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A mean-field theory of the transition from local-moment to heavy-fermion behaviour

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Abstract. We use a slave-boson technique in the mean-field approximation to obtain the temperature (T) dependence of the valence, n_f, the susceptibility, χ_S, and the specific heat, C_V, for a lattice of mixed-valence ions. We find that the mean-field solution is sufficient to extrapolate between the low- and high-temperature regimes giving for example an enhanced Pauli-like susceptibility for low T and a Curie–Weiss-like susceptibility at high T. We consider an extension to the Anderson model in which direct f–f hopping is included and show that such a model exhibits a variety of interesting low-temperature behaviour.

1. Introduction

The mixed-valence and heavy-fermion compounds are characterised by Fermi-liquid-like behaviour at low temperatures going over to local moment behaviour as the temperature is increased. The temperature dependence of the magnetic susceptibility, χ_S, and the specific heat, C_V, clearly shows the crossover between the two types of behaviour (see Laurence *et al* 1981 and Stewart 1984 for reviews).

In this paper we consider the temperature-dependent behaviour using the slave-boson mean-field solution for the periodic Anderson model. The slave-boson technique has had much success in providing a microscopic description for the heavy-fermion compounds in the low temperature strong-coupling regime (Millis and Lee 1987) and we wish to consider to what extent it is successful in describing the high-temperature weak-coupling behaviour as well. At mean-field level self-consistent equations for n_f, the renormalised f-level energy, ϵ_f, and the Fermi level, μ, are found. These can be solved analytically for zero temperature giving rise to renormalised bands with heavy quasiparticles at the Fermi level thus giving the correct low-temperature description. In this paper we solve the equations numerically at finite temperature. We show that for the lattice the mean-field equations are sufficient to produce both high- and low-T behaviour which is in good qualitative agreement with experiment. Our results are compared with the experimentally observed universal 'scaling' relations for χ_S and approximately the correct relations are found. A similar crossover can be found as a function of applied magnetic field. The mean-field solution is thus a very reasonable but simple first approximation to the whole of the temperature regime.

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We note that the mean-field solution gives a state of broken symmetry and a second-order phase transition exists between the low-temperature strong-coupling regime and the high-temperature weak-coupling regime. The phase transition is wiped out when fluctuations about the mean-field level are included. We show that for the lattice this phase transition only occurs for $T \gg T_K$ and in practice it does not restrict our calculations. Despite the fact that we are still below the phase transition and might expect that we are still in the strong-coupling regime the high-temperature behaviour is given correctly. We note that this is in contrast to the single-impurity case where similar calculations have been done. There it is seen that n_f increases rapidly to one and the phase transition occurs for $T \sim T_K$ (Coleman 1985). The mean-field solutions only reproduce the low-temperature behaviour and the crossover to high-temperature behaviour is not obtained. Similarly the high-magnetic-field behaviour cannot be accessed.

Recently an extension to the Anderson model in which direct f–f hopping is included has been considered (Harrington *et al* 1988). At zero temperature it was shown that there is a phase transition as a function of t the bare f–f band width. There is a finite discontinuity in the specific heat at $t = t_c$. This corresponds to a transition from a state in which only the lower band crosses the Fermi level, the upper band being empty, to one in which both bands cross the Fermi level and the density of states becomes continuous. At finite temperature we show that this transition is smoothed out due to the fact that for $T > 0$ the occupation of the upper level is never zero and the distinction between the two cases becomes blurred. We show, however, that near the transition point, $t \sim t_c$, interesting low-temperature behaviour develops. This may be of significance given the variety of low-T behaviour which is in fact observed in the heavy-fermion compounds. The inclusion of t also enables us to widen our parameter space and show that although we have altered somewhat our low-temperature description in a way that makes the Fermi-liquid-like behaviour more apparent the crossover to a local-moment regime still occurs and the high-temperature behaviour is as before.

We perform the calculations for a variety of values of N, the f-level degeneracy, and show that although the behaviour is still qualitatively correct even for small values of N the accuracy of our calculations improves as N increases. The mean-field solution corresponds to working to zeroth order in a $1/N$ expansion so this behaviour is as expected. The case of $N = 2$ with two electrons per site is interesting as here the Fermi energy lies in the hybridisation gap leading to qualitatively different behaviour.

We look now in more detail at the experimental behaviour we would like to explain. At high temperatures there is a Curie–Weiss-like susceptibility. χ_S can be fitted to $(T - \Theta)^{-1}$ where $\Theta < 0$ and there are large effective moments ($> \mu_B$). At low temperatures the behaviour is smooth and the susceptibility tends to a constant value which for the heavy-fermion systems is greatly enhanced over the value expected for a normal metal. This large Pauli-like susceptibility can be characterised by a small energy scale, T_K, by defining $\chi_S(T = 0) = \mu_0^2/(k_B T_K)$ where μ_0 is the effective moment. T_K is known as the 'Kondo' temperature. The low-temperature behaviour is especially interesting as a variety of behaviour is observed. Many of the compounds show a rise in the susceptibility up to a maximum at $T = T_m$. T_K, Θ and T_m are all of the same order of magnitude and experimentally universal 'scaling relations' are found. However, this behaviour is not completely universal and the maximum is not observed in all the compounds. UBe_{13} and $CeCu_2Si_2$, for example, show a monotonic decrease in χ_S as T increases. We can compare the behaviour of UPt_3 and UBe_{13} both of which

