THERMOELECTRICITY AND MODERN TRENDS IN ITS STUDIES[1]

ANDREY VARLAMOV, (*) IOULIA CHIKINA, (**) DAVIDE PEDDIS (***)

SUNTO. – L'effetto termoelettrico è la conversione diretta di una differenza di temperatura in energia elettrica e viceversa. La differenza di temperatura agli estremi di un dispositivo termoelettrico genera una tensione; allo stesso modo l'applicazione di una differenza di tensione nello stesso dispositivo produrrà una differenza di temperatura. A livello microscopico questo fenomeno può essere descritto dalla presenza di un gradiente di temperatura che induce il movimento delle cariche dal lato caldo al lato freddo del dispositivo. Questa relazione comincerà con la discussione di alcuni aspetti storici relativi alla scoperta delle Termoelettricità da parte del Fisico estone *Thomas Johann Seebeck* nel 1821 e delle prime manifestazioni dell'effetto termoelettrico. Oggi con questo termine vengono indicati tre effetti distinti: l'effetto **Seebeck**, l'effetto **Peltier** e l'effetto **Thomson**. L'applicazione del campo magnetico aumenta ulteriormente le possibili manifestazioni della termoelettricità. Tra queste manifestazioni la più conosciuta è l'effetto **Nernst.** Questo fenomeno viene osservato quando un campione conduttore è sottoposto ad un campo magnetico e ad un gradiente di temperatura perpendicolari tra loro. I campi elettrici e magnetici determinano la deriva delle particelle cariche in una direzione perpendicolare ad entrambi. Tale movimento delle particelle cariche è impedito dalla presenza del gradiente di temperatura nella direzione corrispondente nel caso di condizione di circuito aperto. La teoria dei fenomeni termoelettrici e termomagnetici nei metalli e nei semiconduttori, basata sulla teoria quantistica dei solidi, è stata sviluppata a metà del XX secolo. Si è scoperto che nei metalli questi effetti sono trascurabili (per Bismuto il più elevato valore osservato del coefficiente di Seebeck è dell'ordine di $7\mu V/K$). L'effetto termoelettrico aumenta notevolmente nei semiconduttori, che sono per questo utilizzati nella costruzione di generatori termoelettrici (dispositivi a stato solido che convertono un gradiente di temperatura in energia

---

(*) Istituto Lombardo Accademia di Scienze e Lettere, Milano. SPIN-CNR, Roma, Italia - MAGENTA. E-mail: varlamov@ing.uniroma2.it

(**) CEA, Saclay, France - MAGENTA.

(***) ISM-CNR, Roma, Italia - MAGENTA.

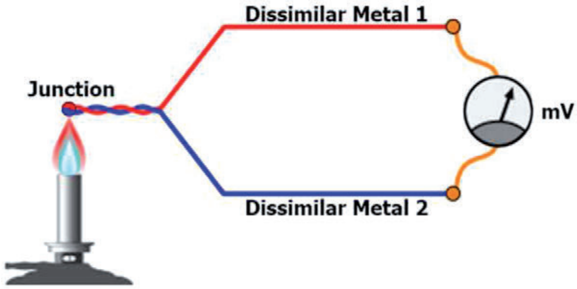
1 This work was partially supported by FET-Proactive Project, MAGnetic nanoparticle based liquid ENergy materials for Thermoelectric device Applications (MAGENTA) [GA 731976].

elettrica). Attualmente la termoelettricità sta riscuotendo un crescente e rinnovato interesse, specialmente in relazione alla scoperta di materiali artificiali con elevate prestazioni termoelettriche: grafene, nuovi superconduttori, polimeri conduttori, elettroliti e ferrofluidi. Le loro proprietà non banali saranno esaminate nella seconda parte della nostra presentazione.

