-liquid behavior at low temperatures for Kondo lattices, i.e., $\chi(T) - \chi_0 \propto T^2$. Therefore, their conclusion is not convincing in our view, especially for Kondo lattices at low temperatures (of course, the experimentally observed scaling law is not in doubt here which we emphasize is consistent with our expression).

IV. CONCLUSIONS

We have clarified the intrinsic energy scale characterizing the Kondo lattices in the presence of small magnetic fields. From it we derive an analytic expression for the heavy-fermion Grüneisen parameter, the same for different physical properties. Provided the energy scale is unique, our results are consistent with the scaling behavior observed experimentally.[5,6] However, these are no longer valid above the field at which the chemical potential moves into the upper ↑-spin band, when the Kondo effect is expected to be largely disrupted. Our expression for the heavy-fermion Grüneisen parameter is *at variance with* the previous belief that Γ is proportional to the enhancement of the quasiparticle mass. We obtain instead only a roughly logarithmic dependence, therefore the largeness of the Grüneisen parameter comes partly from the sensitive volume dependence of the hybridization matrix element. Although our mean-field analyses have been able to cast doubt upon the previous conjecture for Γ, a realistic expression will have to include lattice anisotropy, crystal field, and possible magnetic correlations in the compound. For instance, in the heavy-fermion alloys $U(Pt,Pd)_3$, increasing Pd content has been known to cause an inversion of Γ (see Ref. 19), which is surely beyond the scope of this paper.

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[17]From Eqs. (7) and (12), we know that $\mu+|E_o|$ needs to be much bigger than V^2/W for heavy-fermion compounds, and that $n \gg 2-(|E_o|/W)+(V/W)^2$. For $E_o/W=-1/5$, the lower bound of n is roughly 1.8.

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