Relationship between the thermopower and entropy of strongly correlated electron systems

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A number of recent experiments report the low-temperature thermopower α and specific heat coefficients $\gamma = C_V/T$ of strongly correlated electron systems. Describing the charge and heat transport in a thermoelectric by transport equations, and assuming that the charge current and the heat current densities are proportional to the number density of the charge carriers, we obtain a simple mean-field relationship between α and the entropy density $\mathcal{S}$ of the charge carriers. We discuss corrections to this mean-field formula and use results obtained for the periodic Anderson and the Falicov-Kimball models to explain the concentration (chemical pressure) and temperature dependence of $\alpha/\gamma T$ in $EuCu_2(Ge_{1-x}Si_x)_2$, $CePt_{1-x}Ni_x$, and $YbIn_{1-x}Ag_xCu_4$ intermetallic compounds. We also show, using the 'poor man's mapping' which approximates the periodic Anderson lattice by the single impurity Anderson model, that the seemingly complicated behavior of $\alpha(T)$ can be explained in simple terms and that the temperature dependence of $\alpha(T)$ at each doping level is consistent with the magnetic character of $4f$ ions.

I. INTRODUCTION

Several recent papers[?][?][?] report on a correlation between the low-temperature thermopower α and the specific heat coefficient $\gamma = C_V/T$ for heavy Fermions and valence fluctuating compounds with Ce, Eu, Yb and U ions. The data show that the zero-temperature limit of the ratio $\alpha(T)/C_V(T) = \alpha/\gamma T$ in most systems is about the same, although the absolute values of γ and α/T vary by orders of magnitude[?][?][?][?][?][?][?][?]. At the moment it is not clear if the deviations from universality arise because of insufficient accuracy of the data, or because the 'universal law' is only approximately valid. The difficulty is that neither $\alpha(T)$ nor $C_V(T)$ are linear in the lowest available temperature intervals and to obtain the linear coefficients one has to estimate the functional form of $\alpha(T)$ and $C_V(T)$ before taking the zero-temperature limit. The temperature dependences of $\alpha(T)$ and $C_V(T)$ in various systems might have a different physical origin, and comparing the data on $\alpha(T)/\gamma T$ without a detailed knowledge of the underlying dynamics might lead to erroneous conclusions. Furthermore, the definition of the 'zero-temperature limit' can differ considerably for systems with vastly different characteristic temperatures and at present it is not clear what the error bars are for the $\alpha/\gamma T$ data. We believe, the universality of the $\alpha/\gamma T$ ratio could be tested most directly by performing a pressure experiment which transforms Ce- or Eu-based heavy Fermion materials into valence fluctuators, and Yb-based valence fluctuators into heavy Fermion materials. Pressure can not only change the characteristic temperature of a given compound by several orders of magnitude[?][?] and, with that, change the nature of the ground state, but it has a dramatic effect on the overall shape of the thermopower. Although the low-temperature pressure experiments are less accurate than the ambient pressure ones, the evolution of $\alpha(T)$ or $C_V(T)$ with pressure could be followed and the universality of $\alpha/\gamma T$ studied in a systematic way. Experiments which provide the low-temperature thermopower and the specific heat on the same sample at various pressures are yet to be performed but some data are available on the doping dependence (chemical pressure) of α and γ. For example, doping alters α and γ of $EuCu_2(Ge_{1-x}Si_x)_2$, $CePt_{1-x}Ni_x$ and $YbIn_{1-x}Ag_xCu_4$ intermetallics by more than one order of magnitude[?][?][?][?][?]. while barely affecting the low-temperature ratio $\alpha/\gamma T$. We explain this behavior as a chemical pressure effect.

A simple relation between α and γT is obtained for a free electron gas and for non-interacting electrons on a lattice. The solution of the Boltzmann equation gives, under fairly general conditions, the result[?][?] $\alpha(T) \simeq \mathcal{S}(T)/ne = C_V(T)/ne$, where $\mathcal{S}$ is the entropy density, n the number density of the charge carriers and the second equality holds because the specific heat is linear with T at low T. But non-interacting electrons fail to describe the properties of the compounds mentioned above and the question arises to what extent does the 'universal relation' between α and $\mathcal{S}$ (or C_V) hold for strongly correlated electrons?

On a macroscopic level, an analysis of the charge and heat transport of a thermoelectric in terms of transport equations yields the same relationship between α and $\mathcal{S}$ as the free electron model. This derivation assumes that under isothermal conditions the expectation value of the charge current density is proportional to the expectation value of the heat current density, and we expect it to be valid for Fermi liquids (FL); of course, this is neglecting

other sources of heat transport, such as phonon contributions (but those do not enter into isothermal heat transport unless there are phonon drag effects). In the case of the non-FL compounds, where $C_V(T)/T$ and $\alpha(T)/T$ are temperature-dependent, instead of $\alpha/T\gamma$ one should consider the ratio $\alpha/\mathcal{S}$.