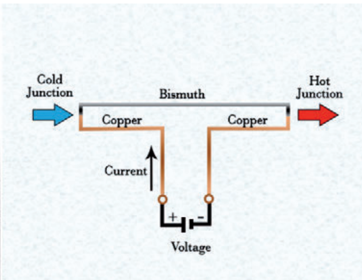
***

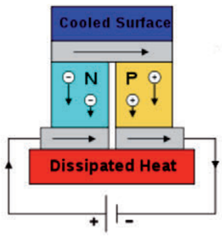
ABSTRACT. – The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the microscopic level of understanding one can say that an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. We will start our discussion from the discovery of the phenomenon of thermoelectricity by the Estonian physicist Thomas Johann Seebeck in 1821 and its early manifestations. Today the term "thermoelectric effect" encompasses three separately identified effects: the **Seebeck effect**, **Peltier effect**, and **Thomson effect**. Application of magnetic field considerably increases the variety of possible manifestations of thermoelectricity. The most known among them is the **Nernst effect** which is nothing else as a thermoelectric effect observed when a conducting sample is subjected to a magnetic field and a temperature gradient perpendicular to each other. The crossed electric and magnetic fields should lead to the drift of a charged particle in the direction perpendicular to both of them. In the case of broken circuit condition such motion of the carriers is prevented by appearance of the temperature gradient in corresponding direction, what is the essence of the **Nernst-Ettingshaus effect,** reciprocal to the **Nernst one.** The theory of thermoelectric and thermomagnetic phenomena in metals and semiconductors, based on the quantum theory of solids, was developed in the middle of XX century. It was found that in metals these effects are negligibly small (for Bi the Seebeck coefficient is maximal and is of the order of $7\mu V/K$). The magnitudes of thermoelectric signals considerably increase in semiconductors what allows to use them as the working elements of thermoelectric generators (solid state devices that convert heat flux (temperature differences) directly into electrical energy), for studies of the scattering mechanisms in semiconductors, etc. Today the interest to the thermoelectricity is very high, especially in view of the possibility to design new artificial materials with tuned high thermoelectric properties: graphene, new generation of superconductors, conducting polymers, electrolytes and ferrofluids. Their non-trivial properties will be reviewed in the second part of our presentation.

The control of heat fluxes and the minimization of related losses are important factors in designing modern elements both of power applications and nano-electronics, including those based on the application of graphene. The thermoelectric effect can find its power applications in auto industry providing up to 1 KW of electric power due to the temperature difference occurring in vehicle and it leads to a significant change in temperature (up to 30%) in the region of contacts in graphene nano-electronics.



The thermoelectric effect (TE), where a junction of dissimilar metals produces an electric current when exposed to a temperature gradient was discovered almost two centuries ago (1821) by Estonian-German scientist, Thomas Johann Seebeck. The inverse thermoelectric effect, *i.e.* the cooling of one junction and the heating of the other when the electric current is maintained in a circuit consisting of two dissimilar materials is called the Peltier effect (1834).





Seebeck effect

Quantitatively, Seebeck effect is characterized by the differential thermopower (the Seebeck coefficient, *i.e.*, the thermo-electromotive force arising in an inhomogeneously heated conductor) divided by the corresponding temperature difference:

$$S = -\frac{\Delta V}{\Delta T} = \frac{E}{\nabla T}$$

The thermo-power of metals is usually small but can be much greater in doped semiconductors and in semimetals.

