Colossal Seebeck Coefficient of Hopping Electrons in $(\mathrm{TMTSF})_2\,\mathrm{PF}_6$

Yo Machida,[1] Xiao Lin,[2] Woun Kang,[3] Koichi Izawa,[1] and Kamran Behnia[2,*]
[1]*Department of Physics, Tokyo Institute of Technology, Meguro 152-8551, Japan*
[2]*LPEM (UPMC-CNRS) ESPCI, 75005 Paris, France*
[3]*Department of Physics, Ewha Womans University, Seoul 120-750, Korea*
(Received 6 January 2016; published 25 February 2016)

We report on a study of the Seebeck coefficient and resistivity in the quasi-one-dimensional conductor $(\mathrm{TMTSF})_2\,\mathrm{PF}_6$ extended deep into the spin-density-wave state. The metal-insulator transition at $T_{\mathrm{SDW}} = 12$ K leads to a reduction in carrier concentration by 7 orders of magnitude. Below 1 K, charge transport displays the behavior known as variable range hopping. Until now, the Seebeck response of electrons in this regime has barely been explored and is even less understood. We find that, in this system, residual carriers, hopping from one trap to another, generate a Seebeck coefficient as large as 400 k_B/e. The results provide the first solid evidence for a long-standing prediction according to which hopping electrons in the presence of the Coulomb interaction can generate a sizable Seebeck coefficient in the zero-temperature limit.

DOI: 10.1103/PhysRevLett.116.087003

The Seebeck coefficient, a measure of entropy per mobile particle [1–4], behaves differently in metals and insulators. In a Fermi-Dirac distribution, entropy is confined to an energy window centered at the Fermi energy with a width of k_BT. A fixed population of mobile electrons share this shrinking entropy when a metal is cooled down. Therefore, the diffusive Seebeck coefficient of a metal, below the degeneracy temperature, has an upper limit of $(\pi^2/3)(k_B/e) \sim 288\ \mu\mathrm{V/K}$, and its linear decrease with temperature reflects the quadratic temperature dependence of the energy shift between the chemical potential and the Fermi energy [3]. In an insulator, both entropy and mobile carriers vanish at zero temperature and the fate of the Seebeck coefficient depends on the relative rate of decrease in these two vanishing quantities. Since there is a well-defined energy gap, Δ, between the chemical potential and the nearest occupied energy level, the Peltier coefficient would be of the order of Δ and the kelvin relation implies that the Seebeck coefficient is proportional to the inverse of absolute temperature [2](see Fig. 1).

Any real insulator cooled down towards zero temperature, however, would end up entering a regime in which electronic transport is governed by carriers trapped in local defects and jumping from one site to another, a regime dubbed variable range hopping (VRH) [see Fig. 1(c)]. Would this impede the survival of a finite Seebeck coefficient in the zero-temperature limit? In spite of several theoretical proposals addressing this question [5–9], no satisfactory response has been given to this question. There is not theoretical consensus, as theorists have variously predicted that in insulators cooled down to the lowest achievable temperature, one is expected to see a vanishing [5], a finite [7], or a diverging (but unmeasurable) [9] Seebeck coefficient. On the experimental side, there is no track of a result providing a definitive answer to this question. A large Seebeck coefficient was found in early experiments on semiconducting silicon and germanium [10,11], but the data acquisition was interrupted at a temperature too high to resolve the asymptomatic response in the zero-temperature limit.