The zero-temperature $\alpha/\gamma T$-ratio has been discussed recently by Miyake and Kohno[?] . They calculate the dynamical conductivity of the periodic Anderson model in the quasiparticle (QP) approximation and obtain the Seebeck coefficient from the canonical formula which expresses $\alpha(T)$ as the ratio of two transport integrals[?] . The universal FL behavior is derived by assuming that in addition to the renormalization effects due to the Coulomb interaction between f-electrons, the charge and heat transport are affected by the scattering of quasiparticles off residual impurities. This scattering dominates the transport relaxation time and gives rise to a finite residual resistivity ρ_0. In the dilute limit, the impurity concentration drops out of the ratio of transport integrals and does not appear in the expression for the Seebeck coefficient.

The exact many-body transport coefficients of the periodic spin-1/2 Anderson model have recently been obtained at finite temperatures by Grenzebach et al.[?] using the dynamical mean field theory (DMFT) which maps the lattice problem onto an auxiliary single impurity model with a self consistency condition. The electron relaxation is solely due to the Coulomb repulsion between f-electrons and the model describes both heavy Fermions and valence fluctuators with vanishing ρ_0. The solution of the auxiliary impurity problem is obtained by the numerical renormalization group (NRG) method, which provides accurate results for the static properties at arbitrary temperature and for the dynamical properties above the FL regime. However, the zero-temperature limit of the transport relaxation time is difficult to obtain by the DMFT+NRG method (due to numerical issues associated with the self-consistency), and the validity of the FL laws for the transport coefficients of strongly correlated electrons has not been clearly established.

In this contribution, we discuss the zero-temperature $\alpha/\gamma T$-ratio for the periodic Anderson model and the Falicov-Kimball model, which describe heavy Fermions and valence fluctuators with crystal field (CF) split $4f$-states. In this limit the excited CF states are not occupied and we calculate the slope of $\alpha(T)$ using the DMFT solution of an effective $\mathcal{M}$-fold degenerate model. The result agrees with that of Miyake and Kohno[?] even though we consider a periodic model with vanishing ρ_0 and have a positive coefficient for the T^2 term of the electrical resistance. We also analyze the influence of CF splittings on the thermopower of the Anderson model above the FL regime. At present, the dynamical properties of such a model cannot be obtained by the exact DMFT mapping and we find the solution using an approximate 'poor man's mapping'. That is, we assume that the conduction electrons scatter incoherently off

the $4f$-ions, relate the transport relaxation time to the single-ion T-matrix, and solve the scattering problem by the non-crossing approximation (NCA), which can properly treat the highly asymmetric limit of the Anderson model and infinite Coulomb repulsion. The results obtained in such a way explain the concentration (chemical pressure) dependence of $\lim_{T\to 0} \alpha/\gamma T$ and the evolution of $\alpha(T)$ in $\mathrm{EuCu}_2(\mathrm{Ge}_{1-x}\mathrm{Si}_x)_2$[? ? ?] $\mathrm{CePt}_{1-x}\mathrm{Ni}_x$[?] , and $\mathrm{YbIn}_{1-x}\mathrm{Ag}_x\mathrm{Cu}_4$[? ? ? ?] . The thermoelectric properties of these systems exhibit all the typical features observed in heavy Fermions and valence fluctuators[? ?] . Our calculations show that the temperature dependence of $\alpha(T)$ at each doping level is consistent with the character of the ground state inferred from the initial thermopower slope.

The rest of this contribution is organized as follows. In Section II, we introduce the macroscopic transport equations, discuss the Seebeck and Peltier experiments, and find the relationship between the thermopower and the entropy. In Section III.1 we calculate the Seebeck coefficient of the periodic Anderson model in the FL regime using the DMFT mapping. In Section III.2 we calculate the finite-temperature behavior using the 'poor man's mapping'. In Section III.3 we discuss the thermoelectric properties of the Falicov-Kimball model using the DMFT approach. In Section IV, we use these results to discuss the experimental data on the intermetallic compounds mentioned above. Our conclusions are presented in Section V.

