Normal-state properties of heavy-electron systems

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A generalization to finite temperatures of the Brinkman-Rice theory of almost-localized-electron systems is presented. It describes a smooth transition from a Fermi-liquid regime at low temperatures to a set of random spins at higher temperatures. The present theory gives a good description of the low-temperature entropy and the specific heat in the normal state of the heavy-electron superconductor UBe_{13}.

The anomalous behavior of the specific heat in the superconducting phase of heavy electrons in the intermetallic compound UBe_{13} has been interpreted by Ott and coworkers[1] as evidence that it is the first example of a p-wave electronic superconductor. The analogy to ^{3}He was stressed and the description of the electrons as almost localized fermions was proposed in Ref. 1 and independently by Anderson.[2] Both authors propose that the Brinkman-Rice[3] theory of almost-localized Fermi liquids should be applicable to the heavy-electron metals. The theory has been successfully applied to ^{3}He by Anderson and Brinkman,[4] and more recently by Vollhardt.[5] It has also been used by Varma[6] in the context of the intermediate-valence problem of f-electron materials. In this paper we present a generalization of the Brinkman-Rice theory to finite temperatures and show that it gives a good description of the thermodynamics of the normal state of the heavy electrons in UBe_{13}. Our model has certain similarities to the periodic Anderson model (see below). We would, however, point out that others[7,8] have concluded that superconductivity in that model would be s wave and driven by electron-phonon interaction and not p wave, driven by spin-fluctuation interactions as suggested in Refs. 1 and 2.

The starting point of the Brinkman-Rice theory is the Hubbard Hamiltonian with a repulsive onsite interaction U. As a ground state of this Hamiltonian, Gutzwiller[9] proposed a variational wave function in which the number of doubly occupied sites is reduced by a projection operator operating on an uncorrelated ground state Φ_0,

$$\Psi_G(\{n(\vec{k},\sigma)\},g)=\left[\prod_i[1-(1-g)n_{i\uparrow}n_{i\downarrow}]\right]\times\Phi_0(\{n(\vec{k},\sigma)\}) \quad , \tag{1}$$

with $n_{i\sigma}$ as the number operator for site i, and in Φ_0 the occupation values $n(\vec{k},\sigma)=1$ for $|\vec{k}|<k_F$ and 0 otherwise. Gutzwiller[9] obtained a relation between the variational parameter g and the concentration of doubly occupied sites d, and an approximate expression for the ground-state energy per site, as

$$E_G=\sum_{k,\sigma}q_\sigma(d,n_\sigma)\epsilon_{\vec{k}}n(\vec{k},\sigma)+Ud \quad . \tag{2}$$

The sum over $\vec{k}$ states is normalized to 1. The function q is given in terms of d and n_σ (the concentration of occupied sites with spin σ) as

$$q_\sigma(d,n_\sigma)=\{[(1-n_\sigma-n_{-\sigma}+d)(n_\sigma-d)]^{1/2}+[d(n_{-\sigma}-d)]^{1/2}\}^2/n_\sigma(1-n_\sigma) \quad . \tag{3}$$

As U increases, so do spatial correlations among the electrons as they try to avoid doubly occupying sites. Thus d decreases from its value of $\frac{1}{4}$ in the uncorrelated state towards zero. If the band is exactly half filled (i.e., $n_\sigma+n_{-\sigma}=1$), then $d\equiv 0$ for

$$U>U_c\left(=8|\bar{\epsilon}|;\ \bar{\epsilon}=\sum_{|\vec{k}|<k_F,\sigma}\epsilon_{\vec{k}}\right) ,$$

all sites are occupied by one electron only, and all electrons are localized. As a result, the system is a Mott insulator.[3] If $U<U_c$, but $U_c-U\ll U_c$, then $d\ll 1$ and $q\approx 8d\ll 1$. In such a state there are very strong spatial correlations among the electrons such that the electrons are almost localized. This almost localized limit has been used by Anderson and Brinkman[4] and by Vollhardt[5] to describe the normal-state Fermi liquid ^{3}He.