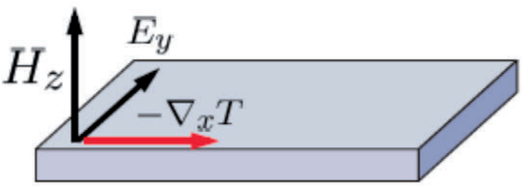
More than a century later, an English scientist, Nevill Mott, found an important relationship between the differential thermopower and the logarithmic derivative of the electric conductivity σ of a metal:

$$S_{ik} = -\frac{\pi^2}{3}\frac{T}{e}\frac{\partial\left(\ln\sigma_{ik}\right)}{\partial\mu},$$

where μ is the chemical potential of the charge carriers and T is the temperature. In metals the Seebeck effect is different from zero due to the electron-hole asymmetry:

$$S_e = -\frac{\pi^2}{3e}\frac{T}{\mu} \sim 10^{-8} T \cdot V / K$$

At present, the Mott formula is the basic in analyzing experiments related to thermoelectricity; however, numerous anomalous situations are known where the behavior of the thermopower cannot be described by the Mott formula. These are phenomena such as an increase in the thermo- power of metals at temperatures close to the Kondo temperature and the anomalies of thermopower at electron topological transitions and its oscillations in strong magnetic fields. One of the factors responsible for the invalidity of the Mott formula is the existence (due to one reason or another) of an essential dependence of the relaxation time of charge carriers on energy.



THERMOMAGNETIC PHENOMENA

They are observed when a sample allowing electrical conduction is subjected to a magnetic field and a temperature gradient perpendicular to each other. Among the variety of known thermomagnetic phenomena, those discussed most frequently are the effects of Nernst and Nernst-Ettingshausen, discovered by Austrian scientists Walter Nernst and Albert von Ettingshausen in 1886. The Nernst effect in metals, which is a thermal analog of the Hall effect, consists in the appearance of an electric field E_y orthogonal to the mutually perpendicular magnetic field H_z and temperature gradient $\nabla_x T$. It is assumed that all electrical circuits are open, *i.e.*, $j_x = j_y = 0$,

and no heat flux is present along the y axis (the adiabaticity condition). Quantitatively, the effect is characterized by the Nernst coefficient

$$N = -\frac{E_y}{H_z \nabla_x T}.$$

Depending on the material, the Nernst coefficient can change within several orders of the magnitude: from $N_m \approx (0.01 - 1) mV / K^{-1}T^{-1}$ for "good" metals to $N_{Bi} \approx 7000 \mu V / K^{-1}T^{-1}$ in bismuth.

The Nernst-Ettingshausen effect is a different experimental realization of the Nernst effect: the electrical current is passed along the y-axis through a sample placed into a magnetic field directed along the z-axis; along the x axis, a temperature gradient arises in this case.

The microscopic nature of the Nernst effect remained unclear up to 1948, until Sondheimer, using a kinetic equation, found an expression for the Nernst coefficient of a degenerate electron gas with impurities by relating the latter to the derivative of the Hall angle with respect to energy:

$$N_n \approx \frac{1}{H_z} \frac{\beta_{xy}\sigma_{xx} - \beta_{xx}\sigma_{xy}}{\sigma_{xx}^2} = -\frac{\pi^2}{3} \frac{cT}{eH_z} \frac{\partial}{\partial \mu} \left(\frac{\sigma_{xy}}{\sigma_{xx}} \right) = -\frac{\pi^2 T}{3m} \frac{\partial \tau(\varepsilon)}{\partial \varepsilon} \bigg|_{\varepsilon = \mu},$$

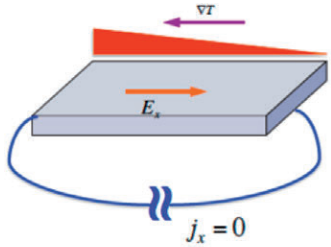
which permitted him to find the relation between these two effects and made the Nernst effect an important tool for studies of the character of scattering of charge carriers in semiconductors. In the above expression m is the effective mass of charge carriers and $\tau(\varepsilon)$ is the energy-dependent relaxation time. Within the Sondheimer theory, the Nernst coefficient is constant in weak fields and decreases as H^{-2} in sufficiently strong fields, when the cyclotron frequency exceeds the inverse relaxation time. In 1964, Obraztsov noted the importance of taking so-called magnetization currents (electric currents arising because of the inhomogeneous magnetization of a sample) into account in discussing the Nernst effect.