II. TRANSPORT EQUATIONS

We consider the macroscopic charge and energy currents which are given by the statistical averages $\mathbf{J} = \mathrm{Tr}\{\rho_\phi \hat{\mathbf{j}}\}$ and $\mathbf{J}_E^\phi = \mathrm{Tr}\{\rho_\phi \hat{\mathbf{j}}_E^\phi\}$, where ρ_ϕ is the density matrix, $\hat{\mathbf{j}}$ the charge current density and $\hat{\mathbf{j}}_E^\phi$ the energy current density operators for a system of charged particles in the presence of an external scalar potential ϕ. These operators are are obtained by commuting the Hamiltonian with the charge and energy polarization operators[?] respectively, which are chosen in such a way that the macroscopic currents satisfy the appropriate continuity equations[?] . Assuming that the external potential couples to the charge density, a direct calculation shows[?] that $\hat{\mathbf{j}}$ is field independent and $\hat{\mathbf{j}}_E^\phi = \hat{\mathbf{j}}_E + \phi \hat{\mathbf{j}}$, where $\hat{\mathbf{j}}_E$ is the energy current density defined by the field-free Hamiltonian. The macroscopic energy current $\mathbf{J}_E = \mathrm{Tr}\{\rho_\phi \hat{\mathbf{j}}_E\}$ does not satisfy the continuity equation in the presence of the external potential but is easily calculated by a perturbative expansion. The gradient expansion of ρ_ϕ produces linearized equations[?] , $\mathbf{J} = L_{11}\mathbf{x}_c + L_{12}\mathbf{x}_E$ and $\mathbf{J}_E = \mathbf{J}_{E_\phi} - \phi\mathbf{J} = L_{21}\mathbf{x}_c + L_{22}\mathbf{x}_E$, where the generalized forces are given by $\mathbf{x}_c = -\nabla\phi - T\nabla(\mu/eT)$ and $\mathbf{x}_E = -\nabla T/T$, μ is the chemical potential and $e = -|e|$ the electron charge. The (linear-response) expansion coefficients are given by the

correlation functions,

$$L_{ij}^{\alpha\beta} = \lim_{s\to 0} \frac{1}{V} \int_0^\infty dt e^{-st} \int_0^\beta d\beta \langle \hat{\mathbf{j}}_i^\alpha(-t-i\beta)\hat{\mathbf{j}}_j^\beta(0)\rangle_0, \quad (1)$$

where $\langle \hat{\mathbf{j}}_i^\alpha \hat{\mathbf{j}}_j^\beta \rangle_0 = \mathrm{Tr}\{\rho\, \hat{\mathbf{j}}_i^\alpha \hat{\mathbf{j}}_j^\beta\}$ denotes the statistical average in the absence of the external potential and $\hat{\mathbf{j}}_1^\alpha$ and $\hat{\mathbf{j}}_2^\beta$ denote the $q = 0$ Fourier components of $\hat{\mathbf{j}}^\alpha(x)$ and $\hat{\mathbf{j}}_E^\beta(x)$, respectively ($\alpha$, β denote the coordinate axes). In what follows, we assume a homogenous and isotropic conductor in the absence of a magnetic field and consider only a single Cartesian component of $\hat{\mathbf{j}}$ and $\hat{\mathbf{j}}_E$ (this is appropriate for cubic systems).

Thermoelectric effects are usually described in terms of the heat current, hence we transform the linearized equations from $\mathbf{J}$ and $\mathbf{J}_E$ to $\mathbf{J}$ and $\mathbf{J}_Q = \mathbf{J}_E - (\mu/e)\mathbf{J}$ to yield[?][?]

$$\mathbf{J} = -\sigma\nabla\phi - \sigma\alpha\nabla T, \quad (2)$$

$$\mathbf{J}_Q = \alpha T\mathbf{J} - \kappa\nabla T, \quad (3)$$

where $\sigma = L_{11}$, $\alpha T = (L_{12}/L_{11} - \mu/e)$, and $\kappa T = (L_{22} - L_{12}^2/L_{11})$. A simple analysis shows that $\sigma(T)$, $\alpha(T)$, and $\kappa(T)$ are the isothermal electrical conductivity, the Seebeck coefficient and the thermal conductivity, respectively[?][?]. The Onsager relation[?] gives $\alpha T = \Pi$, where Π is the Peltier coefficient.

The stationary temperature distribution across the sample is obtained from the total energy current in a field $\mathbf{J}_E^\phi = \mathbf{J}_Q + (\phi + \mu/e)\mathbf{J}$ which satisfies the energy continuity equation[?] $\mathrm{div}\mathbf{J}_E^\phi = 0$ and leads to the Domenicali equation[?],

$$\dot{E}_\phi = \mathrm{div}(\kappa\nabla T) + \frac{\mathbf{J}^2}{\sigma} - T\mathbf{J}\cdot\nabla\alpha = 0. \quad (4)$$

The Joule term (J^2/σ) in Eq. (4) is crucial for the total energy balance and for establishing the correct steady-state temperature distribution.