In the heavy-electron systems, due to the presence of broad conduction bands (e.g., Be-derived bands in UBe_{13}), the number of f electrons on the U ions may not be exactly integer and we shall assume instead that $n_\sigma+n_{-\sigma}=1-\delta$ with $\delta\ll 1$ (the sign of δ is immaterial due to the particle-hole symmetry of the model).[10] In this case, the system never becomes completely localized but for large U (say, $U>U_c$), $d\to 0$, and $q\approx 2\delta$ [see Eq. (3)]. The enhancement of the effective mass m^* over the band mass m ($m^*/m=q^{-1}$) becomes very large, but it is insensitive to U and varies with δ^{-1}.

It is straightforward to evaluate the Landau Fermi-liquid parameters from the expression (2) for the ground-state energy. In this paper we wish to discuss the extension to finite temperatures. From the Gutzwiller form (1) we can define excited-state wave functions by varying the occupation values $\{n(\vec{k},\sigma)\}$ and then calculate the corresponding internal energies from (2). To obtain the free energy, we need an expression for the entropy. We must recognize that the set of excited states determined by varying $\{n(\vec{k},\sigma)\}$ are not mutually orthogonal because of the projection factor. On the other hand, if we hold d fixed, we know the number of excited states that are possible by expanding the excited

states in the site representation. In this way we can easily calculate the number of independent excited states as a function of d and this number varies continuously from four per site in the uncorrelated state ($d=\frac{1}{4}$) to two per site in the almost localized limit ($d\to 0$). However, we know from Landau Fermi-liquid theory that the low-energy excitations are quasiparticles whose entropy is determined by the free fermion entropy formula. Therefore, we make the ansatz that the entropy is determined by introducing a renormalization or weighting factor in $\vec{k}$ space to account for the nonorthogonality and write the electronic entropy as

$$S_e=-k_B\sum_{k,\sigma} w(\vec{k},d,\sigma)\{n(\vec{k},\sigma)\ln n(\vec{k},\sigma) +[1-n(\vec{k},\sigma)]\ln[1-n(\vec{k},\sigma)]\} \quad . \tag{4}$$

To reproduce Landau Fermi-liquid theory, we require that $w\to 1$ as $k\to k_F$. Minimizing the free energy ($E-TS_e$) with respect to $\{n(\vec{k},\sigma)\}$ leads to

$$n(\vec{k},\sigma)=\{\exp[q(\epsilon_{\vec{k},\sigma}-\mu)/w(\vec{k})T]+1\}^{-1} \quad , \tag{5}$$

with μ as chemical potential. In the almost localized limit, $q\ll 1$ and $n(\vec{k},\sigma)\to\frac{1}{2}(1-\delta)$ as T increases beyond qE_F—the renormalized Fermi energy. Then the entropy is

$$k_B\bar{w}[\ln 4-(1-\delta)\ln(1-\delta)-(1+\delta)\ln(1+\delta)]$$

per site ($\bar{w}=\sum_{\vec{k}} w(\vec{k})$). The sum rule on the number of degrees of freedom requires

$$\bar{w}=-\frac{\{(1-\delta-2d)\ln[\frac{1}{2}(1-\delta)-d]+d\ln d+(d+\delta)\ln(d+\delta)\}}{\ln 4-(1-\delta)\ln(1-\delta)-(1+\delta)\ln(1+\delta)} \quad . \tag{6}$$

In the limit d and $\delta\to 0$, $\bar{w}\to\frac{1}{2}$.[11]

In almost localized systems with $q\ll 1$, the temperature dependence of the entropy has two temperature scales. The lower is qE_F, on which scale a total entropy $R\bar{w}\ln 4$ is obtained. The second scale is set by U and for $T\gg qE_F$ one finds

$$d(T)\cong\tfrac{1}{2}[1+\exp(U/2T)]^{-1}+O(\delta) \quad . \tag{7}$$

Thus as $T/U\to\infty$, for $\delta\equiv 0$, $d\to\frac{1}{4}$, $\bar{w}\to 1$, and $S_e(T)$ saturates at the value $R\ln 4$, as it must. In the temperature range with $T\gtrsim qE_F$, the spatial coherence of the quasiparticles and the characteristics of a degenerate Fermi liquid are lost.

