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RESISTIVITY AND THERMOELECTRIC POWER OF HEAVY FERMION SYSTEMS*

G. Czycholl

Institut für Theoretische Physik, Universität Bremen
28359 Bremen, Bibliothekstr. 1, Germany

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Heavy-fermion systems are modelled by the Periodic Anderson Model (PAM) in the limit of infinite dimensions ($d \to \infty$), in which the local approximation for the selfenergy or the Dynamical Mean-Field Theory (DMFT), respectively, become exact. As a consequence, vertex corrections for transport quantities vanish, which means that transport quantities like the conductivity (resistivity) and the thermoelectric power can be calculated from the selfenergy. Different approximations are used to determine the selfenergy, namely the Second Order Perturbation Theory (SOPT) for the PAM and a Modified Perturbation Theory (MPT) within a DMFT-mapping of the PAM on an effective Single-Impurity Anderson Model (SIAM). The MPT reproduces the SOPT for the SIAM for weak interactions and simultaneously fulfills the atomic limit. Both approximations yield an f-electron spectral function at the chemical potential which is strongly temperature dependent and decreases on a characteristic temperature scale T^* approaching a constant value for high temperatures. This characteristic low temperature T^* can be interpreted as the Kondo temperature within these approximations, but T^* does not yet have the characteristic (exponential, non-analytic) dependence on the model parameters expected from the Schrieffer–Wolff transformation. The resistivity $R(T)$ obtained shows qualitatively exactly the behavior, which is characteristic for heavy-fermion systems, namely a low value for zero temperature, a T^2 increase for low temperatures, a maximum exactly at T^*, and $R(T)$ decreases with increasing T for higher temperatures $T > T^*$. The thermoelectric power obtained is absolutely very large (of the magnitude 10^{-4} V/K), and it has an extremum at a temperature, which scales linearly with T^*; the absolute value at the extremum even becomes larger with increasing T^*. The influence of impurity scattering (alloying) was also investigated treating the disorder within the Coherent Potential Approximation (CPA). Possible extensions of these investigations to include crystal-field effects are discussed.

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1. Introduction

The unusual transport properties of Heavy Fermion Systems (HFS) containing Ce and Yb ions are still not properly understood. Pure metallic HFS, for example $\mathrm{CePd_3}$ [1], $\mathrm{CeCu_6}$ [2], have a small zero temperature resistivity $R(T=0)$, a sharp increase of $R(T)$ for low temperature T, a maximum at some characteristic temperature T^*, and a $R(T)$ decreasing with increasing T, *i.e.* a Negative Temperature Coefficient (NTC), for higher temperatures. Another interesting transport quantity is the Thermoelectric Power (TEP); for early monographs on the TEP of metals and alloys see [3]. In HFS the thermoelectric power $S(T)$ is often non-monotonic, and in some systems one observes a sign change at lowest temperatures [4–11]; above 100° K the thermopower can assume giant values, and much of the recent interest in the heavy fermion thermo-electricity is due to the belief that some of the new systems, with the thermopower larger than $150\,\mu\mathrm{V/K}$, might be useful for application. The low temperature behavior can be very sensitive to alloying and external pressure. Substituting Ce-ions in stoichiometric $\mathrm{CePd_3}$ systems by non-magnetic La-ions creates "Kondo holes", and a concentration of only a few percent may be sufficient to obtain a $R(T)$ showing only a NTC [2]. For the TEP the behavior with a negative minimum at low temperatures and a broad positive high-temperature peak between 100° K and 200° K in systems like $\mathrm{CeCu_2Si_2}$, [5], $\mathrm{CeCu_2Ge_2}$, [7], $\mathrm{CePd_2Si_2}$, [7] can change into a behavior with no sign change and two positive maxima or a shoulder on the low temperature side of the large $S(T)$ peak in systems like $\mathrm{Ce}_{1-c}\mathrm{Y}_c\mathrm{Cu_2Si_2}$ [8] or $\mathrm{CeCu_2Ge_2}$ under alloying or under external pressure.

2. Models

It is well accepted that the basic electronic properties of HFS are described by the periodic Anderson model, which contains a conduction band, strongly correlated f-levels localized at the sites of a lattice simulating the rare-earth or actinide ions, and a hybridization between f-states and conduction electron states. For real rare earth or actinide atoms or ions the f-shells are highly degenerate, namely 14-fold degenerate in the bare (hydrogen like) atom, which is splitted into a 6- and an 8-fold degenerate level due to spin-orbit coupling, and this degeneracy is further reduced in a crystal due to crystalline electric fields so that the lowest f-level may be only two-fold degenerate. But the Crystal Field (CF) split level is thermally accessible so that taking into account only a two-fold degenerate f-level is probably not sufficient to account for the full temperature dependence of the relevant physical quantities.