In this Letter, we present a study of electric resistivity and the Seebeck coefficient in $(\mathrm{TMTSF})_2\,\mathrm{PF}_6$, a quasi-one-dimensional conductor known to go through a nesting-driven spin-density-wave (SDW) instability at $T_{\mathrm{SDW}} = 12\,\mathrm{K}$. As the first pressure-induced organic superconductor [12], this Bechgaard salt has been subject to numerous studies during more than three decades (see Refs. [13,14] for recent reviews). According to our findings, below 1 K, electric resistivity displays a VRH temperature dependence and, concomitantly, the Seebeck coefficient rapidly increases with decreasing temperature, attaining a magnitude as large as 37 mV/K at $T \sim 0.1$ K. A quantitative description of our thermoelectric data is missing. Nevertheless, this is the first explicit experimental confirmation of the persistence of a finite Seebeck coefficient in an insulating solid in the zero-temperature limit. We argue that this arises as a consequence of the huge number of configurations available to a hopping electron. Our result is in qualitative agreement with that subset of theoretical proposals [7–9] which does not predict a vanishing fate for the Seebeck coefficient in a zero-temperature insulator.

Figure 2(a) shows the temperature dependence of the resistivity. As found in previous studies [15–18], the SDW transition drastically affects resistivity. Cooling the sample down to 0.2 K leads to a 7-order-of-magnitude enhancement in resistivity. Between 10 and 1 K, it follows that an activated behavior with a temperature dependence expressed as $\rho \propto \exp(\Delta/k_BT)$ and the extracted Δ of 20 K is comparable with what was previously reported and what is expected for a mean-field transition occurring at 12 K.

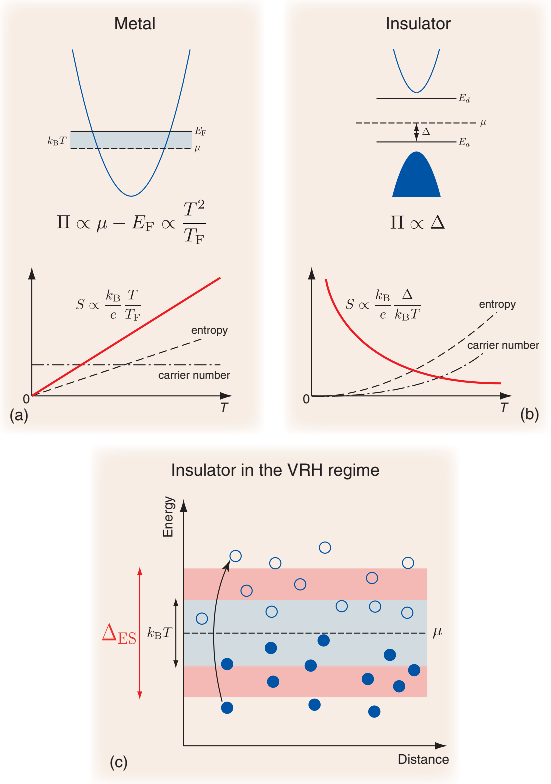

FIG. 1. (a) In a metal, the average thermal energy of a carrier, which sets the Peltier coefficient, Π, is quadratic in temperature. With decreasing temperature, mobile entropy shrinks but carrier number does not change. As a consequence of the kelvin relation ($\Pi = ST$), the Seebeck coefficient is T linear. (b) In an insulator, the average thermal energy of a carrier is T independent, set by the distance between the occupied level closest to the chemical potential. Both the carrier number and entropy vanish at zero temperature. If the carrier number decreases faster, the Seebeck coefficient will increase with decreasing temperature. (c) Real insulators will eventually enter the variable range hopping regime, where Coulomb interaction opens a soft gap (Δ_{ES}) in the vicinity of the chemical potential. What happens to the thermoelectric response at temperatures below this gap?

Below 1 K, we resolve a clear downward deviation from the activated behavior. Note that the millionfold increase in resistivity indicates that the carrier number has dropped to a level where there remains one mobile electron per 10^6 TMTSF. This puts an upper limit on the number of surviving residual carriers after cooling down to this temperature. This is an insulator, in the strict sense of the term: a solid with divergent unsaturated resistivity lacking mobile electrons at zero temperature.