have similar values of T_K and Θ. UPt_{13} has a pronounced maximum at $T \sim 20$ K which would lead us to expect a similar feature for UBe_{13}. This is not observed. Several compounds show more anomalous behaviour. SmB_6, $CeSn_3$ and $CePd_3$ all exhibit a susceptibility 'tail' for very low temperatures (Gschneider 1985, Veenhuizen *et al* 1985, von Molnar *et al* 1982). The susceptibility has a maximum at $T \sim T_K$ which as we further decrease the temperature is followed by a minimum after which there is a sharp upswing as χ_S tends to zero. Experiments have shown that this 'tail' cannot be simply accounted for in terms of magnetic impurities and is an intrinsic feature. The data on the specific heat also shows interesting features. In general C_V varies linearly with temperature at very low temperatures, $C_V = \gamma T$, which is the behaviour expected for a Fermi liquid. γ shows approximately the same enhancement as $\chi_S(T = 0)$. A plot of C_V/T against T tends to have a fairly sharp maximum as we increase from $T = 0$, the area under this anomaly being of the order of the entropy associated with a local moment, $S = k_B \ln N$. The maximum in C_V is at about the same temperature as the maximum in χ_S. Again the behaviour is not universal. UPt_3, for example, shows a rapid downward fall in C_V as T increases (Brodale *et al* 1986). C_V can be fitted to $\gamma T + \delta T^3 \ln T$. Very different behaviour is seen for SmB_6 (von Molnar *et al* 1982). The evidence of a linear T dependence is doubtful and C_V appears to be better fitted to an exponential. This and other evidence suggests that this compound is a semiconductor with the Fermi energy lying in the gap.

The paper is organised as follows. In section 2 we consider the usual mean-field equations and report on the numerical solutions as a function of temperature and also magnetic field. In the next section we introduce the direct f–f hopping parameter t and discuss the effect that this has. Finally we consider the differences between the one-impurity and lattice problems and explain the very different temperature behaviour obtained for the two problems. We discuss also how the temperature dependence of n_f differs for the uranium heavy-fermion compounds.

2. Solving the mean-field equations at finite T and h

The mean-field equations are as follows (Rasul and Desgranges 1986):

$$n_f = -N\rho_0 \int_{-W}^{(N-1)W} A_+(k) f[E_-(k) - \mu] + A_-(k) f[E_+(k) - \mu] \, d\epsilon_k \tag{2.1}$$

$$\epsilon_f = E_0 + \frac{N\Delta_0}{\pi} \int_{-W}^{(N-1)W} \frac{f[E_-(k) - \mu] - f[E_+(k) - \mu]}{E_+(k) - E_-(k)} \, d\epsilon_k \tag{2.2}$$

$$n_f + n_c = N\rho_0 \int_{-W}^{(N-1)W} f[E_-(k) - \mu] + f[E_+(k) - \mu] \, d\epsilon_k = 2 \tag{2.3}$$

where

$$E_\pm(k) = \tfrac{1}{2}\left(\epsilon_k + \epsilon_f \pm \left[(\epsilon_k - \epsilon_f)^2 + 4\tilde{V}^2\right]^{1/2}\right) \tag{2.4}$$

$$A_\pm(k) = -\frac{1}{2}\left(1 \pm \frac{\epsilon_k - \epsilon_f}{\left[(\epsilon_k - \epsilon_f)^2 + 4\tilde{V}^2\right]^{1/2}}\right) \tag{2.5}$$

where E_0 is the bare f-electron energy, V is the hybridisation term (assumed constant), W is the conduction electron bandwidth and ρ_0 is the conduction electron density of

states which is also assumed to be constant. $\tilde{V}^2 = (1-n_f)V^2$, $\Delta_0 = V^2\rho_0/\pi$ and ϵ_f is the effective f-level energy. The Fermi energy μ is measured relative to the Fermi energy of the unhybridised conduction electrons.

These were solved numerically for a variety of values for N keeping the total number of electrons constant (2 electrons per lattice site). For comparison we have also solved (2.1) and (2.2) for $N = 2$ keeping the Fermi level constant. We took $E_0 = -0.8$ eV, $W = 10$ eV and $V = 1$ eV. In figure 1 we show the variation of n_f with temperature in units of T_K, where T_K is defined as $\mu_0^2/[k_B\chi_S(T=0)]$ for $N \neq 2$. The results for $N = 2$, 4 and 6 and for $N = 2$ with μ kept constant (broken curve) are shown. We see that n_f does indeed vary slowly with T and only reaches $n_f = 1$ for $T \sim 10T_K$ (not shown on diagram) where we would expect that the behaviour is that of the weak-coupling regime. The change with temperature becomes slightly faster as N increases. Comparison with the case where μ is kept constant shows the importance of determining the Fermi level accurately. Here n_f reaches 1 for $T \sim T_K$ as in the one-impurity problem. The change in the Fermi level with temperature gives us an important difference between the one-impurity and lattice problems. We note that to a good approximation the Fermi level is given by $\mu = [1-n_f(T)]W$. This is just the value expected for a normal Fermi sea containing $1+(1-n_f)$ non-interacting electrons per site.

