RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 21 1 DECEMBER 1993-I

Thermoelectric power of concentrated Kondo systems

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(Received 28 May 1993; revised manuscript received 28 July 1993)

The thermopower of concentrated Kondo systems based on Ce-Cu, Ce-B, and Yb-Cu intermetallic compounds doped with nonmagnetic impurities like Al, Ag, Au, and Ga, is discussed using the single-impurity Anderson model with more than one scattering channel. Interference between the resonant and nonresonant scattering is important for relating the theory to the experimental data. Correlation effects are present in the resonant channel and are accounted for by a numerical renormalization-group method. The large enhancement of the thermopower over the free-electron values reflects the renormalization of the characteristic energy scale of the elementary excitations from the Fermi energy, ϵ_F, to the Kondo energy, T_K. The characteristic shape of the experimental curves reflects the change in the structure of the low-energy excitations as the temperature passes through the Kondo temperature. The observed sensitivity of the sign of the thermopower to small changes of the local environment around the magnetic ions is attributed to the interference between resonant and nonresonant scattering.

Thermopower measurements provide a sensitive probe of low-energy excitations in metallic systems. The data can be related to the single-particle spectral function and provide evidence for a broad band of quasiparticle excitations.

In heavy fermions the thermopower, $S(T)$, is much larger than in normal metals and as a function of temperature has a more complicated structure.[1–3] As with the specific heat and the magnetic susceptibility, the magnitude and the shape of $S(T)$ in heavy fermions relate to local correlations taking place in $4f$ or $5f$ states. However, the theory of transport coefficients for periodic systems with locally correlated electrons is only recently beginning to emerge[4] and an unambiguous relationship between the data and the underlying elementary excitations has not yet been established.

The complexity of the thermopower data is substantially reduced if we restrict considerations to systems that can be classified as concentrated Kondo systems. That is, we consider only the thermopower of heavy fermions based on Ce-Cu,[1] Ce-B,[2] and Yb-Cu (Ref. 3) intermetallic compounds doped with nonmagnetic impurities such as Al, Ag, Au, and Ga. Typical examples are provided by $Ce(Cu_xM_{1-x})_2$, $Ce(Cu_xN_{1-x})_5$, $Ce(Cu_xAu_{1-x})_6$, or $YbCu_4X$, where M stands for Ag or Ga, N for Al or Ga, and X for Ag and Au. In all these systems the ratio between the residual ($T = 0$) and the room-temperature resistance is of the order of 1, indicating the absence of coherence. The simplifications arise because doping destroys the effects that might be due to the crossover between the high-temperature, incoherent regime and the low-temperature, coherent regime.

An obvious characteristic feature of concentrated Kondo systems is the large slope of $S(T)$ around $T = 0$. Also, the sign of the thermopower seems to be very sensitive to the local environment of magnetic ions. A particularly striking example is provided by $Ce(Cu_xAl_{1-x})_5$ samples[1] in which the slope of the thermopower changes sign as x increases from $x = 0.84$ to $x = 0.88$. However, the temperature dependence of the thermopower of different systems appears quite similar if we plot not just the bare data but rather the ratio of the thermopower and its initial slope. Plotted in such a way the thermopower exhibits a characteristic behavior: it increases up to a maximum at temperature T_M and then decreases down to a minimum at T_m. Above T_m, the thermopower increases further but with a smaller slope than around $T = 0$. In some systems, such as $CeCu_{4.8}Au_{1.2}$,[1] the thermopower changes sign between T_M and T_m. In others, as in $CeCu_{1.4}Ag_{0.6}$ the low-temperature maximum is not well pronounced[1] and only the high-temperature minimum is well resolved. But it seems that the thermopower of most concentrated Kondo systems has a tildelike ($\sim$) shape.