One source of residual carriers at finite temperature is crystal defects, potential wells holding trapped charge carriers. Electric conductivity in this context is described along the lines first drawn by Mott [19] and dubbed variable range hopping [20,21]. In agreement with a previous study [16], we find that resistivity below 1 K can be described by the expression $\rho \propto \exp[(T/T_0)^{-\gamma}]$. However, our results cannot pin down the magnitude of γ, which can be a number between 1/3 and 1/2, as seen in Figs. 2(c) and 2(d).

The temperature dependence of the Seebeck coefficient is illustrated in Fig. 3. As seen in the inset, the SDW transition leads to a jump in the Seebeck coefficient, also reported by previous studies [22–24]. (See the Supplemental Material [25] for a discussion.) The Seebeck anomaly is concomitant with a sharp jump in resistivity and a lambda anomaly in specific heat [26,27], with all three confined to a very narrow window near the critical temperature. Below the SDW transition temperature, the Seebeck coefficient follows an activated behavior $|S| \propto \Delta/k_BT$, with $\Delta \sim$ 20–30 K, comparable with the one extracted from resistivity. A large Seebeck coefficient with a Seebeck coefficient roughly proportional to the inverse of

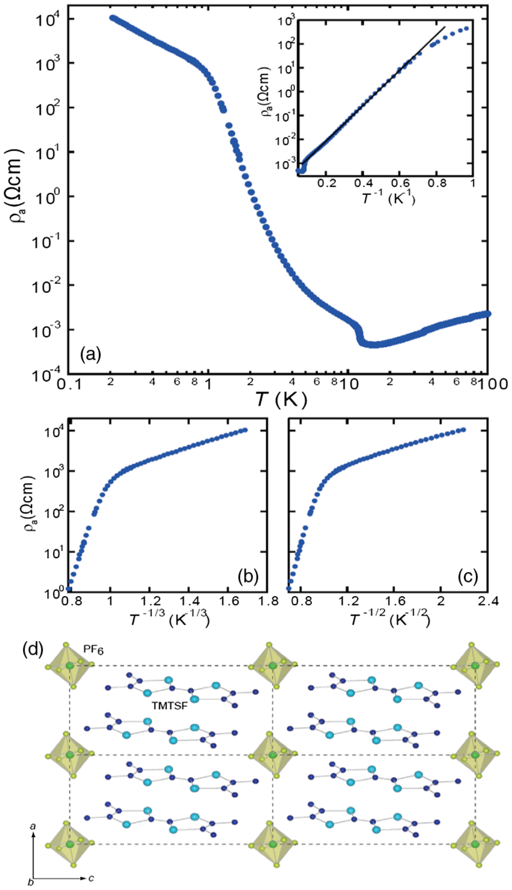

FIG. 2. (a) Temperature dependence of resistivity along the a axis in a logarithmic plot; resistivity increases by more than 7 orders of magnitude. As seen in the inset, over a wide temperature window (10 to 1 K), it follows an activated behavior. (b),(c) Below 1 K, resistivity displays an $\exp[(T/T_0)^{-\gamma}]$ behavior characteristic of VRH. Semilogarithmical plots of ρ vs (b) $T^{-1/3}$ and (c) $T^{-1/2}$ both yield quasistraight lines at the low-temperature end. (d) Crystal structure of the Bechgaard salt $(\mathrm{TMTSF})_2\,\mathrm{PF}_6$.