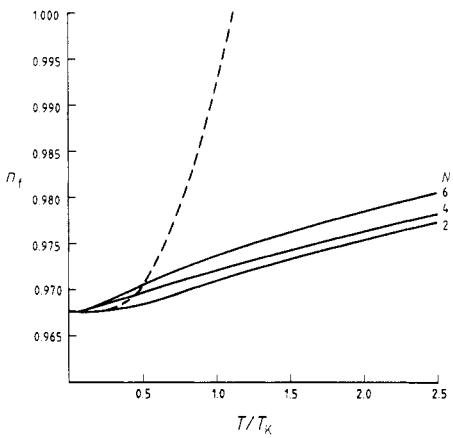

Figure 1. n_f as a function of T/T_K for $N = 2$, 4 and 6. The broken curve shows the result for $N = 2$ with μ kept constant.

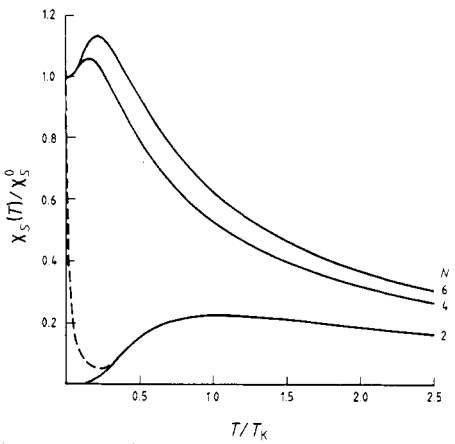

Figure 2. χ_S/χ_S^0 as a function of T/T_K for $N = 2$, 4 and 6. The broken curve shows the results for $N = 2$ and total number of electrons $n_c + n_f = 2.01$.

We can also calculate the magnetic susceptibility and specific heat. We consider first the susceptibility. This can be found by adding a term $h\sum_{im} m f_{im}^\dagger f_{im}$ into the Hamiltonian. The effect is to change $\epsilon_f \to \epsilon_f + hm$. The free energy can be found and differentiating twice with respect to h gives χ_S. We note that only the explicit dependence of F on h has to be considered as we have $\partial F/\partial n_f = \partial F/\partial \epsilon_f = 0$ from the minimisation condition. Strictly speaking we ought also to add in a term coupling the conduction electrons to the field. However at zero temperature the effect is to add a very small correction $O(m/m^*)$ to the susceptibility and we do not expect this to change at higher temperatures.

The expression for the free energy is:

$$F = \Delta F - i\lambda n_f \tag{2.6}$$

where

$$\Delta F = T \sum_{k,i\omega} \sum_{m,\alpha} \ln[i\omega - E_{m\alpha}(k)] \tag{2.7}$$

where $\alpha = \pm$ and $E_{m\pm}(k)$ is found by replacing $\epsilon_f \to \epsilon_f + hm$ in the expression for $E_{\pm}(k)$. This describes the two renormalised bands. Using Poisson's formula we obtain

$$\Delta F = \sum_{m,\alpha,k} \int_{-\infty}^{\infty} d\epsilon \, f(\epsilon) \Theta[\epsilon - E_{m\alpha}(k) + \mu]. \tag{2.8}$$

The sum over k can be performed giving

$$\Delta F = \rho_0 \sum_{m\alpha} \int_{y_{m\alpha}^-}^{y_{m\alpha}^+} d\epsilon \, f(\epsilon) \left(W + \mu + \epsilon + \frac{\tilde{V}^2}{\epsilon_f - \mu + hm - \epsilon} \right) \tag{2.9}$$

where the limits are given by $y_{m\alpha}^+ = E_{m\alpha}[(N-1)W] - \mu$ and $y_{m\alpha}^- = E_{m\alpha}(-W) - \mu$. We can now take the second derivative with respect to h and take the limit $h \to 0$. There are two types of term, one coming from the differentiation of the integrand and the other from the field dependence of the limits. We obtain

$$\chi_S = 2\rho_0 \sum_{m\alpha} m^2 \left\{ \left[\int_{y_{m\alpha}^-}^{y_{m\alpha}^+} d\epsilon \, f(\epsilon) \frac{\tilde{V}^2}{(\epsilon_f - \mu - \epsilon)^3} \right] - \tilde{V}^2 \left[\frac{f(y_{m\alpha}^+)}{(\epsilon_f - \mu - y_{m\alpha}^+)^2} - \frac{f(y_{m\alpha}^-)}{\epsilon_f - \mu - y_{m\alpha}^-} \right] \right\}. \tag{2.10}$$

The contribution to the susceptibility from each band is given by the difference of two terms. We in fact find that the contributions from the upper band, $\alpha = +$, are small and it is the interplay of the two lower-band terms which determines the behaviour. In the integrals $f(\epsilon)$ can be expanded as a series in T^2 and for low T we expect to see a T^2 dependence. The second term comes from band-edge effects. It has an exponential behaviour and in general vanishes as $T \to 0$. We expect an appreciable contribution from excitations to the lower band edge for temperatures $\sim E_-[(N-1)W] - \mu$.