Thermodynamic approach to TE and TM effects

From the constancy of the electrochemical potential in x-direction:

$$\frac{d}{dx}(\mu + e\phi) = 0$$

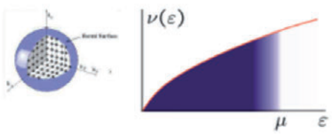
$$E_x = \frac{1}{e}\frac{d\mu}{dx} = \frac{1}{e}\left(\frac{d\mu}{dT}\right)\nabla T$$



$$S = -\frac{\Delta V}{\Delta T} = \frac{E_x}{\nabla T} = \frac{1}{e}\left(\frac{d\mu}{dT}\right)$$

Example: degenerated Fermi system

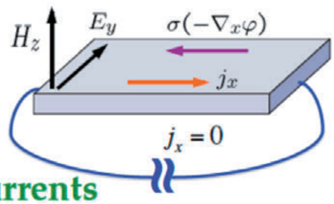
Chemical potential of a degenerate Fermi gas: $\mu(T) = \mu_0 - \frac{\pi^2}{6}T^2\frac{d\ln\nu(\mu)}{d\mu}$



$$S = \frac{1}{e}\frac{d\mu}{dT} = -\frac{\pi^2}{3e}\frac{T}{\mu}$$

Nernst effect & chemical potential

$$j_y = \sigma_{yx}E_x + \sigma_{yy}E_y = j_y^{therm} + j_y^{mag}$$



Thermal contribution

$$N^{(therm)} = \frac{\sigma_{xx}}{ne^2c}\left(\frac{d\mu}{dT}\right)$$

Role of magnetization currents

An additional contribution to the Nernst constant appearing due to the spatial dependence of magnetization in the sample can be found from the Ampere law:

$$\mathbf{j}^{\mathrm{mag}} = \frac{c}{4\pi}\nabla\times\mathbf{B}, \quad \mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \quad j_y^{\mathrm{mag}} = -c\frac{dM}{dT}\nabla T$$

$$E_y^{\mathrm{mag}} = \rho_{yy}j_y^{\mathrm{mag}} \qquad N^{(mag)} = \frac{E_y^{mag}}{(-\nabla T)H} = \frac{c\rho_{yy}}{H}\left(\frac{dM}{dT}\right)$$

Complete expression for Nernst coefficient:

$$N^{(tot)} = \frac{\sigma_{xx}}{ne^2c}\left(\frac{d\mu}{dT}\right) + \frac{c\rho_{yy}}{H}\left(\frac{dM}{dT}\right)$$

Kinetic approach to TE and TM effects

Heat and electric transport equations:

$$\begin{cases} j^e_\alpha = \sigma_{\alpha\beta}E_\beta - \beta_{\alpha\beta}\nabla_\beta T \\ j^Q_\alpha = \gamma_{\alpha\beta}E_\beta - \kappa_{\alpha\beta}\nabla_\beta T \end{cases}$$

Onsager relation: $\gamma_{\alpha\beta}(H) = -\beta_{\beta\alpha}(-H)T$

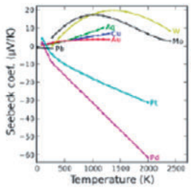
Degenerated Fermi system of carriers:

Mott formula: $\beta_{\alpha\beta} = \frac{\pi^2}{3}\frac{cT}{e}\frac{\partial\sigma_{\alpha\beta}}{\partial\mu}$

Seebeck coefficient : $S_{ik} = -\beta_{il}\sigma^{-1}_{lk} = -\frac{\pi^2}{3}\frac{T}{e}\frac{\partial(\ln\sigma_{ik})}{\partial\mu}$