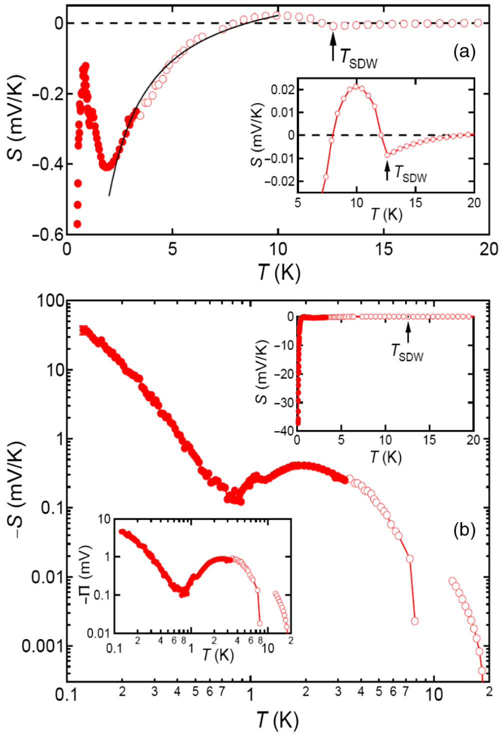

FIG. 3. (a) Temperature dependence of the Seebeck coefficient along the *a* axis in the vicinity of the SDW transition. Below the transition temperature, the Seebeck coefficient follows a T^{-1} dependence, as indicated by a solid line. (Inset) The anomaly at the SDW transition. (b) Temperature dependence of the Seebeck coefficient in a logarithmic plot. The magnitude of the Seebeck coefficient attains 37 mV/K at 0.13 K. (Lower left inset) The temperature dependence of the Peltier coefficient $\Pi = ST$. (Upper right inset) The data in a linear plot. Solid and empty circles represent data obtained on two different samples with two different setups.

the temperature has been seen in several quasi-one-dimensional organic conductors upon the entry of the system in the SDW state [28,29].

The Seebeck coefficient displays a local peak around $T \sim 2$ K. Concomitantly, the Peltier coefficient (extracted using the kelvin relation) peaks to 1 mV [see the lower inset of Fig. 3(b)], which quantifies the average thermal energy carried across the gap. This 2 K peak in thermopower may be related to a number of anomalies seen in the 2–4 K temperature range by magnetotransport [30] and NMR [31] studies. A satisfactory explanation for these anomalies and the significance of this temperature scale are still missing. An incommensurate-to-commensurate SDW transition [31,32] has been invoked to interpret the NMR data.

A more unexpected behavior was detected upon further cooling. A spectacular enhancement in the Seebeck coefficient, with $S \propto T^{-2.5}$, is detectable as soon as the system enters the VRH regime below 1 K. This result, a Seebeck coefficient attaining a magnitude as large as 37 mV/K, almost 400 times k_B/e, is the main new result of this Letter. It is highlighted in the upper inset of Fig. 3(b) by presenting a linear plot of the data. The enhancement below 1 K easily dwarfs the anomaly seen at the SDW transition. The lower inset of Fig. 3(b) presents the temperature dependence of the Peltier coefficient. Its low-temperature magnitude implies that hopping electrons carry an average energy of 4 meV at 0.13 K. Let us examine the possible origins of this colossal thermoelectric response.

Phonon drag, a thermally induced flow of phonons pulling electrons along their way, can lead to a large amplification of the Seebeck coefficient [2,4] in cryogenic temperatures. It is not expected to play a major role in this temperature range, as recently argued [9]. Here, the electron-phonon coupling is weak and lattice thermal conductivity rapidly decreasing, and a sudden emergence of a large phonon drag contribution below 1 K is implausible.

Can the result be an experimental artifact caused by the large resistance of the sample? This is also unlikely. We measured three different samples which yielded comparable results. Moreover, as seen in the figure, there is a satisfactory match between the low-temperature data (obtained in Tokyo on one sample) and the high-temperature data (acquired in Paris on another sample). Our standard one-heater-two-thermometer setup, illustrated in Fig. 4, has been used to measure the subkelvin thermoelectric response in a variety of solids including heavy-electron metals [33,34], superconducting thin films [35], and semimetals [36]. In the case of heavy-fermion $YbRh_2Si_2$, the results were in agreement with those obtained by another group [37]. In the present case, the

