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On the thermoelectricity of correlated electrons in the zero-temperature limit

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Abstract
The Seebeck coefficient of a metal is expected to display a linear temperature dependence in the zero-temperature limit. To attain this regime, it is often necessary to cool the system well below 1 K. We put under scrutiny the magnitude of this term in different families of strongly interacting electronic systems. For a wide range of compounds (including heavy-fermion, organic and various oxide families) a remarkable correlation between this term and the electronic specific heat is found. We argue that a dimensionless ratio relating these two signatures of mass renormalization contains interesting information about the ground state of each system. The absolute value of this ratio remains close to unity in a wide range of strongly correlated electron systems.

1. Introduction

Almost two decades ago, Kadowaki and Woods (KW) noticed a universal correlation between two distinct signatures of electronic correlation in heavy-fermion systems [1]. In these compounds, due to a large density of states at the Fermi energy, both the electronic specific heat ($\gamma = C_{el}/T$) and the T^2 term in the temperature dependence of the resistivity (A with $\rho = \rho_0 + AT^2$) are enhanced. KW defined a ratio linking these two quantities (A/γ^2) and observed that for various heavy-fermion compounds the magnitude of this ratio is close to a value ($a_0 = 1.0 \times 10^{-5}$ $\mu\Omega$ cm (mol K/mJ)^2), which is an order of magnitude higher than the ratio observed in simple metals [1, 2]. It has been argued that the proportionality $A \propto \gamma^2$ ratio reflects the large energy dependence of the conduction electron's self-energy [2]. More recently, Tsujii *et al* [3] have reported that in many Yb-based compounds the KW ratio is considerably smaller. This has been explained by taking into account the orbital degeneracy of the ground state [4].

During recent years, the discovery of T^2 behaviour in other remarkable Fermi liquids, such as $SrRu_2O_4$ [5], LiV_2O_4 [6], $La_{1.7}Sr_{0.3}CuO_4$ [7], and Na_xCoO_2 [8], has led to the extension of the KW plot beyond the heavy-fermion compounds. In many of these metallic oxides, the KW ratio is found to be intriguingly enhanced and the enhancement has been attributed to unusually large electron–electron scattering.

A Fermi liquid is also characterized by the Wilson ratio ($R_W = \frac{\pi^2 k_B^2}{3\mu_B^2}\frac{\chi_0}{\gamma}$, where k_B and μ_B are respectively the Boltzmann constant and the Bohr magneton) which links γ to the Pauli spin susceptibility, χ_0 [9]. This dimensionless number is equal to unity for free electrons and increases up to two for a single Kondo impurity of spin 1/2 [10]. Indeed, such an enhanced Wilson ratio has been observed in a variety of strongly correlated electronic systems [11, 5, 7].

In this paper, we focus on a third ratio connecting two distinct consequences of strong correlations among electrons. We begin by recalling that the thermopower of a free electron gas is linear as a function of temperature. Moreover, the magnitude of the Seebeck coefficient in this regime is directly proportional to the density of states at Fermi energy. A dimensionless ratio links the Seebeck coefficient to the electronic specific heat through the Faraday number and is equal to -1 for free electrons. Our examination of the available experimental data leads to the intriguing conclusion that this ratio remains close to ± 1 for a wide range of strongly interacting electronic systems in spite of their complex band structure. We will argue that scrutinizing this ratio in a given compound is a source of insight into the properties of the ground state.

2. The Seebeck coefficient of the free electron gas

In a Boltzmann picture, the thermo-electric power, also known as the Seebeck coefficient, is given by [12–14]

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\left(\frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon}\right)_{\epsilon_F}. \tag{1}$$

Here, e is the elementary charge and ϵ_F the Fermi energy. The function $\sigma(\epsilon)$, defined as [12]

$$\sigma(\epsilon) = e^2\tau(\epsilon)\int \frac{d\mathbf{k}}{4\pi^3}\delta(\epsilon - \epsilon(\mathbf{k}))v(\mathbf{k})v(\mathbf{k}) \tag{2}$$

yields the dc electric conductivity of the system for $\epsilon = \epsilon_F$, where $\mathbf{k}$ is the electron wavevector and $\tau(\epsilon)$ is the scattering time. Inserting this expression into equation (1) yields [12]

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\left[\left(\frac{\partial \ln \tau(\epsilon)}{\partial \epsilon}\right)_{\epsilon_F} + \frac{\int d\mathbf{k}\,\delta(\epsilon_F - \epsilon(\mathbf{k}))\mathbf{M}^{-1}(\mathbf{k})}{\int d\mathbf{k}\,\delta(\epsilon_F - \epsilon(\mathbf{k}))v(\mathbf{k})v(\mathbf{k})}\right] \tag{3}$$

where $\mathbf{M}_{ij}^{-1}\left(= \pm\frac{1}{\hbar^2}\frac{\partial^2\epsilon(\mathbf{k})}{\partial k_i \partial k_j}\right)$ is the inverse of the effective mass tensor. This expression is a testimony to the difficulty of interpretation of the temperature dependence of thermopower. It contains information on both transport and thermodynamic properties of the system. The scattering time and its energy dependence are only present in the first term of the right-hand side of the equation. The second term is purely thermodynamic.