One can also calculate the spin susceptibility $\chi_s(T)$ by including a coupling term

$$\mu_0 H\left(\sum_{\vec{k}} n(\vec{k},\uparrow)-n(\vec{k},\downarrow)\right)$$

to the external magnetic field H. The calculation is straightforward and gives in the limit ($d\to 0$, δ finite but small)

$$\mu_0^2\chi_s^{-1}(T)=4\delta\sum_{\vec{k},\sigma}\epsilon_{\vec{k}}n(\vec{k},\sigma)+T\left(\sum_{\vec{k},\sigma}[w(\vec{k})]^{-1}n(\vec{k},\sigma)[1-n(\vec{k},\sigma)]\right)^{-1} \quad . \tag{8}$$

In the low-temperature limit $T\to 0$, this reduces to

$$\chi_s=\mu_0^2\frac{N(\mu)}{2\delta}\frac{1}{1+2\bar{\epsilon}N(\mu)} \quad , \tag{9}$$

with $N(\mu)$ the density of states at μ. As stressed by Anderson and Brinkman[4] and Vollhardt,[5] the Stoner enhancement factor is not critical as d and $\delta\to 0$, rather it is the effective mass term which is strongly dependent on d and δ and causes the large susceptibility.

At higher temperatures $T>qE_F$ but still $T\ll U$ we obtain a Curie form

$$\chi_s=\mu_0^2\left(\sum_{\vec{k}}[w(\vec{k})]^{-1}\right)/2T \quad . \tag{10}$$

In this limit, the number of magnetic moments should be simply the number of singly occupied sites. This can be achieved if we set (remembering that $d=0$)

$$\bar{w}_{-1}=\sum_{\vec{k}}[w(\vec{k})]^{-1}=2(1-\delta) \quad . \tag{11}$$

The renormalized Fermi temperature (qE_F) is the crossover temperature between Pauli and Curie behavior. We thus have three conditions that our phenomenological function $w(\vec{k})$ should fulfill, determined from Landau Fermi-liquid theory and sum rules on the entropy and the number of magnetic moments.

Turning to UBe_{13}, we propose to describe the low-temperature thermodynamic properties of the normal state by a $5f$ band whose width is determined by hybridization through the broad conduction bands. Note, however, because of its much larger mass, the $5f$ band rather than the broad conduction band determines the low-temperature thermodynamics. Wuilloud *et al.*[12] concluded from photoemission studies that U ions in UBe_{13} are close to a $5f^3$ configuration. The most reasonable assumption for the ground-state degeneracy of a $5f^3$ configuration in a crystal field is a Kramers doublet which in turn requires that the total entropy of the local moment sites (the analogs of singly occupied sites in the model) is $R\ln 2$. Therefore, it is a prediction of our theory that the electronic entropy at low temperature should saturate at $\bar{w}R\ln 4$ with $\bar{w}\approx\frac{1}{2}$. The above mentioned x-ray photoelectron spectroscopy/bremsstrahlung isochromat spectroscopy study gives no clue with respect to a separation of the occupied and empty $5f$ states due to an intra-atomic Coulomb repulsion U. A U value of 1 eV, consistent with our model, could not be resolved by this experiment but might partially be responsible for the rather large width of 3 eV of the observed structure around E_F.

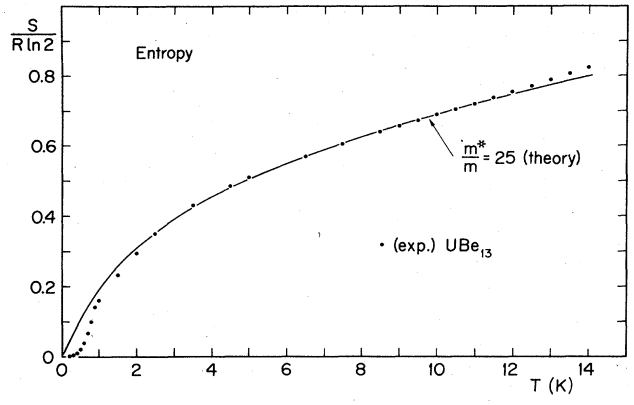

FIG. 1. Temperature dependence of the electronic molar entropy of UBe_{13} below 14 K. T_c for superconductivity is 0.9 K. The solid line is the theoretical curve with a mass enhancement of 25.