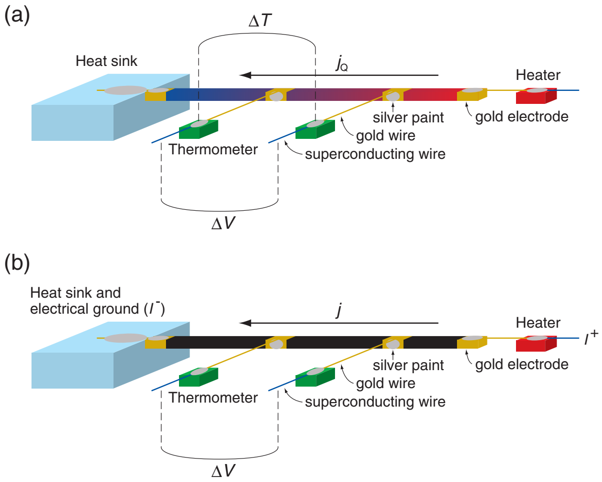

FIG. 4. (a) For measuring the Seebeck coefficient, a heat current was injected into the sample by passing a current though the heater and measuring both the temperature gradient and the voltage difference created by this heat current. (b) For measuring the electrical resistivity, a current was injected into the sample and the voltage difference created by this charge current. In both cases, the voltage was measured in the same way by the same electrodes and the same instrument.

sample resistance becoming as large as 10 MΩ at the lowest temperature remains 2 orders of magnitude lower than the input impedance of the Keithley 2182A nanovoltmeter. The same nanovoltmeter was used to measure the voltage in our resistivity measurement with reliable results. We cannot identify any experimental artifact leading to the large ratio of voltage to thermal gradient observed here (see the Supplemental Material [25]).

The drastic enhancement in the Seebeck coefficient is concomitant with the entry to the VRH transport regime detected by resistivity. It is, therefore, natural to look for an additional source of thermoelectric response associated with this regime. Mott [19] argued that when carriers hop from one site to the other with a probability proportional to $\exp(-W/k_BT - 2R/\xi)$ (W is the energy separation and R the spatial distance between the two sites, while ξ is the localization length of the hopping electron), the expression for electric conductivity in a system with dimension d becomes

$$\sigma \propto \exp[-(T_0/T)^{1/(d+1)}]. \tag{1}$$

Efros and Shklovskii showed that a finite Coulomb interaction leads to a significant depopulation of the occupied sites in the immediate vicinity of the chemical potential and the opening of a soft gap, Δ_{ES} [38]. The resulting expression for electric conductivity is independent of dimensionality:

$$\sigma \propto \exp[-(T_0'/T)^{1/2}]. \tag{2}$$

The presence of this Coulomb gap is expected to become visible when the temperature is low enough such that $k_BT < \Delta_{\mathrm{ES}}$. In practice, as our present data show [see Figs. 2(c) and 2(d)], it is hard to distinguish between the two kinds of stretched exponentials. Burns and Chaikin argued that the fate of the thermopower in the zero-temperature limit is drastically modified by the presence of the Coulomb gap [7]. In the absence of the Coulomb gap, thermopower should be vanishing:

$$S(T)|_{\mathrm{VRH}} \propto T^{(d-1)/(d+1)}. \tag{3}$$

In three dimensions ($d = 3$), this expression is identical to the one first found by Zvyagin [5] [$S(T) \propto (TT_0)^{1/2}$]. On the other hand, Burns and Chaikin argued that, in the presence of the Coulomb gap, thermopower will remain finite in the low-temperature limit:

$$S(T)|_{\mathrm{VRH}}^{\mathrm{ES}} \propto S_0. \tag{4}$$

Later and with detailed calculations, Lien and Toi confirmed this conclusion [8]. However, this theoretical prediction has never been confirmed by experiments. To put it in a few words, can the Seebeck coefficient of a solid remain finite in the zero-temperature limit, the third law of thermodynamics notwithstanding? To the best of our knowledge, this fundamental question is answered for the first time by the observation reported here.