In the simple case of a free electron gas, the second term of equation (3) is equal to $\frac{3}{2\epsilon_F}$ [12, 15]. Moreover, in the zero-energy limit, the energy dependence of the scattering time can be expressed as a simple function [15]:

$$\tau(\epsilon) = \tau_0\epsilon^{\zeta} \tag{4}$$

which yields $\left(\frac{\partial \ln \tau(\epsilon)}{\partial \epsilon}\right)_{\epsilon=\epsilon_f} = \zeta/\epsilon_F$ for the first term. The simplest case implies an energy-independent relaxation time ($\zeta = 0$). However, alternative cases such as $\zeta = -1/2$ are conceivable [15, 14]. The latter corresponds to a constant mean free path, ℓ_e, which implies $\tau = \ell_e/v \propto \epsilon^{-1/2}$.[Note 4]

This leads to a very simple expression for the thermopower of the free electron gas:

$$S = -\frac{\pi^2}{3}\frac{k_B^2}{e}\frac{T}{\epsilon_F}\left(\frac{3}{2}+\zeta\right). \tag{5}$$

This textbook expression gives a correct estimation of the magnitude of thermopower in real metals. It also indicates that whenever the Fermi energy is replaced by a different and smaller energy scale the Seebeck coefficient is expected to increase. The Fermi energy is related to the carrier concentration n and to the density of states, $N(\epsilon)$. For free electrons, the link is given by $N(\epsilon_F) = 3n/(2\epsilon_F)$. Using this expression, equation (5) can be written as

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{N(\epsilon_F)}{n}\left(1+\frac{2\zeta}{3}\right). \tag{6}$$

This equation is strikingly similar to the familiar expression for the electronic specific heat of free electrons [12–14]:

$$C_{el} = \frac{\pi^2}{3}k_B^2 T N(\epsilon_F). \tag{7}$$

In this regime, as Ziman has put it [13], thermopower probes the specific heat per electron. In other words (and assuming $\zeta = 0$): $S = C_{el}/ne$, where the units are V K^{-1} for S, J K^{-1} m^{-3} for C_{el} and m^{-3} for n. However, in order to compare different compounds, it is common to express $\gamma = C_{el}/T$ in J K^{-2} mol^{-1} units. Therefore in order to focus on the S/C_{el} ratio, let us define the dimensionless quantity

$$q = \frac{S}{T}\frac{N_{Av}e}{\gamma} \tag{8}$$

where N_{Av} is the Avogadro number. The constant $N_{Av}e = 9.6\times10^5$ C mol^{-1} is also called the Faraday number. For a gas of free electrons with $\zeta = 0$ (the simplest case), q is equal to -1. In the case of an energy-independent mean free path, implying $\zeta = -1/2$, q becomes equal to $-2/3$. Now, if one imagines replacing the free electrons by free holes (that is assuming a hollow spherical Fermi surface) then q would become equal to +1 and to +2/3.

Note that the conversion factor assumes that there is one itinerant electron per formula unit which is often (but not always) the case. Whenever the density of carriers is lower (higher) than 1 e^-/fu, the absolute magnitude of q is expected to be proportionally larger (smaller) than unity.

Now we turn our attention to the real metals.

3. Thermoelectricity in real metals

At a first glance, the relevance of this picture for a *quantitative* description of thermopower in real metals is far from obvious. Even in alkali metals which present quasi-spherical Fermi surfaces the temperature dependence of the Seebeck coefficient is not linear, and in the case of lithium it is unexpectedly positive (at least down to the lowest temperatures investigated) [15]. There are a number of well known reasons behind this inadequacy.

First of all, a thermal gradient produces a lattice heat current in addition to the electronic one. Due to electron–phonon coupling, this leads to an additional contribution to thermopower dubbed 'phonon drag' [15], which adds up to the 'diffusion thermopower'. The latter is the

[4] In the $T = 0$ limit, an energy-independent ℓ_e, corresponding to the average distance between two defects, is usually taken for granted. This is thought to be the case even in presence of strong correlations [16].

signal generated by the diffusive movement of electrons in the absence of the phononic current. Phonon drag dominates the temperature dependence of many metals in a wide temperature range. (An analogous magnon-drag phenomenon occurs in magnetically ordered metals.) We recall that the phonon-drag term is proportional to the lattice specific heat and the latter varies as T^3 at low temperatures. Therefore, it does not contribute to an eventually linear Seebeck coefficient at very low temperatures and does not constitute a complication in the $T = 0$ limit.

Even the diffusion thermopower of real metals cannot be reduced to the simple picture of the previous section. Since there are different types of scattering centre interacting with various types of carrier, the deconvolution of different contributions is most often an impossible task. The total thermopower is expected to be a weighted sum of different contributions. For example, the Nordheim–Gorter rule, which corresponds to the Matthiessen rule for resistivity, treats the case of a one-band metal in presence of several types of scatterer. According to this rule, $S = \frac{\sum \rho_i S_i}{\sum \rho_i}$, where the index i designates distinct contributions to resistivity, ρ_i, and thermopower, S_i [15]. In the case of several types of carrier, one expects each contribution, S_j, to be weighted by the respective conductivity, σ_j. A combination of the two situations should occur in real multi-band metals [17]. An obvious obstacle for the application of the free-electron-gas picture (even at $T = 0$) to a multi-band metal appears: for each band, thermopower S_j can be positive or negative but the sign of the corresponding electric conductivity (and specific heat) is always positive. Therefore, in principle, the absolute value of the weighted sum which yields the overall thermopower could be considerably reduced compared to the single-band picture. This discrepancy is expected to be particularly large in the case of metals with an even number of electrons per Brillouin zone. Even in the simplest of divalent metals, the Fermi surface presents a remarkably complex structure [12].