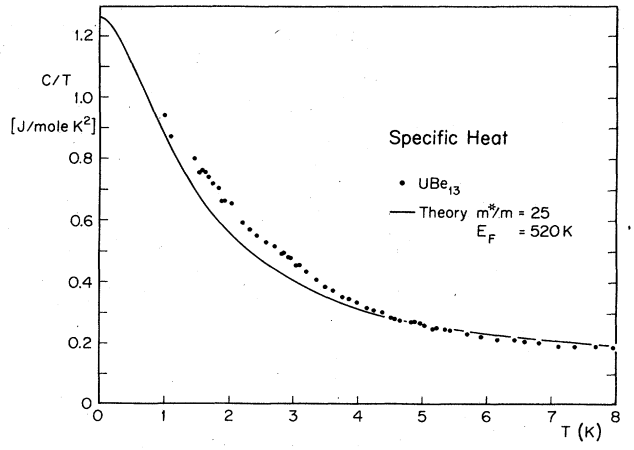

FIG. 2. Temperature dependence of the electronic specific heat of UBe_{13} in the normal state below 8 K. The solid line is the theoretical result.

In Fig. 1, we show a fit to the experimental values of the molar electronic entropy $S_e(T)$ of UBe_{13}. We see that it tends to saturate at $\approx R \ln 2$. The solid line is a fit using as a model band structure a rectangular density of states of width 1070 K (or a bare Fermi energy of ≈ 520 K), and with the choice $\delta = 0.02$ and $d = 0$ (equivalently the mass enhancement $q^{-1} = 25$). A suitable form for the function $w(\epsilon)$ which satisfies the above conditions was found to be $w = 0.6 \exp[-(\epsilon/v)^2] + 0.4$, with $v = 160$ K. The choice of E_F and δ determine the overall temperature scale at the slope of $S_e(T)$ as $T \to 0$, but the vertical scale is fixed absolutely.

Alternatively we can consider the specific heat $C(T)$ in the normal phase, and this is shown in Fig. 2. The overall agreement is also satisfactory especially considering the simplicity of the model. We have not attempted a detailed fit to the susceptibility $\chi_s(T)$ since the comparison of our simplified model to UBe_{13} is complicated by the need to know the g factor and to divide the measured χ into Pauli and van Vleck terms.

In conclusion, we have presented a generalization of the Brinkman-Rice theory to finite temperatures and have shown that it can be used to describe the electronic entropy and specific heat of a heavy-electron system quite accurately. The essential idea is that the large specific heat of the almost-localized Fermi liquid arises from the magnetic entropy of the singly occupied (or local moment) sites which comes out in the Fermi liquid on a temperature scale which is much below the bare Fermi energy. The renormalized Fermi energy is the temperature scale on which the system makes the transition from a coherent quantum Fermi liquid to a set of random spins—a transition which shows up in the spin susceptibility as a change from enhanced Pauli paramagnetism to Curie behavior.

Note added in proof. Related discussions on the heavy-electron systems as almost localized metals with large spin fluctuations have been given by O. T. Valls and Z. Tešanović [Phys. Rev. Lett. **53**, 1497 (1984)] and M. T. Beal-Monod [Phys. Rev. B (to be published)].

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[10]Several authors [see R. M. Martin, Phys. Rev. Lett. **48**, 362 (1982), and references therein] have concluded that in the dense Kondo regime of the periodic Anderson model the average valence is almost, but not exactly integer. This corresponds in our model to a small, but finite δ.

[11]Note that also in the limit $(d, \delta \to 0)$, the entropy sum rule is satisfied for any value of the magnetization $(n_\sigma - n_{-\sigma})$ by choosing $\bar{w} = \frac{1}{2}$. Therefore, in our ansatz we take $w(\vec{k}, d, \delta)$ independent of $(n_\sigma - n_{-\sigma})$.

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