There have been various attempts to explain this temperature dependence. The thermopower of some heavy fermions in the incoherent regime is discussed in terms of the crystal field model: the peak observed at low temperatures is associated with usual Kondo scattering of conduction electrons on the lowest Kramers doublet, while the high-temperature features follow from the scattering on the full crystal field multiplet.[5] The model, however, has difficulties in explaining the variation of the thermopower induced by replacing the nonmagnetic ligands of $4f$ or $5f$ ions with nonmagnetic impurities. Even small changes that could not alter the overall chemical environment and the crystal field of magnetic ions can lead to drastic modifications of the magnitude and the shape of the thermopower.[1]

In a different model, the change of sign of the ther-

mopower observed in many heavy fermions is taken as an indication of the crossover from the paramagnetic Kondo regime to the regime in which the local spins couple by the Ruderman-Kittel-Kasuya-Yosida interaction.[6] The difficulty here, however, is that the change of sign of the thermopower in heavy fermions is often found much above the magnetic ordering temperature.[1] Also, it is observed in some diluted $Ce_xLa_{1-x}Al_3$ heavy fermion systems that do not order magnetically at all.[7]

We believe the similarity of the thermopower data of different concentrated Kondo systems points to a single mechanism being responsible for the observed structure and propose that the seemingly complicated thermopower reflects, as in simple metals, the structure of the elementary excitations. We attribute the diversity to the interplay of two factors: the reduction in characteristic energy scale of the elementary excitations from Fermi energy, ϵ_F, to Kondo energy, T_K, causing the large enhancements over the free electron values, and the scattering of the electrons in the nonresonant channels affecting the sign.

In this paper we consider Ce and Yb based concentrated Kondo systems for which the lowest $4f$ crystal field level is a Kramers doublet well separated from the rest of the multiplet. The low-energy excitations in such systems are well described by the spin-1/2 Anderson model. The sensitivity of the sign of the thermopower on doping by nonmagnetic impurities indicates that the interference between the resonant and the nonresonant scattering should not be neglected. Here, we consider the Anderson model with two scattering channels and evaluate the transport relaxation so as to allow for the interference between the resonant ($l = 0$) and nonresonant ($l = 1$) scattering.[8]

To relate the thermopower to the excitation spectrum we solve the Boltzmann equation in the relaxation time approximation and use the well known expression,

$$S(T) = -\frac{1}{eT}\frac{\int \omega\tau_{\rm tr}(\omega,T)\left(-\frac{\partial f}{\partial\omega}\right)d\omega}{\int \tau_{\rm tr}(\omega,T)\left(-\frac{\partial f}{\partial\omega}\right)d\omega}. \quad (1)$$

In the multichannel scattering problem the transport relaxation time, $\tau_{\rm tr}(\omega,T)$, is obtained by using the generalized phase-shift formula,

$$\frac{1}{\tau_{\rm tr}(\omega,T)} = \frac{1}{\tau^0_{\rm tr}(\omega,T)}\left[\cos 2\eta_1 - \frac{\mathrm{Re}\ G_0(\omega,T)}{\mathrm{Im}\ G_0(\omega,T)}\sin 2\eta_1\right] + \rho_n, \quad (2)$$

which can be derived from the general expressions given in Ref. 9. In (2), $\tau^0_{\rm tr}(\omega,T)$ describes the relaxation time due to the resonant scattering in the absence of the interference effects. For the resonance of width Δ, we have

$$\frac{1}{\tau^0_{\rm tr}(\omega,T)} = -\Delta\ \mathrm{Im}\ G_0(\omega,T), \quad (3)$$

where $G_0(\omega,T)$ is the retarded Green's function, which describes the many-body effects. The square bracket in (2) accounts for the interference between the resonant and the nonresonant scattering. The $l \neq 0$ phase shifts are assumed to be constants, defined by the Friedel sum rule for the screening charge in respective channels, so that ρ_n in (2) is also a constant. In the limit $T = 0$ (but $l \neq 0$) the transport coefficients calculated with (2) reduce to standard phase-shift expressions, while in the limit $\eta_{l\neq 0} \longrightarrow 0$ we recover the usual many-body expression for the Kondo scattering (see, e.g. Ref. 10).

At low temperatures, $T \ll T_K$, the Sommerfeld expansion gives[8]

$$\lim_{T\longrightarrow 0}\frac{3eS}{\pi^2k_B^2}\left[\frac{\sin(2\eta_0-2\eta_1)}{\sin^2(\eta_0-\eta_1)+\rho_n}\right]^{-1} = \gamma\, T, \quad (4)$$

where $\eta_0(\omega) = \tan^{-1}[\mathrm{Im}\ G_0(\omega)/\mathrm{Re}\ G_0(\omega)]$ is the resonant phase shift evaluated at $\omega = \epsilon_F$ in (4) and γ is the enhanced coefficient of the low-temperature specific heat given by the derivative of the resonant phase shift at the Fermi level, $(\partial\eta_0/\partial\omega)_{\omega=\epsilon_F}$ (see Ref. 10).