The Mott formula for transition metals [18, 19] is a celebrated milestone in the understanding of thermoelectricity in multi-band metals. In this two-band picture, light electrons of the band associated with the s orbital coexist with the heavier ones of the d band. The dominant mechanism is the scattering of the light electrons from the wider (s) to the narrower (d) band, due to the larger density of states in the latter. This leads to an additional scattering rate which is proportional to the density of state of the d band: $\frac{1}{\tau} \propto N_{\rm d}(\epsilon_{\rm F})$. As a result of this, the thermopower presents a component proportional to $\left(-\frac{1}{N_{\rm d}(\epsilon)}\frac{\partial N_{\rm d}(\epsilon)}{\partial \epsilon}\right)_{\epsilon=\epsilon_{\rm F}}$ which dominates the free-electron component [15]. The Mott formula provides a qualitative explanation for the enhanced diffusion thermopower in transition metals. It successfully predicts that the sign of the additional contribution is different for elements situated at the beginning and at the end of the series as a result of the occupancy (or vacancy) of the d orbital.

All these considerations indicate that thermoelectricity in usual metals (even at reasonably low temperatures) is dominated by many factors which do not correlate with their specific heat. This may partly explain one curious anomaly. In spite of being known for many decades, widely mentioned [12–14] and commented on in detail [15], the free-electron-gas picture of thermoelectricity has not been *quantitatively* tested. There is no trace of a systematic investigation of real metals verifying the simple correlation between specific heat and thermopower according to equations (6) and (7).

Let us focus on the specific case of heavy-fermion compounds which, due to their giant specific heat, are a natural playground for this concept.

4. Thermoelectricity of heavy electrons in the zero-temperature limit

In heavy-fermion compounds (HFCs), the effective mass, m^*, of quasi-particles is enhanced mainly due to Kondo local fluctuations around each f-electron atom. A new temperature scale,

$T_K \propto 1/m^*$, appears which defines a Fermi energy $\epsilon_f = k_B T_K$ much smaller than in common metals (for a recent review see [20]).

The investigation of thermoelectricity in HFCs started more than two decades ago [21]. An early study on Ce- and Yb-based compounds displaying a moderate mass enhancement (the so-called intermediate-valence compounds) established a number of features in qualitative agreement with an extension of the Mott formula to f electrons [21, 22]. Both the large enhancement of thermopower up to a value close to k_B/e and the occurrence of a maximum at T_{max} corresponding roughly to the bandwidth of f electrons (the latter is inversely proportional to γ) are compatible with the Mott formula. In many cases, S was found to remain linear up to a substantial fraction ($\sim$1/3) of T_{max} and did not show a clear signature of entrance into the Fermi liquid regime. Moreover, the Mott formula provides a natural explanation for the positive (negative) sign of thermopower for Ce- (Yb-) based compounds in a manner analogous to the case of transition metals.

During the last two decades, the exploration of numerous HFCs led to a partial understanding of many features of thermoelectricity in these compounds. At room temperature, the interplay of incoherent Kondo scattering with the crystal field (CF) effect leads to a huge S at room temperature. No experimental systematics appear below the temperature T_{CF} corresponding to the crystal field energy scale. Various interpretations have been proposed to explain why thermopower varies from large and positive (as in the case of $CeCu_6$) to large and negative (as for $CeCu_2Si_2$) among various compounds. On the other hand, high-pressure studies on cerium compounds [23–26] indicate that under pressure the positive sign is systematically favoured, presumably because the system is driven towards an intermediate-valence state (see [26] for a detailed discussion). On the theoretical side, in the absence of a microscopic theory of thermoelectricity in a Kondo lattice, most authors have focused on the single-impurity case [27–29] (for a recent survey on theory see [30]).

Nevertheless, the magnitude of S/T in the zero-temperature limit and its eventual correlation with γ in HFC has not been a focus of attention. Although such a correlation explicitly appears in the papers by Read and his co-workers [28, 29], no experimental study has been devoted to this issue. Furthermore, for a Kondo impurity of spin 1/2 with a complete localization of the $4f^1$ charge (that is when $n_f = 1$), the thermopower is predicted to collapse at very low temperature [30]. As we will see below, this is not the case of cerium Kondo lattices.

With all these considerations in mind, let us examine the magnitude of S/T in the zero-temperature limit from an experimental point of view. In order to address this issue, it is useful to plot the old thermopower data in a different fashion.

Figure 1 displays the temperature dependence of S/T using the previously published data for four different Ce compounds. A polycrystal of $CeCu_2Si_2$ was studied by Sparn *et al* [31]. At zero field, thermopower remains negative down to T_c ($\sim$0.65 K). But, with the application of a magnetic field and the destruction of superconductivity a positive S/T emerges. Measurements on a polycrystal of $CeAl_3$ were reported by Jaccard and Flouquet [33]. Single crystals of $CeRu_2Si_2$ were studied by Amato *et al* [32] and here we have plotted these data for $S \perp c$. Sato *et al* measured a single crystal of $CeCu_6$ with the heat current along the [010] axis [34]. As seen in the figure, in the four cases a finite and positive S/T can be firmly extracted in the zero-temperature limit. Interestingly, in all these systems, the value obtained is not very far from the magnitude of γ/eN_{Av}. In the case of $CeCu_2Si_2$ and $CeAl_3$, the extracted S/T matches $\gamma/N_{Av}e$ within experimental uncertainty ($q \sim 1$). In the other two compounds the extracted magnitudes yield a q close to unity (1.7 for $CeCu_6$ and 0.7 for $CeRu_2Si_2$).