The solution of Eqs. (2)–(4), with appropriate boundary conditions, completely specifies the thermoelectric response of the system. The above procedure connects the theoretical model of a given material with the phenomenological transport coefficients and could be used, in principle, to explain the experimentally established relationship between the thermopower and the specific heat. However, for general many body systems such a program cannot be completed and, at first sight, it is not obvious that the transport coefficients, which depend on the dynamical properties of the system, are simply related to the thermodynamic quantities, which depend only on the static properties[?]. For example, the heat current considered in this many-body theory is just the electronic contribution to the heat transport, hence we only expect it to relate to the appropriate electronic contributions to the entropy. On a macroscopic level, the relationship between α and $\mathcal{S}$ can be obtained by solving Eqs. (2) and (3) once with the boundary conditions corresponding to the measurement of the Seebeck coefficient

and once with those appropriate for the measurement of the Peltier coefficient.

In the Seebeck setup (an open circuit without net charge current), the thermoelectric voltage is induced by the heat flow due to the temperature gradient. The Seebeck voltage appears because the charged particles diffuse from the hot to the cold end and the imbalance of charge gives rise to a potential gradient across the sample. The Seebeck coefficient is obtained from the ratio $\Delta V/\Delta T$, where $\Delta V = -\int_0^a dx\ \nabla\phi(\mathbf{x})$ is the voltage change and $\Delta T = \int_0^a dx\ \nabla T(\mathbf{x})$ the temperature drop between the end-points of a sample of length a. For constant $\alpha(x)$, Eq. (2) gives $\Delta V = \alpha\Delta T$. In a stationary state, a quasiparticle picture says that the electrical energy required to transfer n electrons from the hot end to the cold end against the voltage ΔV is balanced by the change in thermal energy (that is, the heat). Neglecting the shift of the quantum states due to the external potential, we approximate $ne\Delta V \simeq \mathcal{S}_n\Delta T$, where n is the particle density and $\mathcal{S}_n$ the entropy density of the charge carriers. This gives the approximate relationship between the Seebeck coefficient and the entropy as

$$\alpha(T) = \frac{\mathcal{S}_n(T)}{en}. \quad (5)$$

In the Peltier setup, a constant electrical current passing through a junction of two different thermoelectrics gives rise to an additional heat current emanating at the interface of the junction. In a stationary state, the normal component of currents and temperature are continuous across the junction but ∇T and the transport coefficients are discontinuous. Integrating Eq. (4) over a thin volume element containing the interface gives[?],

$$-\kappa_s\nabla T|_s - (-\kappa_l\nabla T|_l) = -\mathbf{J}T(\alpha_s - \alpha_l), \quad (6)$$

where κ_s, $\nabla T|_s$, α_s and κ_l, $\nabla T|_l$, α_l denote the thermal conductivity, temperature gradient and the Seebeck coefficient of the 'sample' and 'leads' in the vicinity of the interface. Eq. (6) shows that the heat brought to and taken from the surface by the thermal conductivity differs by $\Pi_{sl}\mathbf{J}$, where Π_{sl} is the relative Peltier coefficient of the two materials, $\Pi_{sl} = T[\alpha_s(T) - \alpha_l(T)]$. In other words, the junction generates an additional heat current $\Pi_{sl}\mathbf{J}$ which maintains the stationary state by absorbing (or releasing) heat from the environment. The Peltier heat appears because the excitation spectra on the two sides of the interface are different, so that the charge transfer produces a reversible entropy change. (The entropy of n particles is determined by the structure of the energy levels over which the current carriers are distributed.)

Under stationary isothermal conditions, and for currents flowing in the x-direction, Onsager's relation gives

$$\alpha(T) = \frac{J_Q}{TJ}, \quad (7)$$

where J_Q is the Peltier heat current. Neglecting the Joule heat and assuming that the stationary state is maintained

by a heat source at one end and a sink at the other end of the sample, we can simplify Eq. (7) using div $\mathbf{J} = 0$ and div $\mathbf{J}_Q = 0$. For such divergence-free currents, we assume that the charge and heat flow uniformly with a drift velocity $\mathbf{v}$ and write $\mathbf{J} = ne\mathbf{v}$ and $\mathbf{J}_Q = Q_n\mathbf{v}$, where $Q_n = \alpha Tne$ is the Peltier heat generated at the lead-sample interface and transported by the current in the lead to the sink. Defining the reversible thermoelectric entropy density as $\mathcal{S}_n(T) = Q_n/T$, we reduce Eq. (7) to Eq. (5). Finally, multiplying both sides of Eq. (5) by $N_A e$, where N_A is Avogadro's constant, and dividing by the molar entropy $\mathcal{S}_N(T) = \mathcal{S}_n(T)\Omega$, where Ω is the molar volume of the material under study, we obtain a dimensionless parameter