Nevertheless, for the actual calculations presented in this paper the standard PAM with only a two-fold degeneracy of the f-levels has been used, *i.e.*

$$\begin{aligned} H &= \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \\ &+ \sum_{\vec{R}\sigma} \left[E_f f^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} + \frac{U}{2} f^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} f^{\dagger}_{\vec{R}-\sigma} f_{\vec{R}-\sigma} + V \left(c^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} + \text{c.c.} \right) \right], \end{aligned} \tag{1}$$

where $\varepsilon_{\vec{k}} = 2t \sum_{l=1}^{d} \cos(k_l a)$ denotes the band electron dispersion (t — nearest neighbor hopping, a — lattice constant), for which a tight-binding model on a simple-cubic lattice in dimension d is assumed. To calculate transport quantities one needs also the current operator, and for the current operator being consistent with the PAM the component in x-direction is given by

$$j_x = \sum_{\vec{k}\sigma} \frac{\partial \varepsilon_{\vec{k}}}{\partial k_x} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \left[+ \underbrace{\frac{\partial V_k}{\partial k_x} \left(f^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} + \text{c.c.} \right)}_{=0,\ \text{if } V\ k\text{-independent}} \right]. \tag{2}$$

So for k-independent hybridization V one has in site representation

$$j_x = ita \sum_{\vec{R}\Delta_x\sigma} \left(c^{\dagger}_{\vec{R}+\Delta_x\sigma} c_{\vec{R}\sigma} - c^{\dagger}_{\vec{R}\sigma} c_{\vec{R}+\Delta_x\sigma} \right), \tag{3}$$

(i — imaginary unit, t — hopping, a — lattice constant).

The influence of alloying with non-HFS systems can be studied by considering the following generalization of the PAM

$$\begin{aligned} H &= \sum_{\vec{k}\sigma} \varepsilon_{\vec{k}} c^{\dagger}_{\vec{k}\sigma} c_{\vec{k}\sigma} \\ &+ \sum_{\vec{R}\sigma} \left[E_{Rf} f^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} + \frac{U}{2} f^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} f^{\dagger}_{\vec{R}\bar{\sigma}} f_{\vec{R}\bar{\sigma}} + V_R (c^{\dagger}_{\vec{R}\sigma} f_{\vec{R}\sigma} + \text{c.c.}) \right], \end{aligned} \tag{4}$$

where

$$E_{Rf} = \begin{cases} E_f & \text{with probability} \quad 1 - c\,, \\ E_f + \Delta E_f & \text{with probability} \quad c\,. \end{cases} \tag{5}$$

For large ΔE_f the f-level remains unoccupied meaning physically that there is no rare-earth ion at this site with probability c, which corresponds to the concentration of the non-rare-earth constituent.

Being interested in transport quantities two-particle Green functions for the PAM have to be calculated. To calculate the conductivity we start from the Kubo formula for the (diagonal element of the) frequency (ω-) dependent conductivity (tensor), which (according to standard linear response theory [12–14]) is given by the current–current response function:

$$\sigma_{xx}(\omega) = -\frac{1}{\omega + i0}\,\mathrm{Im}\,\chi_{j_x,j_x}(\omega + i0)\,, \tag{6}$$

$$\chi_{j_x,j_x}(z) = \ll j_x; j_x \gg_z = -i\int_0^\infty dt' \mathrm{e}^{izt'}\langle [j_x(t'), j_x(0)]_-\rangle\,. \tag{7}$$

The static conductivity can be obtained as the zero frequency ($\omega \to 0$) limit of the dynamical conductivity and then the TEP follows by means of the standard Mott relation [15]. So one must determine two-particle Green functions of the kind $\ll c^\dagger_{\vec{k}\sigma}c_{\vec{k}\sigma}; c^\dagger_{\vec{k}\sigma'}c_{\vec{k}\sigma'} \gg_z$. Using standard relations of many-body theory [12] the two-particle Green functions can be obtained from (products of) one-particle Green functions and additional vertex corrections. The one-particle Green functions are defined by

$$G^{ab}_{\vec{k}\sigma}(z) = \ll a_{\vec{k}\sigma}; b^\dagger_{\vec{k}\sigma} \gg_z = -i\int_0^\infty dt' e^{izt'}\left\langle \left[a_{\vec{k}\sigma}(t'), b^\dagger_{\vec{k}\sigma}(0)\right]_+\right\rangle \tag{8}$$