The persistent variation of S/T in the sub-kelvin temperature range indicates that the so-called Fermi-liquid regime in these cases is established only at very low temperatures. This is backed by a very careful study of thermopower down to 14 mK in $CeCu_6$ [34]. Indeed,

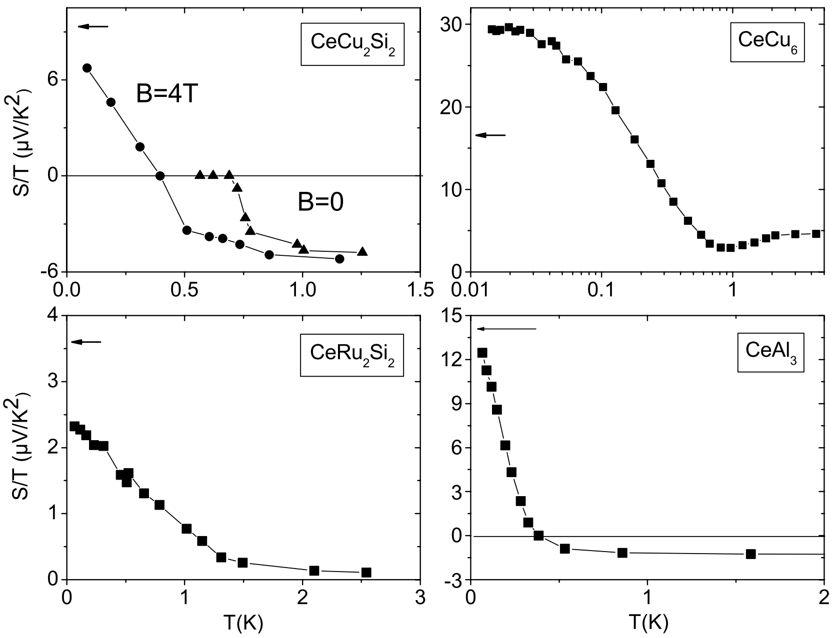

Figure 1. S/T as a function of temperature for four different Ce-based compounds using previously published data by three different groups [31–34]. In each panel, the horizontal vector points to the value corresponding to $\gamma/(N_{Av}e)$. Note the semi-logarithmic scale in the case of $CeCu_6$.

Sato *et al* reported that S/T becomes constant only below 30 mK, which is also the temperature associated with the emergence of a purely T^2 resistivity [34][5].

5. A short survey of various families

The specific heat of many remarkable metals is well documented in technical literature. This is not, however, the case for thermoelectric power. In particular, the magnitude of S/T in the zero-temperature limit is almost never explicitly reported. In table 1, we have compiled the reported data for a number of compounds. We have tried to restrict ourselves to the cases where the extrapolation of data at the lowest reported temperature to $T = 0$ does not appear to produce any significant change in the sign and/or magnitude of S/T. In the case of low-dimensional systems, we have taken the *in-plane* value. As seen in the table, in most cases the coefficient q is not very far from unity. This can also be seen in figure 2 which plots S/T as a function of γ. Each data point represents a compound and together they constitute a cloud around a straight line representing $N_{Av}e/\gamma$. Below, we consider different families of compounds represented in table 1.

Heavy fermions

In all Ce-based compounds listed in the table, the ratio q remains close to unity. As γ extends over two orders of magnitude from $CeSn_3$ to $CeCu_6$, this correlation between specific heat and

[5] The carefully extracted A-term in $CeCu_6$ [34] (71 $\mu\Omega$ cm K^{-2}) yields an anomalously large KW ratio. Interestingly, however, the discrepancy vanishes if one directly computes the ratio $A/(S/T)^2$ using values obtained below 30 mK. The anomaly seems to stem from the anisotropy of transport. It is greatly reduced when one compares γ with values of S/T and A averaged along in-plane and out-of-plane directions.

Table 1. Reported magnitudes of linear thermopower and specific heat for a number of metals. The significance of the coefficient $q = \frac{S}{T}\frac{N_{Av}e}{\gamma}$ is discussed in the text.

Compound	S/T (μV K^{-2})	Remarks	γ (mJ mol K^{-2})	q
$CeCu_2Si_2$ ($B = 4$ T)	9 [31]	Polycrystal	950 [53]	0.9
$CeCu_6$	29 [34]	Along [010]	1600 [54]	1.7
$CeAl_3$	14 [33]	Polycrystal	1400 [33]	1.0
$CeRu_2Si_2$	2.4 [32]	In-plane	350 [55]	0.7
$CeCoIn_5$ ($B = 6$ T)	6 [56]	In-plane	650 [57]	0.9
$CePt_2Si_2$	2 [58]	Along [110]	130 [59]	1.5
$CeSn_3$	0.18 [60]	Polycrystal	18 [61]	1.0
CeNiSn	50 [62]	Polycrystal	45 [63]	107
$YbCu_{4.5}$	−7 [64]	Polycrystal	635 [65]	−1.1
YbCuAl	−3.6 [66]	Polycrystal	267 [67]	−1.3
$YbCu_4Ag$	−3.6 [68]	Polycrystal	200 [69]	−1.7
$YbCu_2Si_2$	−1 [21, 70]	Polycrystal	135 [71]	−0.7
$YbAl_3$	−0.6 [21]	Polycrystal	45 [72]	−1.3
$YbInAu_2$	−0.75 [70]	Polycrystal	40 [73]	−1.8
UPt_3	Unknown	None observed [36]	430 [36]	—
UBe_{13} ($B = 7.5$ T)	−12 [37]	Polycrystal	1100 [74]	−1.1
UNi_2Al_3	0.24 [38]	Polycrystal	120 [75]	0.2
UPd_2Al_3	0.4 [38]	$S \perp c$	150 [76]	0.3
URu_2Si_2	−3 [39]	$S \perp c$	65 [77]	−4.5
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br	−0.4 [42]	In-plane	22 [78]	−1.7
κ-(BEDT-TTF)$_2$Cu(NSC)$_2$	−0.15 [43]	In-plane	25 [79]	−0.6
(TMTSF)$_2$ClO$_4$	Unknown	No report found	11 [80]	—
Sr_2RuO_4	0.3 [45]	In plane	38 [5]	0.8
$SrRuO_3$	Unknown	No report found	30 [81]	—
$Sr_3Ru_2O_7$	Unknown	No report found	38 [82]	—
$SrRhO_3$	0.03 [83]	Polycrystal	7.6 [84]	1.3
Na_xCoO_2	0.4 [46]	In-plane	48 [47]	0.8
$La_{1.7}Sr_{0.3}CuO_4$	0.18 [48]	Ceramic	6.9 [7]	2.5
$Bi_2Sr_2CuO_{6+\delta}$	−0.25 [49]	Ceramic	8.7 [85]	−2.8
$NbSe_2$	0.3 [52]	In-plane	17 [86]	1.7
Pd	−0.08 [17]	Polycrystal	9.5 [87]	−0.8
Cu	−0.028 [51]	Along [231]	1.6 [12]	−1.7
Constantan (43% Ni–57% Cu)	−0.25 [15]	Wire	27.4 [88]	−0.9