$$q = N_A \frac{e\alpha(T)}{\mathcal{S}_N(T)} = (\frac{N}{N_A})^{-1}, \qquad (8)$$

which characterizes the thermoelectric material in terms of an effective charge carrier concentration per formula unit (or the Fermi volume V_F of the charge carriers). For Fermi liquids, $\mathcal{S}(T) = \gamma T$ at low temperature and we obtain

$$q = N_A e \frac{\alpha(T)}{\gamma T}, \qquad (9)$$

which is the quantity defined by Behnia, *et al.*[?]. Throughout this paper, α is expressed in [μV/K], C_V and $\mathcal{S}$ in [J/(K mol)], and the Faraday number is $N_A e = 9.6 \times 10^4$C/mol.

Before proceeding, we should comment on the validity of the above approximations. As mentioned already, the entropy of the charge carriers in the steady state which characterizes the Seebeck setup is not the same as the equilibrium entropy, because the steady-state potential is different at the hot and the cold end. As regards the Peltier setup, the average value of the current density operator is not simply proportional to the particle density, and the definition used in Eq. (8) neglects all the operator products which lead to higher-order powers in the particle density. This amounts to describing the low-energy excitations of the system by quasiparticles and approximating the many-body interactions by self-consistent fields.

Furthermore, we should take into account that the entropy $\mathcal{S}_n$ in Eq. (5) or $\mathcal{S}_N$ in Eq. (8) is not the full entropy $\mathcal{S}$ of the system, but only the entropy of the charge carriers appearing in the transport equations. For example, the total entropy $\mathcal{S}$ might have contributions $\mathcal{S}_M$ coming from additional degrees of freedom, like localized paramagnetic states, magnons or phonons, which do not participate in the charge transport and are only weakly coupled to the charge carrying modes. Assuming $\mathcal{S} = \mathcal{S}_N + \mathcal{S}_M$ but neglecting the contribution of these additional degrees of freedom to the charge transport, we get the experimentally determined quantity

$$\tilde{q} = N_A \frac{e\alpha(T)}{\mathcal{S}(T)} = \frac{N_A}{N} \frac{1}{1 + \mathcal{S}_M(T)/\mathcal{S}_N(T)}, \qquad (10)$$

which could be much reduced with respect to $q = N_A/N$ given by Eq. (8). The experimental values $\tilde{q}$ depend not only on the concentration of carriers but also on temperature, and to get the universal ratio one might need a very low temperature, where $\mathcal{S}_M \ll \mathcal{S}_N$. This behavior is similar to deviations of the Wiedemann-Franz law from ideal metallic behavior whenever the phonon contribution to the heat current is substantial—in order for Wiedemann-Franz to hold, we need to have the phonon contribution to the thermal conductivity be much smaller than the electronic contribution.

The Seebeck coefficient appearing in Eqs. (5)—(10) should also be treated with care. If there are several conductivity channels, the total thermopower is a weighted sum of all the components $\sigma\alpha = \sum_j \sigma_j \alpha_j$, where $\sigma = \sum_j \sigma_j$, and there might be some cancellations in the thermopower sum. But $\mathcal{S}$ has different vertex corrections and the specific heat is not affected by these cancellations. Similarly, if there are several scattering channels for conduction electrons, vertex corrections give rise to interferences which affect the thermopower (like in the Friedel phase shift formula[?]). Even if we neglect interference effects and use the Nordheim-Gorter rule[?] ($\rho\alpha = \sum_j \rho_j \alpha_j$, where $\rho = \sum_j \rho_j$ and ρ_j and α_j are the resistivity and thermopower due to the j-th scattering channel), the α_j-terms in the weighted sum might have different signs and cancel. Thus, unless one of the channels dominates, $\tilde{q}$ is non-universal and temperature-dependent, and the interpretation becomes difficult. We also remark that the heat conductivity of magnons and phonons can give rise to phonon-drag and spin-drag contributions to $\alpha(T)$, which are not included in Eqs. (8) or (10). However, at low temperatures, those contributions are expected to be small.

III. CALCULATION OF THE SEEBECK COEFFICIENT

Considering the limitations and uncertainties mentioned above, it is somewhat surprising that in many correlated systems the low-temperature ratio of the thermopower and the specific heat comes quite close to the universal value given by Eq. (9). In what follows, we show that the universal law of Sakurai[?] and Behnia[?] holds for the periodic Anderson model with on-site hybridization. We also show that this model explains the full temperature dependence of the Seebeck coefficient observed in the intermetallic compounds with Ce, Eu and Yb ions.