At higher temperatures (4) is no longer valid and the thermopower has to be evaluated numerically from (1). This requires an accurate expression for the Green's function, $G_0(\omega,T)$, over a range of frequencies and temperatures. Various approaches have been used to extract this Green's function, including $1/N$ expansions[11,12] and quantum Monte Carlo methods.[13] Here, the numerical renormalization group,[14] which has recently been extended to the calculation of both finite and zero-temperature Green's functions,[15,16] is used to calculate $G_0(\omega,T)$. Results for the transport coefficients of the Anderson model,[17] with only resonant scattering, have shown that this approach satisfies all the exact Fermi liquid relations for transport properties at low temperature[15,17] and that it is valid in the crossover and high-temperature regimes.[16] These calculations are now extended so as to take into account the effects of nonresonant scattering which is necessary to explain the observed sensitivity of the sign of the thermopower to small changes of the local environment around the magnetic ions.

The numerical renormalization-group analysis is performed for a fixed value of the Coulomb correlation, $U = 4\pi\Delta$, and for several values of the resonant charge, n_0. For a given value of n_0 the thermopower is calculated from (1) and (2) for several values of the nonresonant phaseshifts.

In Fig. 1, we show the single-particle spectral density $\rho_0(\omega,T)$ for the $l = 0$ channel obtained via the numerical renormalization group at several temperatures, and for $n_0 = 0.78$ ($T_K = 0.18\Delta$). The Kondo resonance shows a strong temperature dependence and is seen to disappear almost completely for $T/T_K \geq 10$. It should be noted that the slope of the spectral density at the Fermi level changes sign from a large positive value for $T \ll T_K$ to a negative value for $T > T_K$. Not shown in Fig. 1 are the high-energy atomiclike resonances of width Δ at ϵ_d and $\epsilon_d + U$. These peaks acquire some temperature dependence when $T \approx \Delta$ and there is a shift in spectral weight from the low-energy to the high-energy peak. The above features of the spectral density of the asymmetric model in the Kondo regime are completely general and do not depend on the choice of parameters (see Refs. 18

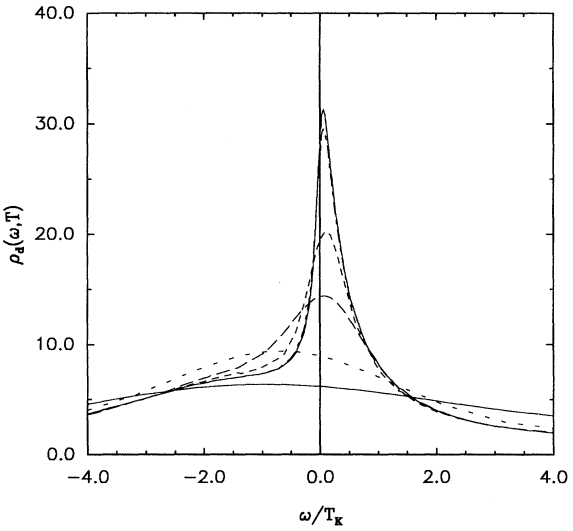

FIG. 1. The single-particle spectral density of the Anderson model for energies, $-4 \leq \omega/T_K \leq +4$ and reduced temperatures, $T/T_K = 0.025$, 0.129, 0.653, 1.468, 4.955, and 11.149. The Kondo peak at the Fermi level ($\omega = 0$) monotonically decreases in height with increasing temperature.