The results are shown in figure 2 where we have plotted $\chi_S(T)/\chi_S^0$ against T/T_K where χ_S^0 is the zero-temperature limit of χ_S for $N \neq 2$. We see that $N = 2$ is a special case. Here the lower band is completely full so the Fermi level is in the gap at $T = 0$ giving zero susceptibility. This comes from a complete cancellation of the two terms in (2.10). The susceptibility then rises to a maximum at $T \sim T_K$ which corresponds to excitations across the gap. Although for $N = 2$ the results cannot be considered to be accurate, we nonetheless expect that this is at least qualitatively correct. For $U = 0$, where U is the on-site Coulomb repulsion for the f electrons, the case of $n = 2$ has the Fermi level lying in the gap and we have an insulator. By Luttinger's theorem we must then also have an insulator even as $U \to \infty$. For the other cases the low-T dependence is $\sim T^2$. This can be found analytically and shown to scale as T_K^{-2}. At higher temperatures the contribution from the band edge starts to play an increasingly important role and brings the susceptibility down. We see the characteristic maximum in the susceptibility at temperatures $\sim 0.2T_K$. As N increases the position and height of the maximum increases. This is due to the position of the band edge increasing relative to the Fermi level meaning that the exponential terms are only becoming important at

higher temperatures. Plotting $1/\chi_S$ against T we see that the behaviour is linear above the maximum T_m and that the low-temperature part of the curve deviates above the high-temperature extrapolation. The curve extrapolates to a negative intercept on the T axis. The intercept is given by $\Theta \sim 0.5T_K$ in all the cases. The gradient of the line is not exactly k_B/μ_0^2, differing from $\sim 50\%$ for $N = 2$ to $\sim 8\%$ for $N = 8$. This systematic decrease in the discrepancy as N increases appears to be connected to the fact that we are using the zeroth-order solution in a $1/N$ expansion. We note that the three characteristic temperatures T_K, Θ and T_m are all of the same order of magnitude with $T_m < \Theta < T_K$. The results can be compared with the experimental scaling relations $T_K \simeq 2\Theta$ and $T_m \simeq \frac{2}{3}\Theta$ (Laurence *et al* 1981). Considering the approximations made the agreement is seen to be remarkably good especially for the first of these relations. We note that as N increases T_m also increases which will tend to improve the agreement for the second. These relationships are universal which would mean that solving the equations for arbitrary E_0, i.e. arbitrary $n_f(0)$, and plotting our results as $\chi_S(T)/\chi_S(0)$ against T/T_K ought to give us identical results. We have looked at $E_0 = -0.6$ and $E_0 = -0.4$. The first gives $n_f(0) \simeq 0.82$ which can be compared to $n_f(0) \simeq 0.97$ which was found for $E_0 = -0.8$. The zero-temperature susceptibilities differ by a factor of 8 which is appreciable. The curves differ only slightly and to a good approximation the same relationships between T_K, T_m and Θ hold. For $E_0 = -0.4$ we obtain $n_f(0) \simeq 0.5$ and $\chi_S(0)$ is about 60 times smaller than that for $E_0 = -0.8$. Here the difference in the curves is greater and the relationships are $T_m = 0.25T_K$ and $\Theta = 0.6T_K$. The theory does not give exact universality as we go into the mixed-valence regime but the differences in the renormalised values are not great especially for n_f close to one.

We can compare our results with those for several mixed-valence compounds (see e.g. Wohlleban 1983 for a review of experimental data for YbCuAl) and get good agreement. We can also compare our results with those for the heavy-fermion compound, UPt_3. The situation is complicated as there is a slight curvature in the plot of χ_S^{-1} against T which persists to very high temperatures. This is due to crystal field effects. If we extrapolate from the very-high-temperature region then the deviation from linear behaviour begins for T significantly greater than T_m and falls below the extrapolation. This is not consistent with what we find. However, if we extrapolate from smaller values of T, e.g. $T \sim 300$ K, the deviation only starts to be seen for T close to T_m and is above the extrapolated curve which is in agreement with our result.

We note that experimentally there is no evidence for any of the compounds having zero susceptibility which would seem to exclude the $N = 2$ result. It is interesting to note however that if we add or subtract a small number of electrons (i.e. $n_f + n_c = 2 + \eta$) then this is sufficient to push the Fermi level into one of the bands where there is a large density of states giving a large zero-T susceptibility. The susceptibility decreases rapidly (approximately exponentially) due to the band-edge effects which dominate because the Fermi level lies so close to the band edge. At higher T however the behaviour is virtually indistinguishable from that for $N = 2$. This gives us the distinctive susceptibility 'tail' followed by a minimum and then a maximum as T increases. In figure 2 the results for $N = 2$ and $n_c + n_f = 2.01$ are shown by the broken curve. We note that within our theory we need only add an arbitrarily small number of electrons to see this effect. To some extent this is an artefact of our theory where we have taken a square density of states for the conduction band which leads to sharp band edges. A more realistic density of states would smooth the bands at the edge and η would need to be finite for a significant $\chi_S(0)$ to be seen. Nonetheless, we would expect that for η reasonably small the same effect would be produced.

It is also possible to calculate the specific heat or equivalently the entropy S. S is most easily calculated from $S = (F - U)/T$ where F can be calculated as above and U is given by

$$U = N\rho_0 \sum_{\alpha} \int_{-W}^{(N-1)W} E_\alpha(\epsilon_k) f[E_\alpha(k) - \mu] \, d\epsilon_k - i\lambda n_f. \tag{2.11}$$

The results are shown in figure 3 where we have plotted $S/(k_B \ln N)$ against T/T_K for $N = 2$, 4 and 6. At low T there is a linear T dependence. S increases rapidly saturating at $T \sim T_K$. Although the entropy rapidly increases towards its high-T value, $S = k_B \ln N$, it appears to stop a little short. Presumably the extra entropy would be recovered if we went beyond mean-field theory. This suggestion is borne out by the observation that the accuracy with which the entropy is given increases with increasing N.