The Hamiltonian is **(what follows is not very clear)**

$$H_A = H_c + H_f + H_{cf}, \qquad (11)$$

where H_c describes the (conduction) c-electrons hopping on the lattice, H_f describes the $4f$ states localized at each lattice site, and H_{cf} describes the hybridization of electrons between $4f$ and c-states. The total number of c- and f-electrons per site is n_c and n_f, respectively. The c-

and *f*-electrons have $\mathcal{L}$ internal degrees of freedom (channels) and we consider the model with an infinitely strong Coulomb repulsion between *f*-electrons (or *f*-holes) which does not allow two *f*-electrons to occupy the same channel or the same lattice site. We strictly enforce the constraint $n_f \leq 1$ (or $n_f^h \leq 1$), choose $n_c \leq 1$, and conserve the total number of electrons $n = n_c + n_f$. The unrenormalized density of states (DOS) of the conduction electrons in each channel is $\mathcal{N}_c^0(\epsilon) = \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}})$, where $\epsilon_{\mathbf{k}}$ is the conduction-electron dispersion. We assume $\mathcal{N}_c^0(\epsilon)$ to be a symmetric, slowly varying function of half-width D, which is the same in all channels, and measure all the energies, except ω, with respect to its center. In the case of heavy Fermions and valence fluctuators with Ce ions the magnetic state is represented by the CF levels which are occupied by a single *f*-electron. We consider $M-1$ excited CF levels separated from the CF ground state by energies $\Delta_i \ll |E_f|$, where $i = 1, \ldots, M-1$. Each CF state belongs to a given irreducible representation of the point group Γ_i and its degeneracy is $\mathcal{L}_i$, such that $\mathcal{L} = \sum_i \mathcal{L}_i$. The spectral functions of the unrenormalized *f*-states are given by a set of delta functions at E_f^i and $E_f^i = E_f^0 + \Delta_i$. The mixing matrix element V_i connects the *c*- and *f*-states belonging to the same irrep and, for simplicity, we consider the case $V_i = V$ for all channels, i. e. the hybridization is characterized by the parameter $\Gamma = \pi V^2 \mathcal{N}_c^0(0)$. The *c*- and *f*-states have a common chemical potential μ. The properties of the model depend in an essential way on the coupling constant $g = \Gamma/\pi|E_f - \mu|$, where $E_f = \sum_i \mathcal{L}_i E_f^i/\mathcal{L}$ and on the CF splittings. For $\mathcal{L} > 2$ and strong correlation between the *f*-electrons, the condition $n_f \leq 1$ makes the model extremely asymmetric; $n_f \simeq 1$ can only be reached for very small g. An increase in g gives rise to a monotonic reduction of n_f. An application of pressure or chemical pressure (doping) to Ce systems is modeled by an increase of the bare coupling g, which decreases n_f. In the case of Europium the non-magnetic $4f^6$ state is a Hund's singlet and the magnetic state is a degenerate $4f^7$ Hund's octet with full rotational invariance. The Eu ion fluctuates between the two configurations by exchanging a single electron with the conduction band and we model the pressure effects in the same way as for Ce. In the case of Ytterbium, the non-magnetic state is the full-shell $4f^{14}$ configuration and the magnetic one is the $4f^{13}$ configuration, which can be split by the CF. Here, pressure or chemical pressure reduce g and enhance the number of *f*-holes.

For constant hybridization, the charge current density operator is given by

$$\hat{\mathbf{j}} = e \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}, \qquad (12)$$

where σ labels the symmetry channels (irreducible representations to which the *c*-electrons belong) and $\mathbf{v}_{\mathbf{k}} = \nabla \epsilon(\mathbf{k})$ is the velocity of unperturbed *c*-electrons. Calculating the heat current density operators for a constant hybridization in $\mathbf{k}$-space we verify explicitly the Jonson-

Mahan theorem[?] and find for each symmetry channel the static conductivity satisfies

$$\sigma(T) = \int d\omega \left(-\frac{df}{d\omega}\right) \Lambda(\omega, T) \qquad (13)$$

and the thermopower satisfies

$$\alpha(T) = -\frac{1}{|e|T} \frac{\int d\omega \left(-\frac{df}{d\omega}\right) \omega \Lambda(\omega, T)}{\int d\omega \left(-\frac{df}{d\omega}\right) \Lambda(\omega, T)}. \qquad (14)$$