Many questions remain unanswered. Is this result generic to all semiconductors cooled below their Coulomb gap in the VRH regime? Available reports on thermoelectric response in archetypal semiconductors such as silicon [11,39] and germanium [10,40,41] resolve a large Seebeck coefficient down to the lowest temperature of measurement. However, the data stop above 5 K. Only in metallic samples of silicon [42] or germanium [41] (that is, with carrier density above the threshold of the metal-insulator transition), a vanishing thermopower in the low-temperature limit has been resolved. Therefore, the thermoelectric response of band insulators in the VRH limit remains an open question [25]. Here, the robust insulating ground state owes its existence not to a band gap, but to a many-body gap opened by a SDW transition. Does this matter? This is another open question. Because of the incommensurability of the SDW order in $(\mathrm{TMTSF})_2\mathrm{PF}_6$, one expects the presence of collective excitations known as phasons deep inside the ordered state [32]. We note also that another unsolved enigma is the electric-field dependence of nonlinear conductivity below 1 K [18]. One may wonder about the relevance of these other puzzling features of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ to the observation reported here.

If a large Seebeck coefficient happens to be a generic feature of an insulator cooled below the temperature corresponding to its Coulomb gap, then a new research avenue opens up. How do we quantify the Seebeck coefficient of hopping electrons in each system? The Heikes formula [43] is often used to describe the magnitude of the thermoelectric response by hopping electrons. As Mott noted long ago [19], this formula assumes a single hopping probability for all sites, and therefore it cannot be readily used in the VRH regime. The connection between the energy landscape carved by defects in a real insulator and the low-temperature thermoelectric response is an unexplored field of research. The configurational entropy of each hopping electron is the information which travels with it. Therefore, there are potential links to the emerging field of thermodynamics of information [44].

In summary, we measured the Seebeck coefficient $(\mathrm{TMTSF})_2\mathrm{PF}_6$ down to very low temperatures and found that the entry to the VRH regime is concomitant with a very large enhancement of the Seebeck coefficient, which attains a magnitude as large as 37 mV/K, implying that a finite Seebeck coefficient can persist in a solid in the zero-temperature limit.

This work was supported in Japan by JSPS KAKENHI Grants No. 25400361, No. 23340099, and No. 15K05884 (J-Physics), in France by ANR through the SUPERFIELD project, and in Korea by the NRF grants funded by the Korea Government (MSIP) (Grants No. 2015-001948 and No. 2010-00453).

[*] kamran.behnia@espci.fr

[1] H. B. Callen, Phys. Rev. **73**, 1349 (1948).

[2] D. K. C. MacDonald, *Thermoelectricity: An Introduction to the Principles* (John Wiley & Sons, New York, 1962).

[3] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1964).

[4] K. Behnia, *Fundamentals of Thermoelectricity* (Oxford University Press, Oxford, 2015).

[5] I. P. Zvyagin, Phys. Status Solidi (b) **58**, 443 (1973).

[6] T. E. Whall, J. Phys. C **14**, L887 (1981).

[7] M. J. Burns and P. M. Chaikin, J. Phys. C **18**, L743 (1985).

[8] N. Van Lien and D. Dinh Toi, Phys. Lett. A **261**, 108 (1999).

[9] G. D. Mahan, J. Electron. Mater. **44**, 431 (2015).

[10] T. H. Geballe and G. W. Hull, Phys. Rev. **94**, 1134 (1954).

[11] T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

[12] D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. (Paris), Lett. **41**, 95 (1980).

[13] D. Jérome, J. Supercond. Novel Magn. **25**, 633 (2012).

[14] S. Brown, Physica (Amsterdam) **514C**, 279 (2015).

[15] P. M. Chaikin, P. Haen, E. M. Engler, and R. L. Greene, Phys. Rev. B **24**, 7155 (1981).

[16] Y. M. Kim, G. Mihály, H. W. Jiang, and G. Grüner, Synth. Met. **70**, 1287 (1995).