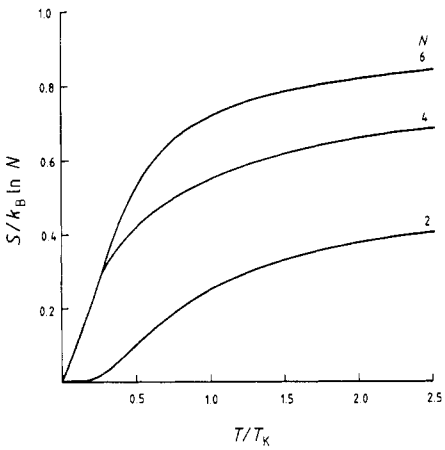

Figure 3. $S/(k_B \ln N)$ as a function of T/T_K for $N = 2$, 4 and 6.

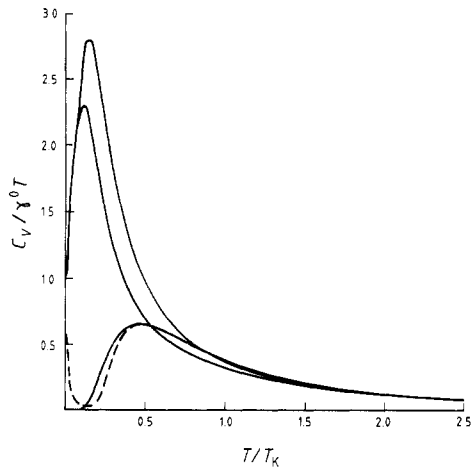

Figure 4. $C_V/(\gamma^0 T)$ as a function of T/T_K for $N = 2$, 4 and 6. The broken curve shows the result for $N = 2$ and $n_c + n_f = 2.01$.

C_V can be found from this and the results are shown in figure 4 where we have plotted $C_V/(\gamma^0 T)$ against T/T_K where γ^0 is the zero-temperature limit of C_V/T for $N \neq 2$. We note the increase in the Wilson ratio (i.e. the dimensionless ratio of $\chi_S(0)$ to γ) as T is increased from zero. There is a sharp maximum for T somewhat smaller than T_K which gets larger as N increases. From the form of the equations we can see that there will be no $T^3 \ln T$ term. This term only arises when we go beyond mean-field level (Rasul and Desgranges 1986). For some of the compounds we are losing an important piece of the low-temperature physics by considering only the mean-field solutions. The $N = 2$ case is again interesting. There is no evidence for a linear T dependence and the behaviour is dominated by exponential terms. Again the results are not accurate but we expect them to be qualitatively correct. They are in agreement with experimental results for SmB_6. We note that there is evidence that the Fermi level lies in or near the hybridisation gap for this compound thus explaining this unusual dependence. For $N = 2$ and $n_c + n_f = 2.01$ we find evidence of a small specific heat 'tail' similar to that for the susceptibility (broken curve in figure 4). The high-T dependence

is again just that for $n_c + n_f = 2$. Experimentally the specific heat data below 15 K is difficult to analyse and is extremely sample dependent. The relation $C_V = \gamma T + \beta T^3$ is not obeyed over any reasonable range of T. Nonetheless, a linear term in C_V/T against T^2 is found as $T \to 0$, where γ can be large. The values for γ vary widely from sample to sample. These results are consistent with our theoretical picture where the susceptibility tail is due to the Fermi level lying very close to the gap giving us very anomalous low-temperature behaviour. We note that within our theory the 'tail' arises due to a small perturbation from the case where $n_c + n_f = 2$, and we would expect a large sample dependence.

We consider now a different type of crossover. So far we have looked at the crossover from the Fermi-liquid region to the local-moment behaviour as a function of temperature. A similar type of crossover can be observed as a function of applied magnetic field. If we apply a large enough magnetic field we will force the f electrons to behave like local moments. This problem has also been considered for the one-impurity case where, as before, the occurrence of a phase transition prevented the high-magnetic-field weak-coupling regime being investigated.

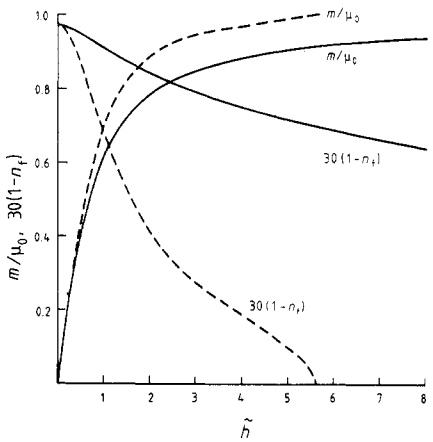

Figure 5. m/μ_0 and $30(1 - n_f)$ as a function of magnetic field h. The broken curve shows the results when μ is kept constant.

The equations we have are similar to those we had previously for the susceptibility except that we no longer take the limit $h \to 0$. The results of solving them numerically at zero temperature are shown in figure 5 where we plot m_f/μ_0 against $\tilde{h}$ where m_f is the moment induced on the f electrons, μ_0 is the value expected for the local moment and $\tilde{h} = h/k_B T_K = g\mu_B H/k_B T_K$. We compare two cases: the case where the field dependence of the Fermi level is properly taken into account and the case where μ is replaced by a constant value. The effect is analogous to that found before. For μ held constant n_f increases to $n_f = 1$ for $h \sim 6T_K$ at which point $m_f/\mu_0 = 1$ also. There is a phase transition at this point and the weak-coupling regime is not seen. This is analogous to the behaviour of the single impurity where we note that a magnetic field on the f electrons does not have a significant effect on the Fermi level. For the proper calculation the field dependence of the Fermi level must be taken into account and this has the effect of slowing down the increase in both n_f and m_f. As a result of this the high-field weak-coupling regime can be accessed by the mean-field solution.