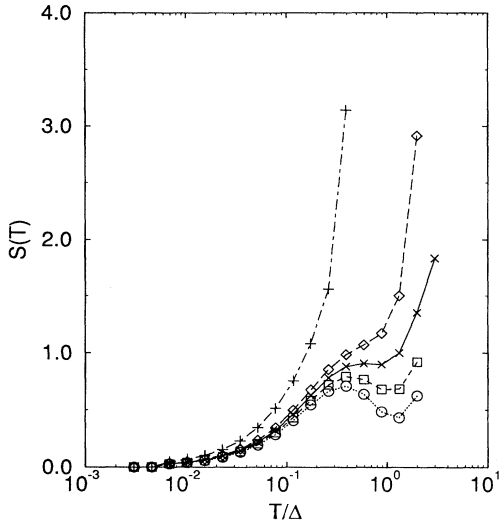

FIG. 3. The thermopower $S(T)$ over the full temperature range in the valence fluctuation ($\epsilon_d = 0$) regimes and for $U/\pi\Delta = 4$ is plotted versus T/Δ. The various curves correspond to $\eta_1 = -0.02\pi$ (o), $\eta_1 = -0.01\pi$ (□), $\eta_1 = 0$ (×), $\eta_1 = 0.01\pi$ (◇), and $\eta_1 = 0.02\pi$ (+), respectively.

and 19 for details).

Figure 2 shows the thermopower of the Anderson model in the Kondo limit (parameters as in Fig. 1), while Fig. 3 shows the results for parameters corresponding to the valence fluctuation regime ($n_0 = 0.45$, $T_K = \sqrt{2\pi}\Delta$). The results are plotted on a reduced temperature scale, defined by the characteristic energy of the low lying excitations. The slopes of the low-temperature curves on Figs. 2 and 3, evaluated on an absolute temperature scale, differ by Δ/T_K, i.e., the Kondo effect leads to a substantial enhancement of the thermopower. The effect of the nonresonant scattering is shown for several values of η_1. Since we keep $n_0 < 1$ [$\eta_0(\epsilon_F, T = 0) < \pi/2$], the interference enhances the effect of local correlation for $\eta_1 < 0$ and reduces it for $\eta_1 > 0$. The increase of the nonresonant screening can make the valence fluctuation curves assume the Kondo shape or the shape typical of an empty orbital, depending on the sign of η_1. Note, the thermopower of a valence fluctuator, shown in Fig. 3, exhibits only a shallow minimum and does not change sign. For a given value of the Coulomb correlation, the interference effects are most pronounced for systems with the local resonance at half-filling ($n_0 = 1$), i.e., for systems with the smallest Kondo temperature or largest specific-heat coefficient γ. In the absence of such interference effects, the thermopower would vanish at half-filling due to particle hole symmetry, since then the spectral density and transport time would be even functions of energy and the numerator in (1) would be identically zero. The inclusion of nonresonant scattering is important for relating the theory to the experimental data. The interference effects explain the sensitivity of the sign of the thermopower on doping with nonmagnetic ions, as observed in some concentrated Kondo systems. Small changes in the local environment of magnetic ions modify the nonresonant scattering and could give rise, provided $n_0 \sim 1$, to large differences found in the thermopower of $Ce(Cu_xAl_{1-x})_5$ as x changes from $x = 0.84$ to $x = 0.88$.[1]

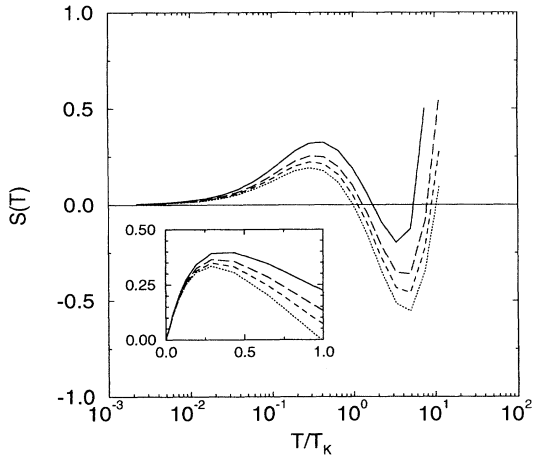

FIG. 2. The thermopower $S(T)$ over the full temperature range in the Kondo ($\epsilon_d = -2\Delta$) regimes and for $U/\pi\Delta = 4$ is plotted versus T/T_K ($T_K = 0.18\Delta$). The various curves correspond to $\eta_1 = -0.02\pi$ (dotted), $\eta_1 = -0.01\pi$ (dashed), $\eta_1 = 0$ (long dashed), and $\eta_1 = 0.01\pi$ (solid), respectively. The inset is for $S(T)/\left[\frac{\sin(2\eta_0 - 2\eta_1)}{\sin^2(\eta_0 - \eta_1) + \rho_n}\right]$ and shows the linear in T Fermi liquid behavior and the universality for $T \ll T_K$.