[17] K. Petukhov and M. Dressel, Phys. Rev. B **71**, 073101 (2005).

[18] G. Grüner, Rev. Mod. Phys. **66**, 1 (1994).

[19] N. F. Mott, J. Non-Cryst. Solids **1**, 1 (1968).

[20] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1984).

[21] O. Agam and I. L. Aleiner, Phys. Rev. B **89**, 224204 (2014).

[22] K. Mortensen, Solid State Commun. **44**, 643 (1982).

[23] M.-Y. Choi, M. J. Burns, P. M. Chaikin, E. M. Engler, and R. L. Greene, Phys. Rev. B **31**, 3576 (1985).

[24] Y. S. Chai, H. S. Yang, J. Liu, C. H. Sun, H. X. Gao, X. D. Chen, L. Z. Cao, and J. C. Lasjaunias, Phys. Lett. A **366**, 513 (2007).

[25] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.116.087003 for experimental details and available thermoelectric data on semiconductors.

[26] J. Coroneus, B. Alavi, and S. E. Brown, Phys. Rev. Lett. **70**, 2332 (1993).

[27] D. K. Powell, K. P. Starkey, G. Shaw, Y. V. Sushko, L. K. Montgomery, and J. W. Brill, Solid State Commun. **119**, 637 (2001).

[28] K. Mortensen, E. M. Conwell, and J. M. Fabre, Phys. Rev. B **28**, 5856 (1983).

[29] K. Mortensen and E. M. Engler, Phys. Rev. B **29**, 842 (1984).

[30] S. Uji, J. S. Brooks, M. Chaparala, S. Takasaki, J. Yamada, and H. Anzai, Phys. Rev. B **55**, 12446 (1997).

[31] S. Nagata, M. Misawa, Y. Ihara, and A. Kawamoto, Phys. Rev. Lett. **110**, 167001 (2013).

[32] E. Barthel, G. Quirion, P. Wzietek, D. Jérome, J. B. Christensen, M. Jørgensen, and K. Bechgaard, Europhys. Lett. **21**, 87 (1993).

[33] K. Izawa, K. Behnia, Y. Matsuda, H. Shishido, R. Settai, Y. Onuki, and J. Flouquet, Phys. Rev. Lett. **99**, 147005 (2007).

[34] Y. Machida, K. Tomokuni, C. Ogura, K. Izawa, K. Kuga, S. Nakatsuji, G. Lapertot, G. Knebel, J.-P. Brison, and J. Flouquet, Phys. Rev. Lett. **109**, 156405 (2012).

[35] A. Pourret, H. Aubin, J. Lesueur, C. A. Marrache-Kikuchi, L. Bergé, L. Dumoulin, and K. Behnia, Nat. Phys. **2**, 683 (2006).

[36] Z. Zhu, H. Yang, B. Fauqué, Y. Kopelevich, and K. Behnia, Nat. Phys. **6**, 26 (2010).

[37] S. Hartmann, N. Oeschler, C. Krellner, C. Geibel, S. Paschen, and F. Steglich, Phys. Rev. Lett. **104**, 096401 (2010).

[38] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, L49 (1975).

[39] L. Weber and E. Gmelin, Appl. Phys. A **53**, 136 (1991).

[40] H. P. R. Frederikse, Phys. Rev. **92**, 248 (1953).

[41] J. F. Goff and N. Pearlman, Phys. Rev. **140**, A2151 (1965).

[42] P. Ziegler, M. Lakner, and H. von Löhneysen, Europhys. Lett. **33**, 285 (1996).

[43] R. R. Heikes and R. W. Ure, Jr., *Thermoelectricity: Science and Engineering* (Interscience Publishers, New York, 1961).

[44] J. M. R. Parrondo, J. M. Horowitz, and T. Sagawa, Nat. Phys. **11**, 131 (2015); E. Lutz and S. Ciliberto, Phys. Today **68**, 30 (2015).