3. Including direct f–f hopping

We consider now what happens when we include a direct f–f hopping term into our Hamiltonian. It has been shown that such a term can have a large effect on the zero-temperature linear coefficient of specific heat, γ (Harrington *et al* 1988).

The term we add is $\sum_{i,j,m} t_{ij} f_{im}^{\dagger} f_{jm}$. We specialise to the case of nearest-neighbour hopping only and assume the same dispersion relation for t_k as for ϵ_k. With these conditions the additional term in the mean-field Hamiltonian becomes

$$\sum_{km} \frac{\tilde{t}}{W} \epsilon_k f_{km}^{\dagger} f_{km} \tag{3.1}$$

where $\tilde{t} = (1 - n_f)t$. The main effect of this term is simply to renormalise $\epsilon_f \to \epsilon_f + \beta\epsilon_k$ in the expressions for $E_{\pm}(k)$ and $A_{\pm}(k)$ where $\beta = \tilde{t}/W$. The following additional term also comes into the RHS of the expression for ϵ_f:

$$+Nt \int_{-W}^{(N-1)W} \frac{\epsilon_k}{W} \{A_+(k) f[E_-(k) - \mu] + A_-(k) f[E_+(k) - \mu]\} \, \mathrm{d}\epsilon_k. \tag{3.2}$$

If the linear coefficient of specific heat is now calculated as a function of t there is a point at which there is a crossover from a density of states with a gap in it (which is what we expect from an ordinary Anderson model) to a continuous density of states (more reminiscent of a Hubbard model). At this point there is a discontinuity in γ. In the Anderson-like region the mass enhancement is given approximately by $\tilde{V}^2/\epsilon_f^2$ with small corrections of order β while in the Hubbard-like regime the mass enhancement is approximately β^{-1} with small corrections depending on $\tilde{V}$. We note that to some extent the phase transition is an artefact of the theory. It is the sharp band edges, which as mentioned previously comes from using a constant conduction electron density of states, that are the origin of the discontinuity. A conduction electron density of states which was smoothed off at the edges would lead to renormalised quasiparticle bands which were also smoothed off slightly at the edges. This would mean that there was no discontinuity in γ. Nonetheless the density of states would increase very rapidly as we moved away from the band edges and C_V would vary very rapidly with t in the vicinity of $t \sim t_c$. Qualitatively the effects would be the same.

It is interesting to ask what happens to this picture as the temperature is increased. Clearly the distinction between the two cases will be blurred out as at finite temperature both bands have a finite occupation, whichever regime we are in. We might, however, expect to get some interesting temperature-dependent behaviour for $t \sim t_c$. Solving for n_f and ϵ_f we find a smooth variation of n_f with t even for $T = 0$. ϵ_f, however, varies sharply at $t = t_c = 0.101$. As T increases this is smoothed out. In figure 6 we show the T/T_K dependence of n_+ where n_+ is the number of f electrons in the upper band and T_K is defined for $t = 0$. The diagrams for n_+ show clearly the effects of the transition. For $t = 0$, n_+ is zero at $T = 0$ and increases slowly with T; for $t = 0.095$, which is just below the critical value for t, n_+ is again zero for $T = 0$ but increases much more rapidly with increasing T. For $t = 0.105$, which is just above t_c, n_+ has a small finite value even at $T = 0$ but the higher-T behaviour is very similar to that for $t = 0.095$. Finally when t is appreciably bigger than t_c there are a reasonable number of f electrons in the upper band even for $T = 0$.

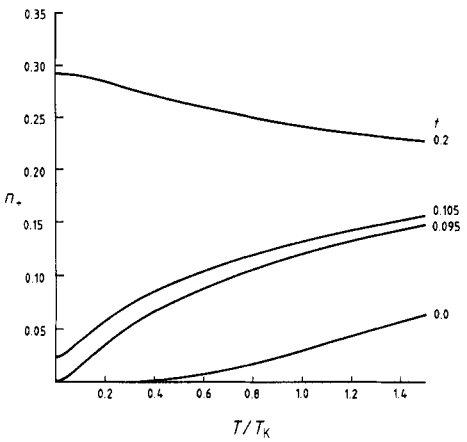

Figure 6. The number of electrons in the upper band, n_+, as a function of T/T_K for a variety of values of t.

With these extra features the expression for the free energy becomes

$$F = \rho_0 \sum_{m\alpha} \int_{y^-_{m\alpha}}^{y^+_{m\alpha}} d\epsilon \, f(\epsilon)(W + \mu + \epsilon_\pm) \tag{3.3}$$

where

$$\epsilon_\pm = -\frac{1}{2\beta}\left\{\epsilon_f - \epsilon(1+\beta) \pm \left[(\epsilon_f - \epsilon(1-\beta)^2 + 4\beta\tilde{V}^2\right]^{1/2}\right\}. \tag{3.4}$$

As before this can be differentiated twice with respect to h and χ_S found.