(with a, $b \in \{c, f\}$). The f-electron selfenergy is defined by:

$$\begin{pmatrix} \ll c_{\vec{k}\sigma}; c^\dagger_{\vec{k}\sigma} \gg_z & \ll c_{\vec{k}\sigma}; f^\dagger_{\vec{k}\sigma} \gg_z \\ \ll f_{\vec{k}\sigma}; c^\dagger_{\vec{k}\sigma} \gg_z & \ll f_{\vec{k}\sigma}; f^\dagger_{\vec{k}\sigma} \gg_z \end{pmatrix} = \begin{pmatrix} z - \varepsilon_{\vec{k}} & -V \\ -V & z - E_f - \Sigma_{\vec{k}f}(z) \end{pmatrix}^{-1} \tag{9}$$

and for the model(s) defined above one has to expect a correlation- (interaction-) and a disorder- (impurity-) contribution to the selfenergy:

$$\Sigma_{\vec{k}f}(z) = \Sigma^{\mathrm{corr}}_{\vec{k}f}(z) + \Sigma^{\mathrm{imp}}_{\vec{k}f}(z)\,. \tag{10}$$

3. Approximations

We study the PAM in the limit of infinite dimension $d \to \infty$, $t \to 0$ keeping $dt^2 = \mathrm{const.}$ [16]; in this limit certain simplifications become exact, which extremely simplify practical calculations. It has been shown [17] that these simplifications are already a reasonable additional approximation for realistic dimension $d = 3$, *i.e.* 3-dimensional systems behave already similar as systems in the mathematical limit $d \to \infty$. The most important simplification is that the selfenergy becomes site-diagonal (k-independent), *i.e.* the so called "local approximation" becomes exact for large dimension d and is a reasonable approximation for $d = 3$. Consistent with the site diagonality of the self energy is the vanishing of vertex corrections for the current–current response functions. Then the static (zero frequency) conductivity is simply given by [18]

$$\sigma_{xx} = \frac{e^2 a^{2-d}}{2\pi\hbar} t^2 \int dE \left(-\frac{df}{dE}\right) L(E)\,, \tag{11}$$

where a is the lattice constant, d the dimension, t the hopping matrix element of the band electrons, $f(E)$ the Fermi function, and the function $L(E)$ is defined by

$$L(E) = \frac{2}{N} \sum_{\vec{k}\sigma} \left(\operatorname{Im} G^c_{\vec{k}\sigma}(E + i0)\right)^2\,, \tag{12}$$

where

$$G^c_{\vec{k}\sigma}(z) = \frac{1}{z - \dfrac{V^2}{z - E_f - \Sigma_f(z)} - \varepsilon_k}\,, \tag{13}$$

is the band electron Green function of the PAM and $\Sigma_f(z)$ the (k-independent) f-electron selfenergy. The TEP is also determined by the function $L(E)$ according to [15]

$$S = \frac{\int dE \left(-\frac{df}{dE}\right)(E - \mu)L(E)}{\mathrm{e}T \int dE \left(-\frac{df}{dE}\right) L(E)}\,. \tag{14}$$

Therefore, in the limit $d \to \infty$ the transport quantities of interest can be obtained from the one-particle Green functions or the (k-independent) selfenergy alone.

But a full exact solution of the PAM is not possible even in infinite dimensions and one needs additional approximations. We have applied the standard selfconsistent second order perturbation theory with respect to the Coulomb correlation U. The SOPT is the simplest non-trivial extension of the Hartree–Fock approximation, and it has the advantage that Fermi liquid properties (Luttinger sum rules) are automatically fulfilled within this approach. Furthermore, a selfconsistent mapping on an effective single-impurity Anderson model, *i.e.* the "dynamical mean-field theory" becomes exact in infinite dimensions [19]. The DMFT selfconsistency relation reads

$$\begin{aligned} G_R^{f\mathrm{SIAM}}(z) &= \frac{1}{z - E_f - \Sigma_f(z) - \Delta(z)} \\ &= \frac{1}{N} \sum_{\vec{k}} \frac{1}{z - E_f - \Sigma_f(z) - \frac{V^2}{z - \varepsilon_{\vec{k}}}}\,. \end{aligned} \tag{15}$$