The excitation energy ω is measured with respect to μ, $f(\omega) = 1/[1 + \exp(\beta\omega)]$ is the Fermi-Dirac distribution function and $\Lambda(\omega, T)$ is the charge current - charge current correlation function[?] (our result differs from Mahan's by an additional factor of e^2 from the charge current operators). Note, the factor $(-df/d\omega)$ restricts the integration range in (13) and (14) to the Fermi window, $|\omega| \leq k_B T$. The main contribution to transport integrals comes from the $\mathbf{k}$-points in the vicinity of the renormalized Fermi surface (FS) In the low-temperature FL limit, the charge current - charge current correlation function is approximately found from the reducible vertex function by

$$\Lambda(\omega, T) = \frac{e^2}{V} \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}}^2 G_c^\sigma(\mathbf{k}, \omega + i\delta) G_c^\sigma(\mathbf{k}, \omega - i\delta)$$
$$\times \quad \gamma^\sigma(\mathbf{k}, \omega + i\delta, \omega - i\delta). \qquad (15)$$

Here $G_c^\sigma(\mathbf{k}, \omega \pm i\delta)$ are the momentum and energy-dependent retarded and advanced Green's function of the conduction electrons and $\gamma^\sigma(\mathbf{k}, \omega + i\delta, \omega - i\delta)$ is the analytic continuation from the imaginary axis into the complex plane of the (reducible) scalar vertex function $\gamma^\sigma(\mathbf{k}, i\omega_n)$, which is defined by the diagrammatic expansion of the current-current correlation function[?] . It is a challenge to determine the conductivity and the thermopower for the periodic Anderson model with the crystal field split states, which satisfy the constraint $n_f \leq 1$, and we perform the calculations for two simplified cases.

In the case of a short mean-free path, the thermopower is obtained by the 'poor man's' mapping, which takes into account the CF splitting but neglects the coherence. That is, the scattering of conduction electrons on the $4f$ ions, which gives rise to a low conductivity, is treated as an impurity problem. Using the identity $G_c(\mathbf{k}, \omega^+) G_c(\mathbf{k}, \omega^-) = -A_c(\mathbf{k}, \omega)/\text{Im } \Sigma_c(\omega^+, T)$, where Σ_c is the self-energy and

$$A_c(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im } G_c(\mathbf{k}, \omega^+) \qquad (16)$$

the spectral function of *c*-electrons, obtains

$$\Lambda(\omega, T) = \frac{-e^2}{V \text{ Im} \Sigma_c(\omega^+, T)} \sum_{\mathbf{k}} v_{\mathbf{k}}^2 A_c(\mathbf{k}, \omega). \qquad (17)$$

This can be further simplified taking into account that in the narrow region of $(\mathbf{k}, \omega)$–space we approximate $v_{\mathbf{k}}^2$ by its FS average, $\langle v_{k_F}^2 \rangle$. This gives the usual result,

$$\Lambda(\omega, T) = e^2 \langle v_{k_F}^2 \rangle \mathcal{N}_c(\omega) \, \tau(\omega, T), \qquad (18)$$

where the renormalized c-DOS is defined by

$$\mathcal{N}_c(\omega) = \sum_{\mathbf{k}} A_c(\epsilon_{\mathbf{k}}, \omega), \qquad (19)$$

and the transport relaxation time is

$$\tau(\omega, T) = \frac{1}{-\mathrm{Im}\ \Sigma_c(\omega^+, T)}. \qquad (20)$$

When the mean free path is long, which is the case of the stoichiometric compounds at low temperatures, the coherent scattering has to be taken into account. However, in this temperature range the excited CF states are unoccupied and the calculations can be performed using the spin-degenerate periodic Anderson model. The effective low-temperature degeneracy is determined by the CF ground state. The charge current - charge current correlation function is determined exactly within DMFT, where the vertex corrections vanish[?] and

$$\Lambda(\omega, T) = \frac{e^2}{V} \sum_{\mathbf{k}\sigma} \mathbf{v}_{\mathbf{k}}^2 \left[\mathrm{Im} G_c^\sigma(\mathbf{k}, \omega + i\delta) \right]^2. \qquad (21)$$

This form is particularly useful if $G_c^\sigma(\mathbf{k}, \omega + i\delta)$ is known for all $\mathbf{k}$ and ω points; we use it for evaluating the Falicov-Kimball model[? ?], since it does not have FL behavior in general. For the FL at low temperature we use Eq. (15) instead of Eq. (21) since it is the dominant contribution when $T \to 0$.

In what follows we provide the details the 'poor man's' and the FL approach. The overall behavior of the periodic Anderson model is then easily obtained by interpolating between the low-temperature FL solution and the high-temperature 'poor man's' solution.