At zero temperature the integrals can be performed analytically and comparison with γ shows that the Wilson ratio is equal to one for all t as expected. The discontinuity arises due to the term in $f(E_+(-W) - \mu)$ which jumps discontinuously from 0 to 1 as the Fermi level crosses the upper band. Previously it was only the contribution from the lower band which determined the behaviour but here we expect the upper band to play a crucial role too.

In figure 7 we show χ_S/χ_S^0 as a function of t for several values of temperature, where χ_S^0 is the zero-temperature value for $t = 0$. We see how the discontinuity is smoothed out as T increases until at high temperatures χ_S looses all dependence on t. We note that as $n_f \to 1$, $\beta \to 0$ and the model reduces to the ordinary Anderson model.

The behaviour of χ_S as a function of T is interesting. For $t \ll t_c$ we have a T^2 rise in the susceptibility up to a maximum. As t approaches t_c the rise in χ_S becomes more rapid as here positive exponential terms from the upper band edge begin to play a part. For t just bigger than t_c, χ_S has a rapid decrease with decreasing temperature and there is no maximum. Finally for $t \gg t_c$ there is a small T^2 dependence but the maximum is much less pronounced. In figure 8 we show the T dependence of χ_S^{-1} for different values of t, $t = 0$, $t = 0.095$, $t = 0.105$ and $t = 0.2$ as before. The features mentioned above are clearly seen. We find also that the deviation from the high-temperature extrapolation occurs at higher temperatures when t is included. For $t = 0$ the deviation only occurs for T close to T_m while for the higher values of t it occurs for $T > T_K$. We note in particular that the behaviour for $t = 0.105$ is reminiscent of those heavy-fermion

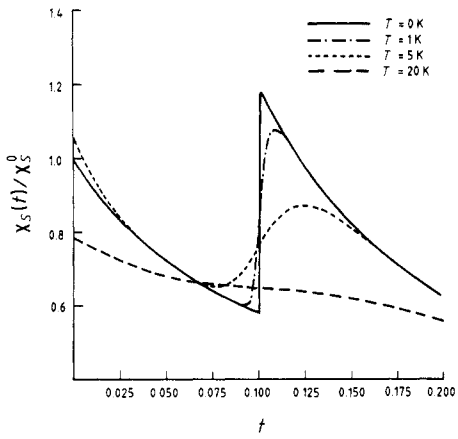

Figure 7. χ_S/χ_S^0 as a function of t for a variety of temperatures.

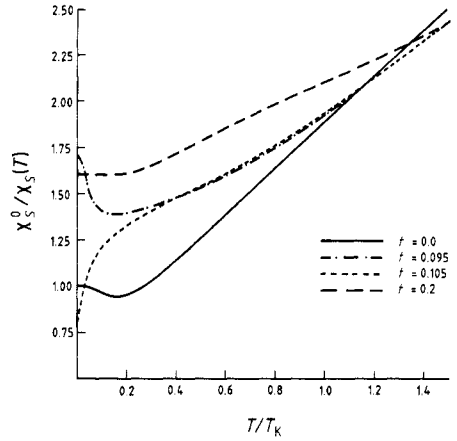

Figure 8. $(\chi_S/\chi_S^0)^{-1}$ as a function of T/T_K for a variety of values of t.

compounds which do not show a maximum in their susceptibilities e.g. UBe_{13}. The inverse susceptibility deviates above the high-T extrapolation as expected for this case.

The entropy and specific heat can also be calculated. The entropy rises to the same high-T limit as previously but does so more slowly. The specific heat has a maximum at a similar value of T but the maximum is less pronounced and much broader. These features can be understood in the following way. With direct f–f hopping we expect the 'Fermi-liquid' nature of the f electrons to be more pronounced and this is manifested by a slower crossover to the local-moment behaviour. The entropy rises more slowly and the high-temperature Curie–Weiss-like behaviour only occurs for higher temperatures. It is difficult to compare the specific heat results with experimental data as the usual experimental plot is C_V/T against T^2. If we plot this we find that the maximum gets lost (as it does in the experimental plots) and the differences between the different values of t become much less pronounced.

4. Comparison with the single impurity

We have shown that the temperature-dependent properties of the mean-field solution for the lattice are different to those for the single impurity. Our results have shown that is important to determine the Fermi level correctly and include its temperature dependence. These effects are not present in the one-impurity problem and it is this which appears to be the important distinction between the two cases. We discuss here why the Fermi level plays such an important role.

We consider first the variation of the valence n_f with temperature for the one-impurity problem. n_f has to be chosen to minimise the free energy F. From the definition, $F = U - TS$, we see that the minimum is determined by the interplay of the entropy which we want to make as large as possible and the internal energy which we want to be small. For small T the entropy is given by $S = \gamma T$ which increases rapidly as n_f approaches one. This leads us to expect that n_f will increase with temperature. We now need to consider the role of the energy. As n_f varies the number of conduction electrons changes which tends to change the Fermi level μ. For

a collection of non-interacting impurities the change in the Fermi level gives rise to a term in the energy

$$\Delta U \sim \delta W[n_f(T) - n_f(0)] \tag{4.1}$$

where δ is the impurity concentration (Newns *et al* 1983). This acts in opposition to the entropy effects and it is advantageous for n_f to remain close to its zero-temperature value. We note that the condition that a number of impurities can be considered as independent is $\delta \ll \epsilon_f/W$ (Nozières 1985) so the above effect is likely to be small. Furthermore (4.1) is likely to be an overestimate. The picture we have is of a single impurity being screened by an electron cloud which contains precisely n_f electrons. This screening is local so any change in n_f produces a change in the concentration of conduction electrons only in the vicinity of the impurity. This has the effect of pinning the Fermi level to the impurity level and μ remains constant. The temperature dependence of n_f is controlled by entropy considerations and n_f increases rapidly to one.