The inset in Fig. 2 shows that the thermopower, normalized by the low-temperature phase factor [square bracket in (4)], exhibits universal low-temperature behavior in the Kondo regime. For $T \geq T_K/10$ the universal behavior terminates, as expected. For the choice of parameters used in Fig. 2, the thermopower assumes a maximum at about $T_M = T_K/3$ and changes sign above T_K. As temperature increases further the thermopower

passes through a broad minimum. The calculations with different parameters have shown that the crossover temperature decreases with T_K but not in a universal way.

The behavior of the thermopower can be be understood from the temperature dependence of the spectral density as follows. For the asymmetric model in the Kondo regime and for temperatures $T \ll \Delta$ the behavior of the transport integrals in (1) are dominated by the Kondo resonance and in particular its slope at the Fermi level. As discussed above, the slope of the Kondo resonance at the Fermi level is large ($\sim 1/T_K$) and positive at $T = 0$, then decreases with increasing temperature, and eventually becomes negative (see Fig. 1). This gives rise to the maximum of the thermopower at $T \approx T_K/3$ and to the sign change at $T > T_K$. For $T \approx \Delta$ the Kondo resonance has completely disappeared. Charge fluctuations become important and there is a transfer of spectral weight from the low-energy to the high-energy atomiclike peak in the spectral density. The effect of this is to increase the thermopower as can be seen from (1) noting that $\tau_{\rm tr}(\omega, T) \sim 1/\rho_0(\omega, T)$. This increase gives rise to the minimum at $T \approx \Delta$. For the valence fluctuation regime, the resonance of width Δ associated with the bare level $\epsilon_d \approx 0$ is renormalized by the interactions to lie above the Fermi level at all temperatures, hence its slope is always positive (for details see Ref. 19). There is also a resonance in the spectral density at $\epsilon_d + U$, but this carries little weight and is not important here. For $T \approx \Delta$ the resonant level at $\tilde{\epsilon}_d > 0$ depends on temperature and its height decreases monotonically with temperature. At low temperature $T < \Delta$ the sign of the thermopower is governed by the slope of the renormalized resonance at the Fermi level and is therefore positive. At higher temperatures $T > \Delta$ the factor governing the sign of $S(T)$ is the spectral weight, which lies predominantly above the Fermi level, and again from (1) this leads to a positive thermopower. For $T \approx \Delta$ the resonant level is temperature dependent, the slope at the Fermi level is decreasing, and this gives rise to the minimum of $S(T)$ at $T \approx \Delta$.

To summarize, in concentrated Kondo systems the enhancement of the specific heat and of the low-temperature thermopower is determined by the elementary excitations in the resonant channel. Above the Kondo temperature, the transport current relaxes due to the incoherent scattering of conduction electrons on $4f$ spins of Ce ions and the thermopower reflects the excitation spectrum of localized spins weakly coupled to the conduction sea. At temperatures low with respect to the Kondo temperature, the localized spins are screened and the current relaxes via excitations in the local Fermi liquid formed by the Kondo screening. The thermopower assumes a typical $\sim$ shape which is directly related to the structure of the excitation spectrum as the system is cooled from high to low temperatures. The low-temperature maximum at $T \approx T_0/3$, where $T_0 = T_K$ for Kondo systems and $T_0 = \Delta$ for mixed valent systems, is a result of the renormalized Fermi liquid ground state and the broad minimum at $T \approx \Delta$ reflects the importance of charge fluctuations at higher temperatures. Interference effects due to nonresonant scattering of conduction electrons were shown to influence the sign of the thermopower and could be important in relating the theory to experiment, in particular in explaining the sensitivity of the sign of the thermopower to small changes in the local environment around magnetic ions as observed in systems such as $Ce(Cu_xAl_{1-x})_5$.[1]

Our analysis indicates that the low-temperature thermopower of concentrated Kondo systems, normalized by a phase factor that depends on the screening charge only, exhibits universal features if plotted as a function of γT. The overall shape of the thermopower curves calculated for the Anderson model with two scattering channels resembles quite strikingly the experimental data.

We acknowledge the SERC for financial support and the CSI for computer equipment. One of us (T.A.C.) would also like to thank Professor Müller-Hartmann for an invitation to the Institut für Theoretische Physik, Cologne where part of this work was carried out.

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