METAL OR ALLOY	SEEBECK COEFFICIENT (mV/C) vs. PURE PLATINUM
Bismuth	-0.0734
Constantan	-0.0351
Nickel	-0.0148
Cobalt	-0.0133
Alumel	-0.0129
Mercury	-0.0060
Palladium	-0.0057
Calcium	-0.0051
Gold-chromium	-0.0017
Thorium	-0.0013
Platinum	0
Alloy 11	+0.0013
Tantalum	+0.0033

In normal metals



$S(T) = -\frac{\pi^2}{3e}\frac{T}{\mu} \sim -(1-100)\mu V/K$

Manifestation of thermoelectricity in different systems

Mott formula: $S_{ik} = -\beta_{il}\sigma^{-1}_{lk} = -\frac{\pi^2}{3}\frac{T}{e}\frac{\partial(\ln\sigma_{ik})}{\partial\mu}$

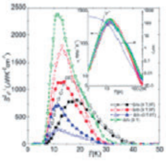
Free electron theory $\sigma = \frac{Ne^2\tau}{m}$

$N \sim p_F^3 \sim \mu^{3/2}$ $\Rightarrow$ $S = -\frac{\pi^2}{3}\frac{T}{e}\frac{\partial(\ln\mu)}{\partial\mu} = -\frac{\pi^2}{3e}\frac{T}{\mu}$

Elastic scattering : $\tau \sim \mu^{-1/2}$ What coincides with the thermodynamic approach

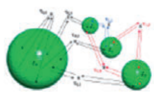
Yet, already in the case of more complicated scattering mechanisms: $\tau \sim \mu^{-1/2+\alpha}$ $S = -\frac{\pi^2}{3e}\frac{T}{\mu}(1+\alpha)$

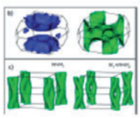
In the cases of Kondo, problem

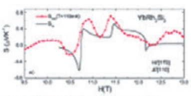


A.Bentien et al., 2007 Colossal Seebeck coefficient in strongly correlated semiconductor $FeSb_2$

Giant Seebeck signal close to Lifshitz Transition







A.Pourret et al, 2017, Transport Spectroscopy of a field induced Cascade Lifshitz Transitions,

Giant Seebeck effect in graphene

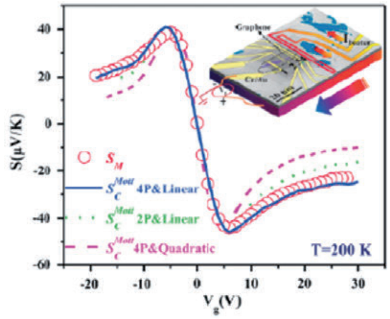


FIG. 1. (Color online) Comparison of experimentally measured Seebeck coefficient S_M (open circles) and three Seebeck curves S_C^{Mott} calculated from measured electrical conductivity using the Mott relation. The solid line is calculated with the 4P resistivity and a linear dispersion relation; the dotted line is with the two-point (2P) resistivity and a linear dispersion relation; and the dashed line is with the 4P resistivity and a quadratic dispersion relation. μ_c of this device is ~1500 cm^2/Vs. The inset shows a false colored scanning electron microscopy image.

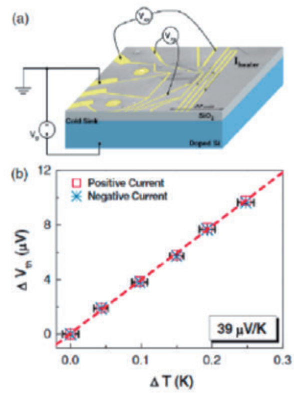
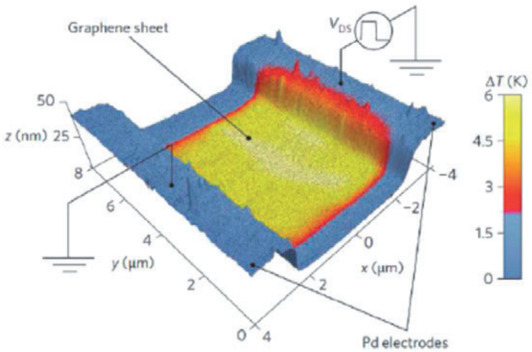


FIG. 1 (color). (a) SEM image and circuit schematic of a graphene device for thermoelectric measurements. (b) ΔT vs thermovoltage change ΔV_{th} for a series of heater power steps at 255 K and zero gate voltage. The linear fit of this curve gives the thermopower of 39 μV/K.