Here the "bath" Green function $\Delta(z)$ (*i.e.* the effective SIAM conduction band Green function) has to be determined selfconsistently. The selfenergy for the effective SIAM has to be determined either by numerical methods (quantum Monte Carlo or numerical renormalization group) or by a suitable approximation for the SIAM. We have applied the "modified perturbation theory", which starts from the following Ansatz [20–22]

$$\Sigma_f(z) = Un_{f-\sigma} + \frac{\alpha\Sigma_f^{\mathrm{SOPT}}(z)}{1-\beta\Sigma_f^{\mathrm{SOPT}}(z)}\,, \tag{16}$$

where $\Sigma_f^{\mathrm{SOPT}}(z)$ is the SIAM selfenergy in second order in U relative to the Hartree–Fock solution and the parameters α, β can be determined by the condition that the atomic limit (of vanishing V) and an additional criterion (Fermi liquid sum rule, reproduction of the first four moments) are fulfilled. The MPT has the advantage that it is exact up to order U^2 and the atomic limit is fulfilled simultaneously.

Concerning the disorder contribution to the selfenergy the coherent potential approximation (CPA) becomes exact in the large-d limit. Therefore, the exact selfconsistency relation for the impurity selfenergy reads

$$\Sigma^{\mathrm{imp}}(z) = \overline{\frac{E_{Rf}}{1-(E_{Rf}-\Sigma^{\mathrm{imp}}(z))G_R^{ff}(z)}}\,, \tag{17}$$

where the bar denotes the configurational average. For $\Delta E_f \to \infty$, *i.e.* for non-magnetic impurities with unoccupied f-shell, this leads to [23]

$$\Sigma^{\mathrm{imp}}(z) = E_f - \frac{c}{G_R^{ff}(z)}\,, \tag{18}$$

where c is the concentration of the impurities.

4. Results

Within the SOPT the selfenergy imaginary part at the Fermi energy vanishes at zero temperature T in accordance with the Luttinger theorem leading to a mass enhancement of the quasi particles at low temperatures, *i.e.* "heavy quasiparticles" are easily reproduced within this approach. As a consequence the f-electron Density Of States (DOS) at the chemical potential μ is strongly temperature dependent and decreases on a characteristic low temperature scale T^* towards an asymptotic T-independent value. Therefore, T^* can be defined as the half width of the T-dependent part of the f-DOS at μ. This temperature T^* can be interpreted as Kondo temperature;

however, within the SOPT treatment it is not yet of the correct (Schrieffer–Wolff) form and magnitude, which cannot be expected in a weak-coupling expansion like the SOPT.

When calculating the T-dependence of the resistivity $R(T) = 1/\sigma_{xx}$ from (11), one obtains for most choices of the parameters the following characteristic behavior: A residual resistivity approaching zero for $T \to 0$, a T^2-dependence for very low T as expected for Fermi liquids, a nearly linear increase with increasing T for $T < T^*$, a maximum of $R(T)$ exactly at T^*, and an $R(T)$ decreasing with increasing T (and thus behaving similarly as in the case of incoherent scattering from magnetic impurities) for $T > T^*$. This can be seen from Fig. 1, where we show $R(T)$ for the model with 2.2 electrons per site, an f-occupancy $n_f = 1.1$, and for different hybridization V. For fixed other parameters the hybridization V determines the low temperature scale T^*. The calculations are performed for $U = 1$. Remarkably, as long as there is a maximum in $R(T)$ it is very close to T^* as determined by the f-DOS criterion described above. For too large V and T^* (and corresponding less strong mass enhancement) there is no longer a true maximum but only a plateau behavior in $R(T)$.