thermopower is indeed remarkable. Note that the sign of thermopower is positive for all Ce-based compounds. On the other hand, the thermopower of Yb compounds which often display a clearly linear temperature dependence in a reasonable temperature window is negative. In all cases the magnitude of a S/T yields $q \sim -1$.

The table also includes CeNiSn, a so-called 'Kondo insulator'. Given the extremely low carrier density of the system, the very large magnitude of q ($\sim$107) is not a surprise. The Hall data suggest a carrier density of 0.01 e^-/fu at 5 K and still lower below [35]. The magnitude of q is in good agreement with this estimation.

The situation is different for the U-based compounds. An early study of UPt_3 did not detect a finite S/T at sub-kelvin temperatures [36]. (The magnitude of S/T above T_c yields $q \sim 0.2 - 0.3$.) In UBe_{13} thermopower changes strongly with magnetic field. The largest field applied (7.5 T) in the only reported study [37] was not enough to destroy superconductivity.

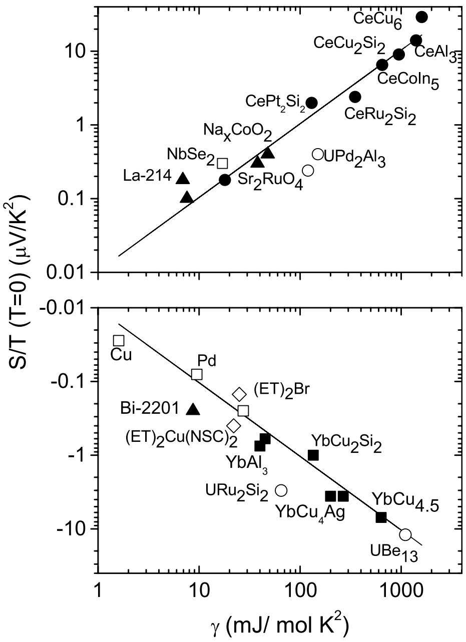

Figure 2. S/T versus γ for the compounds listed in table 1. Solid circles (squares) represent Ce (Yb) heavy-fermion systems. Uranium-based compounds are represented by open circles, metallic oxides by solid triangles, organic conductors by open diamonds, and common metals by open squares. For some data points, due to the lack of space, the name of the compound is not explicitly mentioned. See table 1 for the missing names. The two solid lines represent $\pm\gamma/(eN_{\text{Av}})$.

Taking the value of S/T in the presence of such a field at $T \sim 0.8$ K yields a $q \sim -1$. For the other U-based compounds of the list, no data are available for low temperatures and in the presence of a magnetic field needed to destroy superconductivity. In the $T = 0$ limit, the magnitude (and the sign) of S/T in UPd_2Al_3 and UNi_2Al_3 could be somewhat different from what is given in table 1, which gives the zero-temperature extrapolation of the data reported for $T > 2$ K [38]. In the case of URu_2Si_2 [39] there is a simple reason for expecting a q much larger than unity. Indeed, both Hall effect measurements [40] and band calculations [41] indicate that the carrier density at low temperatures is very small (about 0.05 e^-/U atom). Thus the apparently large q (∼4.5) is a consequence of an enhanced conversion factor between γ and S/T. In fact, given such a small carrier density in URu_2Si_2, a q as large as 20 and sensibly larger than what is given in the table is expected. Clearly, a fresh look at the thermopower of U-based compounds in the subkelvin regime would be very useful. Even at this stage, however, the problem of the 4f-electron localization in uranium compounds appears to be more complex than in the case of Ce and Yb compounds. Notably, the sign of the thermopower is strikingly different among different compounds.

Organic superconductors

Few studies of thermoelectricity in organic superconductors are available. The table indicates data found in literature for two members of the κ-(BEDT-TTF)$_2$X family of quasi-two-dimensional superconductors. While γ is roughly the same in κ-(BEDT-TTF)$_2$Cu(NSC)$_2$ and in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, two different groups report sensibly different values of thermopower at the onset of superconductivity for each compound [42, 43]. In neither case is S purely linear at this temperature. The reported results point to a q in the 0.6–1.7

range. Note that the in-plane thermopower of these compounds is anisotropic and the values of the table correspond to the (larger) negative ones attributed to the carriers associated with the quasi-one-dimensional sheet of the Fermi surface [44]. Determination of the magnitude of the low-temperature S/T in the metallic state of the Bechgaard salts (the $(TMTSF)_2X$ family) would be very useful for the purpose of this investigation. The zero-temperature thermoelectricity of organic conductors with their simple and well defined Fermi surfaces appears to be largely unexplored.