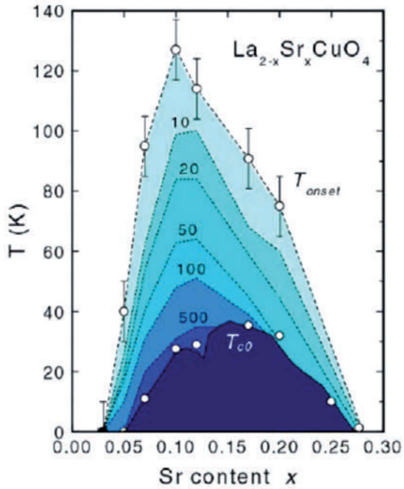
Large role of thermoelectric effect in graphene



$$W = \sigma j^2 + T(S_a - S_b)$$

The experiments [K. Grosse et al., Nature Nanotechnology (2011)] indicate that thermo-electric effect in graphene accounts for up to one-third of the contact temperature changes and thus it can play significant role in cooling down of such systems.

Nernst effect in pseudogap phase of cuprates



Y. Wang et al. (2001)

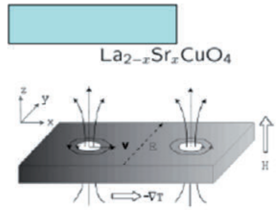
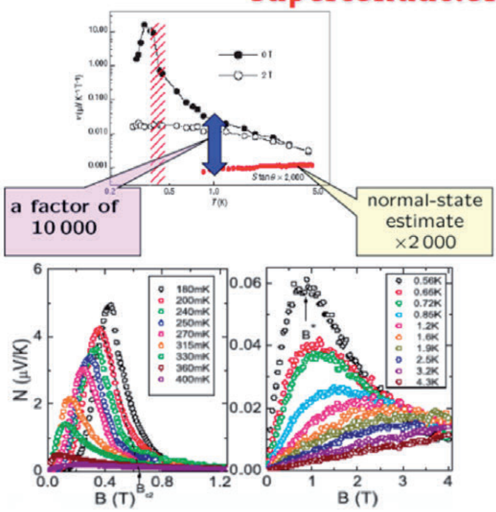


FIG. 1. The vortex-Nernst effect in a type-II superconductor. Concentric circles represent vortices.

$$N_{pg}^{\max} \approx 1 \mu V / K^{-1} T^{-1}$$

Nernst effect in fluctuating conventional superconductors



A. Pourret et al.,
Nature Phys. (2006);
Phys. Rev. B (2007)

$Nb_{0.15}Si_{0.85}$ film

thickness
$d = 35$ nm
$T_c = 0.38$ K
$R_{\square} = 350$ Ohm

$$N_{NbSi}^{\max} \approx 15 \mu V / K^{-1} T^{-1}$$

Applications

Thermoelectric devices are used to build refrigerators or to convert thermal energy into electric one. Other usage of this technology is applied to generate power for satellites or space shuttles because the battery life is not sufficient. Central Processing Units for PC have also benefited from the Peltier effect. Thermomagnetic phenomena (TM) are observed when a sample allowing electrical conduction is subjected to a magnetic field and a temperature gradient perpendicular to each other (Nernst-Ettingshausen effect), or vice versa, electric current flowing through a sample perpendicularly to magnetic field generates the temperature gradient (Nernst effect).