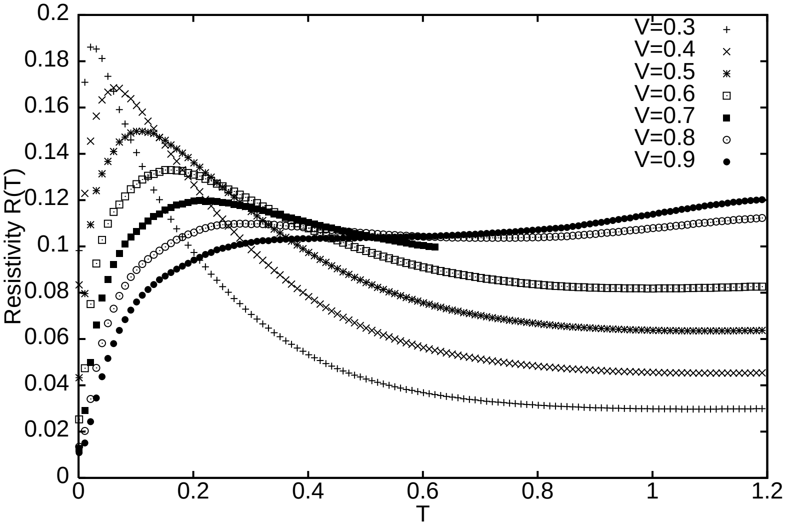

Fig. 1. Temperature dependence of the resistivity $R(T)$ obtained withion the SOPT for the PAM for different hybridizations, a total number of 2.2 electrons per site, and an f-electron number of $n_f = 1.1$.

Corresponding results for the thermopower are shown in Fig. 2. Here, $S(T)$ is measured in units of $k_{\mathrm{B}}/e \approx 86\mu\mathrm{V/K}$. Obviously $S(T)$ is strongly temperature dependent and absolutely very large, namely of the magnitude

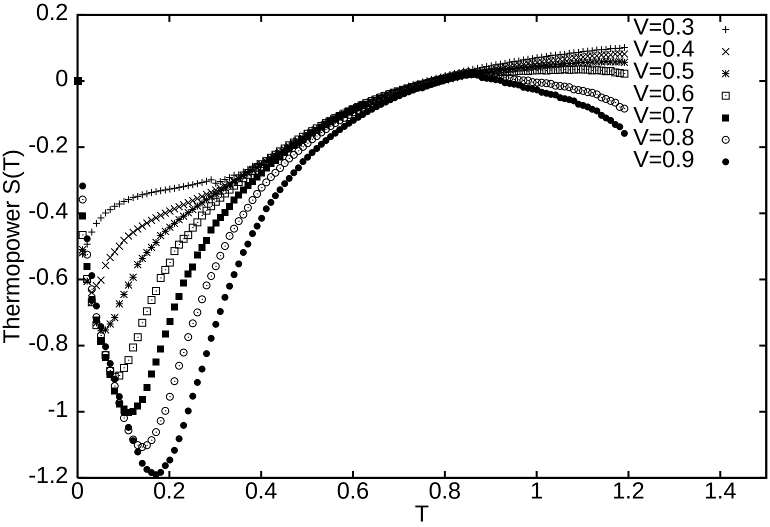

Fig. 2. Temperature dependence of the resistivity $R(T)$ obtained within the SOPT for the PAM for different hybridizations, a total number of 2.2 electrons per site, and an f-electron number of $n_f = 1.1$.

50–100 μV/K. It has an extremum (negative minimum in the plot) at a temperature T_1, which scales linearly with T^*, *i.e.* $T_1 = AT^*$. For the parameters used for the figure we have $A \approx 0.5$, but the exact value of A depends on the other parameters (U, n_f *etc.*) This extremum in $S(T)$ also exists in the situation when the resistivity $R(T)$ exhibits no maximum but only a plateau behavior. The absolute value $|S(T_1)|$ at the extremum even slightly increases with increasing T^*, *i.e.* according to this result it is not necessarily the most "heavy" fermion systems which exhibit the largest values of the TEP. In any case, in the low temperature regime $T \leq T^*$ this approach yields a TEP of the correct absolute magnitude and the qualitative behavior, in particular an extremum, which is characteristic for the TEP experimentally observed in many heavy fermion systems. Of course, for intermediate and high T the features due to the CF splitting cannot be reproduced within this SOPT treatment of the PAM, as only the two-fold degenerate PAM was used, which has no higher CF-split f-levels included.

Results for another set of parameters are shown in the following figures. Here I chose E_f positive (*i.e.* within the upper half of the conduction band) and a total filling of 2.4. Then the conduction band is more than half filled, which has influence on the zero temperature sign of $S(T)$, and the f-occupation is smaller than 1. The resistivity shows again the characteristic behavior mentioned above with a maximum and a NTC. The TEP,