Metallic oxides

The table includes a number of metallic oxides known to be remarkable Fermi liquids. The thermopower of Sr_2RuO_4 has been studied down to 4.2 K [45]. It displays an almost linear temperature dependence over an extended temperature range. Taking the value of S/T at 4.2 K yields $q = 0.8$. We did not find any report on the thermoelectricity of two other ruthenate compounds displaying a comparable mass enhancement in their specific heat. It is interesting to observe that available data for thermopower [46] and specific heat [47] of the recently discovered cobaltite compound (Na_xCoO_2) also points to a q close to unity. Ando *et al* [47] have already made a qualitative link between the giant thermopower and the enhanced specific heat in this case.

Let us underline the interesting case of the heavily overdoped cuprate $La_{1.7}Sr_{0.3}CuO_4$. At this doping level, superconductivity is completely absent and resistivity displays a purely T^2 temperature as expected for a Fermi liquid [7]. Now, a study of thermopower in $La_{2-x}Sr_xCuO_4$ reports that for $x = 0.3$, in contrast with lower doping levels, thermopower becomes almost linear below 20 K with $S/T \sim 0.18\ \mu V\ K^{-2}$ [48]. This, combined with $\gamma \sim 6.9$ mJ mol^{-1} K^{-2} [7], yields $q \sim 2.5$. The result is far from anomalous and is to be compared with 3.3, which is the expected value of q for a system with a carrier density of 0.3 e^-/unit cell. Interestingly, a linear term, slightly larger and *with an opposite sign*, can be extracted from the data reported for overdoped Bi-2201 at a comparable doping level ($p = 0.29$). Future studies on single crystals would be very useful to refine the issue. An intensive debate on thermopower of the cuprates has focused on the influence of the doping level on the magnitude of Seebeck coefficient at high temperatures [50].

Common metals

The extraction of an intrinsic linear thermopower is particularly difficult in simple elemental metals. This is due to the small magnitude of thermopower at low temperatures and its sensitivity to the presence of a small concentration of impurities. We have found compelling data for very pure Cu [51] and for hydrogen-free Pd [17]. The value of S/T has been taken at the lowest reported temperature (1.5–2 K) which is below the last low-temperature structure in S. Interestingly, constantan, a Cu–Ni alloy widely used as a thermocouple, presents a linear S up to room temperature. Taking this quasi-constant S/T and γ yields a q close to -1. It is tempting to attribute the absence of any detectable phonon drag in this alloy to the presence of strong disorder which kills electron–phonon coupling. Finally, we have also included the data from a recent study on the charge-density-wave compound $NbSe_2$ [52] which presents a positive thermopower and $q \sim 1.7$.

6. Discussion and unanswered questions

The principal observation reported in this paper is presented in figure 2. Most of the systems considered lie close to the two lines representing $\pm\frac{\gamma}{N_{Av}e}$. In other words, in a wide range of different metals, one finds $0.5 < |q| < 2$. Moreover, in other cases which appear not to follow this general trend, the number of carriers per formula unit gives a satisfactory explanation for the magnitude of q.

Let us stress that, in spite of its conformity to the free-electron-gas picture, this observation does not lie on a solid understanding of microscopic properties. Many of the systems considered here have notoriously complicated Fermi surfaces. In a naive multi-band picture, the contribution of holelike and electron-like carriers would cancel out and lead to a more or less homogenous distribution of points between the two $\pm\frac{\gamma}{N_{\mathrm{Av}}e}$ lines. Clearly, this is not the case.

One may invoke an inherent asymmetry of mass renormalization between electrons and holes in each system. Take the case of cerium and ytterbium compounds. In Ce compounds, the *occupancy* of the f-level orbital is expected to lead to the formation of a narrow band which has a curvature opposite to the one formed in Yb compounds. Now, it is a tiny vacancy (ϵ) in the $4f^1$ content ($n_{\mathrm{f}} = 1 - \epsilon$) of the 4f shell which is responsible for the Kondo dressing and for the positive sign of the thermoelectric power in Ce compounds. In the Yb case, on the other hand, the excess in the 4f content (with respect to the trivalent state Yb^{3+}) leads to the negative sign of S. Note that such an explanation is quite different from the one resulting from the extension of the Mott formula which also correctly predicts the positive (negative) sign of thermopower for Ce (Yb) compounds. According to the latter, the sign of the thermopower is determined by $\partial N(\epsilon)/\partial\epsilon$ since it affects *the energy dependence of the scattering rate of the light electrons*. In other words, the sign of S is imposed by the first term of equation (3) and not the second which prevails in the simple free-electron-gas picture. Clearly, a rigorous theoretical investigation of this issue is required.

Let us also note that, within the current resolution, the experimental data presented in figure 2 do not allow us to detect any deviation from the general tendency for different families of correlated-electron systems. This is also remarkable, since large deviations from the KW value (from 0.04 a_0 in several Yb compounds [3] to 50 a_0 in Na_xCoO_2 [8]) have been reported. This may not be as surprising as it appears. There is a fundamental difference between the KW ratio and q. While the former compares the size of *inelastic* electron–electron scattering with the density of states at Fermi energy, the latter is a ratio of two zero-energy properties of the system. In this regard, it is more akin to the Wilson ratio. However, in contrast to the latter, it should mirror those anomalous transport properties which affect the energy dependence of the scattering rate.

Finally, we should mention that the observation reported here can be used as a tool for tracking non-trivial physics associated with an anomalous value of q at very low (yet finite) temperature. This is the case of several HF superconductors such as $CeCoIn_5$, UBe_{13} and $CeCu_2Si_2$ at the onset of superconductivity.