For the lattice the situation is rather different. The position of the Fermi level is likely to be of greater importance and it will clearly vary by a greater amount when there is a contribution from each site. We expect the extra term in the energy to be larger and the screening effect to be much smaller since the number of electrons in the screening cloud is much less than one (Millis and Lee 1987).

For the lattice we obtain at zero temperature

$$\mu = W[1 - n_f(T)]. \tag{4.2}$$

This can be shown analytically for $T = 0$ (provided W is large) but is in fact a very good approximation for finite temperature as well. The effect of this change in μ on the internal energy is not however $W[n_f(T) - n_f(0)]$ as might have been expected. This is due to the fact that the change in the total energy from the conduction electrons exactly cancels the change from the shift in the f-level position. Nonetheless, the temperature dependence of μ is significant. The effect of a decrease in μ is to increase ϵ_f and so reduce n_f. This 'negative feedback' tends to keep n_f at its initial value. This can be compared to the case where we keep μ constant where there is no such increase in ϵ_f and we expect n_f to increase at a similar rate to the single-impurity problem.

The energy effects cannot be ignored for the lattice and the tendency is for n_f to change much more slowly with temperature meaning that we only get to $n_f = 1$ for much higher temperatures. The mean-field solutions continue to work into the high-temperature regime.

The model can be extended to describe the uranium compounds where the valence fluctuations are between f^2 and f^3 (Rasul and Harrington 1987). Both the valence states are magnetic and the behaviour is symmetric in both integral valence limits. The low-T entropy diverges as $n_f \to 2$ or 3 and has a minimum at $n_f = 2.4$. For $n_f(0) > 2.4$ we expect n_f to increase with T while for $n_f < 2.4$ we expect it to decrease. However, if $n_f(0)$ is in the middle of the valence regime then we are close to a fairly shallow minimum in S and the entropy effects are small. This is the relevant situation for the uranium heavy-fermion compounds which have $n_f \sim 2.5$. We, therefore, might expect that the T dependence of n_f is very small in both the lattice and one-impurity cases. Our results are easily extended to show that this is indeed the case. At the mean-field level the equations for uranium can be solved at finite temperatures and the results show a very slow variation of n_f with temperature both for the one-impurity problem and for the lattice with and without μ being kept constant.

5. Conclusions

We have considered the temperature dependence for the valence, susceptibility and specific heat for a mixed-valence lattice using the slave-boson technique. We show that the mean-field solutions which describe correctly the low-temperature Fermi-liquid behaviour are also sufficient to give us the high-temperature local-moment behaviour and to extrapolate smoothly between the two regimes. The high-magnetic-field behaviour is also obtained. This is in marked contrast to the one-impurity problem where the high-temperature and magnetic-field behaviour is not given by the mean-field solution. We show that the important factor in giving this different behaviour is the change of the Fermi level with temperature or field which is appreciable for the lattice but very small in the one-impurity case. We consider also the case of the uranium systems. There are important differences and for $n_f(0) \sim 2.5$ the high-temperature behaviour can be obtained even for the one-impurity problem.

The crossover between strong- and weak-coupling behaviour is central to the heavy-fermion problem and it is interesting to see this arising naturally out of a relatively simple approach. We note that the slave-boson mean-field solution gives us a Hamiltonian which is bilinear in fermion operators with renormalised parameters and it therefore automatically gives us quasiparticle bands and Fermi-liquid-like behaviour at low temperatures. It is not clear, however, that this will lead to the correct local-moment behaviour at high temperatures. It is interesting to note that we are getting the correct weak-coupling behaviour even though we are below the phase transition and might have thought we were still in the strong-coupling regime.

Despite the simplicity of the approach the results are in good qualitative agreement with experiment. At high temperatures we observe a Curie–Weiss susceptibility $\chi_S \sim (T - \Theta)^{-1}$ where Θ is negative and is in good agreement with the observed scaling relation $\Theta = 2T_K$. The effective moments are somewhat smaller than the local moments of the free ions but tend towards the value expected as N increases. Similarly the values for the position of the low-T maximum in χ_S agree better with experiment as N gets large. This is as expected since we are using the zeroth-order solution in a $1/N$ expansion.

We show that interesting behaviour occurs when the number of electrons is close to the number of states in a band. This appears to explain the susceptibility 'tail' seen in several compounds and the specific heat data for SmB_6.

The behaviour of the specific heat agrees qualitatively with what is seen for those compounds where the $T^3 \ln T$ term is not dominant. The entropy under the low-T anomaly is $\sim k_B \ln N$, the agreement again improving as N increases. It is interesting that in an approximation which we know misses an important part of the low-T physics (i.e. the $T^3 \ln T$ term) we nonetheless get behaviour which is qualitatively correct.

Including direct f–f hopping extends our parameter space and produces a much richer model with a variety of low-T behaviour. We show that this may be significant, given the different behaviour which is in fact observed. The Fermi-liquid-like behaviour is more apparent at low temperatures and the crossover to the high-temperature regime is somewhat slower. Nonetheless, at sufficiently high temperatures local-moment behaviour is again observed.

Acknowledgments

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