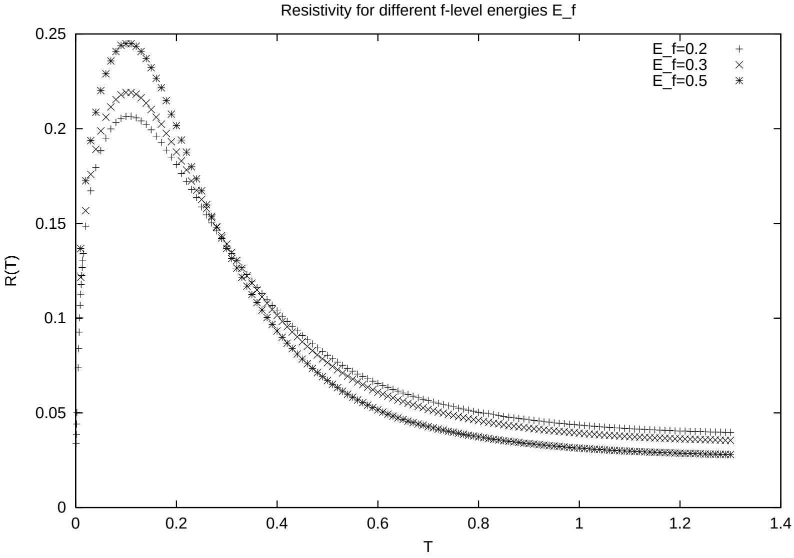

Fig. 3. Temperature dependence of the resistivity $R(T)$ obtained within the SOPT for the PAM for different f-level positions E_f for hybridization $V = 0.5$ and a total number of 2.4 electrons per site.

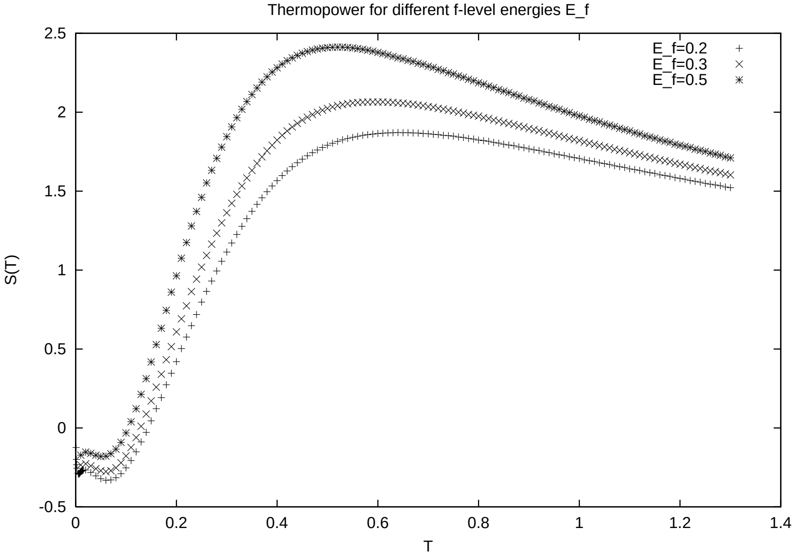

Fig. 4. Temperature dependence of the thermopower $S(T)$ obtained within the SOPT for the PAM for different f-level positions E_f for hybridization $V = 0.5$ and a total number of 2.4 electrons per site.

however, is negative for small T and has a change of sign at low temperatures T, so it is qualitatively similar as that observed experimentally in some HFS. Increasing E_f (with respect to the conduction band center) leads to smaller f-occupations, *i.e.* to a transition from the Kondo into the more mixed valence regime, and may simulate the influence of external pressure. Obviously the negative low-T minimum of $S(T)$ becomes more shallow with increasing E_f, and for even larger E_f (not shown in the figure) it disappears and only a positive TEP is obtained, which may have some fine structure at very low T. Note that the TEP is zero for temperature $T = 0$ also within the used approximation; the apparant non-zero value of $S(T)$ for small T is due to the finite temperature resolution of the presented calculations, which for numerical reasons have not yet been done at the lowest temperatures $T < 0.02$.

5. Conclusion

The most characteristic features observed in the T-dependence of the resistivity and the thermopower of HFS can qualitatively be reproduced within simple approximations of the PAM, in particular within the U-perturbation approach, *i.e.* the SOPT. It has been shown already for the resistivity [23] that also the effects of alloying can be reproduced; applications of this investigation (using additionally the CPA for disordered systems) to the TEP are presently in progress. Applications of the MPT within the DMFT scheme (recently done but not presented in this manuscript) can give qualitatively similar behavior, only the characteristic low temperature T^* comes out different within the MPT approach than within the SOPT. I expect that the proper inclusion of orbital degeneracy and crystal field effects will allow for the description and understanding also of the details in the low T behavior of the thermoelectric power.

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