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References

[1] Kadowaki K and Woods S B 1986 *Solid State Commun.* **58** 507
[2] Miyake K, Matsuura T and Varma C 1989 *Solid State Commun.* **71** 507
[3] Tsujii N, Yoshimura K and Kosuge K 2003 *J. Phys.: Condens. Matter* **15** 1993
[4] Kontani H 2004 *J. Phys. Soc. Japan* **73** 515
[5] Maeno Y *et al* 1997 *J. Phys. Soc. Japan* **66** 1405

[6] Urano C, Nohara M, Kondo S, Sakai F, Takagi H, Shiraki T and Okubo T 2000 *Phys. Rev. Lett.* **85** 1052
[7] Nakamae S, Behnia K, Mangkorntong N, Nohara M, Takagi H, Yates S J C and Hussey N E 2003 *Phys. Rev.* B **68** R100502
[8] Li S Y, Taillefer L, Hawthorn D G, Tanatar M A, Paglione J, Sutherland M, Hill R W, Wang C H and Chen X H 2004 *Preprint* cond-mat/0401099
[9] Wilson K E 1975 *Rev. Mod. Phys.* **47** 773
[10] Yamada K 1975 *Prog. Theor. Phys.* **53** 970
[11] Lee P A, Rice T M, Serene J W, Sham L J and Wilkins J W 1986 *Comm. Cond. Matt.* **12** 99
[12] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (Philadelphia, PA: Saunders)
[13] Ziman J M 1972 *Principles of the Theory of Solids* (Cambridge: Cambridge University Press)
[14] Abrikosov A A 1988 *Fundamentals of the Theory of Metals* (Amsterdam: North-Holland)
[15] Barnard R D 1972 *Thermoelectricity in Metals and Alloys* (London: Taylor and Francis)
[16] Millis D A and Lee P A 1987 *Phys. Rev.* B **35** 3394
[17] Fletcher R, Ho N S and Manchester F D 1970 *J. Phys. C: Solid State Phys.* **3** S59
[18] Mott N F 1935 *Proc. R. Soc.* **47** 571
[19] Colquitt L, Fankhauser H R and Blatt F J 1971 *Phys. Rev.* B **4** 292
[20] Flouquet J 2004 *Progress in Low Temperature Physics* ed P W Halperin (Amsterdam: Elsevier) at press
[21] Jaccard D and Sierro J 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 409
[22] Mott N F 1982 *Valence Instabilities* ed P Wachter and H Boppart (Amsterdam: North-Holland) p 402
[23] Jaccard D, Mignot J M, Bellarbi B, Benoit A, Braun H F and Sierro J 1985 *J. Magn. Magn. Mater.* **47/48** 23
[24] Fierz C, Jaccard D, Sierro J and Flouquet J 1988 *J. Appl. Phys.* **63** 3899
[25] Jaccard D, Behnia K and Sierro J 1992 *Phys. Lett.* A **163** 475
[26] Link P, Jaccard D and Lejay P 1996 *Physica* B **225** 45
[27] Bickers N E, Cox D L and Wilkins J W 1985 *Phys. Rev. Lett.* **54** 230
[28] Newns D M and Read N 1987 *Adv. Phys.* **36** 799
[29] Houghton A, Read N and Won H 1987 *Phys. Rev.* B **35** 5123
[30] Zlatić V, Horvatić B, Milat I, Coqblin B, Czycholl G and Grenzebach C 2003 *Phys. Rev.* B **68** 104432
[31] Sparn G, Lieka W, Gottwick U, Steglich F and Grewe N 1985 *J. Magn. Magn. Mater.* **47/48** 521
[32] Amato A, Jaccard D, Sierro J, Lapierre F, Haen P, Lejay P and Flouquet J 1988 *J. Magn. Magn. Mater.* **76/77** 263
[33] Jaccard D and Flouquet J 1985 *J. Magn. Magn. Mater.* **47/48** 45
[34] Sato H, Zhao J, Pratt W P, Onuki Y and Komatsubara T 1987 *Phys. Rev.* B **36** 8841
[35] Iga T F *et al* 1998 *J. Magn. Magn. Mater.* **177–181** 277
[36] Sulpice A, Gandit P, Chaussy J, Flouquet J, Jaccard D, Lejay P and Tholence J L 1986 *J. Low Temp. Phys.* **62** 39
[37] Jaccard D, Flouquet J, Fisk Z, Smith J L and Ott H R 1985 *J. Phys. Lett.* **46** L-811
[38] Grauel A, Fromm D, Geibel C, Steglich F, Sato N and Komatsubara T 1993 *Int. J. Mod. Phys.* B **7** 50
[39] Sakurai J, Hasegawa K, Menovsky A A and Schweizer J 1988 *Solid State Commun.* **97** 689
[40] Schoenes J, Schoneneberger C, Franse J J M and Menovsky A A 1987 *Phys. Rev.* B **35** 5375
[41] Yamagami H and Hamada N 2000 *Physica* B **284/288** 1295
[42] Yu R C, Williams J M, Wang H H, Thompson J E, Kini A M, Carlson K D, Ren J, Whangbo M H and Chaikin P M 1991 *Phys. Rev.* B **44** 6932
[43] Sasaki T, Ozawa H, Koakutsu M and Fukase T 1993 *Synth. Met.* **103** 1944
[44] Mori T and Inokuchi H 1988 *J. Phys. Soc. Japan* **57** 3674
[45] Yoshino H, Murata K, Shirakawa N, Nishihara Y, Maeno Y and Fujita T 1996 *J. Phys. Soc. Japan* **65** 1548
[46] Terasaki I, Sasago Y and Uchinokura K 1997 *Phys. Rev.* B **56** R12685
[47] Ando Y, Miyamoto N, Segawa K, Kawata T and Terasaki I 1999 *Phys. Rev.* B **60** 10580
[48] Elizarova M V and Gasumyants V E 2000 *Phys. Rev.* B **62** 5989
[49] Konstantinovic Z, Le Bras G, Forget A, Colson D, Jean F, Collin G, Ocio M and Ayache C 2002 *Phys. Rev.* B **66** 020503
[50] Obertelli S D, Cooper J R and Tallon J L 1992 *Phys. Rev.* B **46** 14928
[51] Rumbo E R 1976 *J. Phys. F: Met. Phys.* **6** 85
[52] Bel R, Behnia K and Berger H 2003 *Phys. Rev. Lett.* **91** 066602
[53] Bredl C D, Horn S, Steglich F, Lüthi B and Martin R M 1984 *Phys. Rev. Lett.* **52** 1982
[54] Löhneysen H v, Pietrus T, Portisch G, Schlager H G, Schröder A, Sieck M and Trappmann T 1994 *Phys. Rev. Lett.* **72** 3262
[55] Lacerda A, de Visser A, Haen P, Lejay P and Flouquet J 1989 *Phys. Rev.* B **40** 8759