1. The 'poor man's' solution

The 'poor man's' solution of the periodic Anderson model is defined by the approximation $\Sigma_c(k, \omega^+) \simeq n_i T_{kk}(\omega^+)$, where $T_{kk}(\omega^+)$ is the single-ion scattering matrix on the real axis. The concentration of $4f$ ions is set to $n_i = 1$, and the transport relaxation time is obtain from Eq. (20). We can justify this approach if the mean free path of conduction electrons is sufficiently short, such that the coherent scattering can be neglected. Recent solution of the spin-1/2 model obtained by the DMFT+NRG shows[?] that the electrical resistance $\rho(T)$ increases rapidly and is very large at the temperature T_K at which $\alpha(T)$ has a maximum. For $T \geq T_K/2$ the DMFT+NRG shows that $\alpha(T)$ is very similar to the exact results[?] obtained for the single impurity spin-1/2 Anderson model. This indicates that the 'poor man's' approach provides a reliable description of the stoichiometric compounds above the FL regime and can be used to approximate $\alpha(T)$ for $T \geq T_K/2$. However, the single impurity model has to be solved by methods which can deal with large Coulomb correlation and the CF splitting.

The experimental results on the heavy Fermion and valence fluctuators provide additional support for the single impurity approach. The data show that the residual resistance of ternary and quaternary compounds like $EuCu_2(Ge_{1-x}Si_x)_2$, $CePt_{1-x}Ni_x$ and $YbIn_{1-x}Ag_xCu_4$ grows rapidly with x and for $0.3 \leq x \leq 0.8$ the mean free path is reduced by disorder to about a single lattice spacing. In these random alloys the electron propagation is incoherent even at $T = 0$ and the experimental data are very well described by the single impurity model down to lowest temperatures. At low doping and in stoichiometric heavy Fermion compounds with small ρ_0 the impurity description breaks down in the low-temperature regime. However, in these systems $\rho(T)$ and $\alpha(T)$ grow rapidly towards room temperature (RT) and attain large maxima at T_K^ρ and T_K, respectively. In the case of the degenerate f-states or small CF splitting, the data show[? ? ?] $T_K^\rho < T_K < RT$ and for $T \geq T_K^\rho/2$ there is not much difference between the stoichiometric compounds and doped systems. In the presence of the CF splitting, $\rho(T)$ has two maxima: a low-temperature one at T_K^ρ and a high-temperature one at T_ρ. The thermopower also exhibits two maximal[?] : a low-temperature one at $T_K > T_K^\rho$ and a high-temperature one at T_S. Since the mean free path is short for $T \geq T_K/2$, it is not really surprising that the thermopower of periodic systems and random alloys exhibit the same qualitative features above the FL regime. The experimental data also show that the functional form of $\alpha(T)$ is strongly affected by pressure or chemical pressure. The fact that all the qualitative features of the pressure-induced variations of $\alpha(T)$ are completely accounted for by the 'poor man's mapping' justifies, a posteriori, the approximation which neglects the coherent scattering of conduction electrons on the lattice of f-ions.

In the case of a single scattering channel (no CF splitting) the vertex corrections to the T-matrix vanish by symmetry and the conduction electron's self energy is given by $\Sigma_c(\omega^+) = V^2 G_f(\omega^+)$, where $G_f(\omega^+)$ is the retarded Green's function of the effective $\mathcal{L}$-fold degenerate single impurity Anderson model. In the case when the degeneracy is lifted by the CF splitting the vertex corrections do not vanish but we neglect them anyway and use

$$\Sigma_c(\omega^+) = \sum_{\Gamma} V_{\mathbf{k}\Gamma_i} G_{\Gamma_I}(\omega^+) V_{\Gamma_i \mathbf{k}'}. \qquad (22)$$

$V_{\Gamma \mathbf{k}} = \langle \Gamma | V | \mathbf{k} \rangle$ is the matrix element for the scattering between the conduction state $\mathbf{k}$ and the f-state belonging to the irrep Γ, and $G_\Gamma(\omega^+)$ is the corresponding Green's function of the single impurity Anderson model with the CF splitting. We calculate $G_\Gamma(\omega^+)$ by the NCA and obtain $\alpha(T)$ from Eqs. (14) and (18).

In the limit of large asymmetry and infinite correlation, the NCA solution shows that the single impurity Anderson model has a universal low-temperature scale, given by the Kondo temperature T_K. The T_K is large for large $\mathcal{L}$ and small Δ_{CF}, and T_K is small for small $\mathcal{L}$ and large Δ_{CF}. This shows that T_K decreases rapidly as the