[56] Bel R, Behnia K, Nakajima Y, Izawa K, Matsuda Y, Shishido H, Settai R and Onuki Y 2004 *Phys. Rev. Lett.* **92** 217002

[57] Bianchi A, Movshovich R, Vekhter I, Pagliuso P G and Sarrao J L 2003 *Phys. Rev. Lett.* **91** 257001

[58] Bhattacharjee A K, Coqblin B, Raki M, Forro L, Ayache C and Schmitt D 1989 *J. Physique (France)* **50** 2781

[59] Ayache C, Beille J, Bonjour E, Calemczuk R, Creuzet G, Gignoux D, Najib A, Schmitt D, Voiron J and Zerguine M 1987 *J. Magn. Magn. Mater.* **63/64** 329

[60] Sakurai J, Kamimura H and Komura Y 1988 *J. Magn. Magn. Mater.* **76/77** 287

[61] Ikeda K and Gschneidner A A Jr 1982 *Phys. Rev.* B **25** 4623

[62] Hiess A, Geibel C, Sparn G, Bredl C D, Steglich F, Takabatake T and Fujii H 1994 *Physica* B **199/299** 437

[63] Izawa K, Suzuki T, Fujita T, Takabatake T, Nakamoto G, Fujii H and Maezawa K 1999 *Phys. Rev.* B **59** 2599

[64] Spendeler L, Jaccard D, Sierro J, François M, Stepanov A and Voiron J 1994 *J. Low Temp. Phys.* **94** 585

[65] Amato A, Fisher R A, Phillips N E, Jaccard D and Walker E 1990 *Physica* B **165/166** 389

[66] Jaccard D, Flouquet J and Sierro J 1985 *J. Appl. Phys.* **57** 3084

[67] Pott R, Schefzyk R, Wohlleben D and Junod A 1981 *Z. Phys.* B **44** 17

[68] Casanova R, Jaccard D, Marceneat C, Hamdaoui N and Besnus M J 1990 *J. Magn. Magn. Mater.* **90/91** 587

[69] Bauer E 1991 *Adv. Phys.* **40** 417

[70] Alami-Yadri K, Jaccard D and Andreica D 1999 *J. Low Temp. Phys.* **114** 135

[71] Sales B C and Viswanathan R 1976 *J. Low Temp. Phys.* **23** 449

[72] Havinga E E, Buschkow K H J and Vandal H J 1973 *Solid State Commun.* **13** 621

[73] Besnus M J, Kappler J P, Ravet M F, Meyer A, Lahiouel R, Pierre J, Siaud E, Nieva G and Sereni J 1986 *J. Less Common Met.* **120** 101

[74] Graf M J, Fortune N A, Brooks J S, Smith J L and Fisk Z 1989 *Phys. Rev.* B **40** 9358

[75] Geibel C *et al* 1991 *Z. Phys.* B **83** 305

[76] Geibel C *et al* 1991 *Z. Phys.* B **84** 1

[77] Maple M B, Chen J W, Dalichaouch Y, Kohara T, Rossel C, Torikachvili M S, McElfresh M W and Thompson J D 1986 *Phys. Rev. Lett.* **56** 185

[78] Andraka B, Jee C S, Kim J S, Stewart G R, Carlson K D, Wang H H, Crouch A V S, Kini A M and Williams J M 1991 *Solid State Commun.* **79** 57

[79] Andraka B, Kim J S, Stewart G R, Carlson K D, Wang H H and Williams J M 1989 *Phys. Rev.* B **40** 11 345

[80] Garoche P, Brusetti R and Bechgaard K 1982 *Phys. Rev. Lett.* **49** 1346

[81] Allen P B, Berger H, Chauvet O, Forro L, Jarlborg T, Junod A, Revaz B and Santi G 1996 *Phys. Rev.* B **53** 4393

[82] Perry R S *et al* 2001 *Phys. Rev. Lett.* **86** 2661

[83] Yamaura K, Huang Q, Young D P, Noguchi Y and Takayama-Muromachi E 2002 *Phys. Rev.* B **66** 134431

[84] Yamaura K and Takayama-Muromachi E 2001 *Phys. Rev.* B **64** 224424

[85] Mayama H, Okajima Y and Yamaya K 1998 *Phys. Rev.* B **57** 14470

[86] Sanchez D, Junod A, Muller J, Berger H and Lévy F 1995 *Physica* B **204** 167

[87] Mizutani U, Massalski T B, Bevk J and Vandervoort R R 1977 *J. Phys. F: Met. Phys.* **7** L63

[88] Ho James C, O'Neal H R and Phillips N E 1963 *Rev. Sci. Instrum.* **34** 782