In metals the TE and TM phenomena usually are directly related to the electron-hole asymmetry (Seebeck coefficient, characterizing the strength of TE, *S~T / EF*) and they are very weak, producing the voltage only of the order of millivolts when the temperature difference of the order of 100 ^{0}C is applied to the thermocouple. This value increases one-two orders in degenerated semiconductors, making them the basis of low power applications.

The efficiency of a thermoelectric device

$$\eta = \frac{\text{energy provided to the load}}{\text{heat energy absorbed at hot junction}}$$

$$\eta = \frac{V^2 \Delta t}{R} / (qA\Delta t) = \frac{AS^2 (\Delta T)^2 \Delta t}{\rho l q A \Delta t} = \frac{S^2 (\Delta T)^2}{\rho l \kappa (\Delta T)/l} = \frac{\sigma S^2 \Delta T}{\kappa} = (ZT)\frac{\Delta T}{T}$$

The dimensionless figure of merit: $ZT = \frac{\sigma S^2}{\kappa}$ characterizes the efficiency of thermoelectric device

$$\eta_{max} = \frac{T_h - T_c}{T_h} \frac{(1+ZT_{av})^{1/2} - 1}{(1+ZT_{av})^{1/2} + \frac{T_c}{T_h}}$$

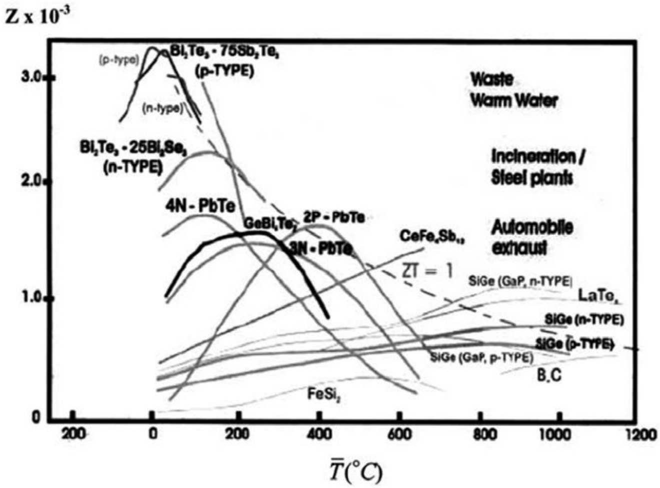
Dealing with the degenerated electron systems one has to recall Wiedemann-Franz law:

$$\frac{\sigma_e T}{\kappa_e} = \frac{3e^2}{\pi^2}$$

where from

$$\frac{\sigma_e T}{\kappa_e + \kappa_{ph}} < \frac{3e^2}{\pi^2}$$

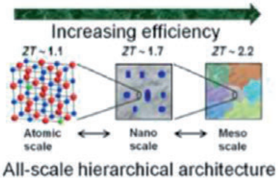
Device is effective if ZT > 4. Current records are ZT ~ 2



New Materials for Thermoelectricity

$$ZT = \frac{\sigma S^2}{\kappa}$$

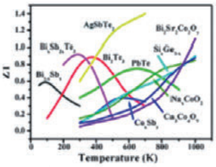
The reduction of thermal conductivity is highly related to the material's structure, from atomic-level features to meso- and microscale structures. It can be achieved by invoking all-length scales in bulk thermoelectrics. This "panoscopic" tailoring of materials microstructures enhances phonon scattering across different wavelengths, yet preserves their electronic transport, leading to high-performance thermoelectric materials. Heat-carrying phonons with short mean free paths can be scattered by nanoscale precipitates embedded in the matrix, and ones with long mean free paths can be scattered by controlling and fine-tuning the meso-scale architecture of the nanostructured thermoelectric materials.



Shih-Han Lo, Northwestern University
(http://materialsforenergy.typepad.com)

Strategies to improve thermoelectric materials are going towards both advanced bulk materials and the use of low-dimensional systems.

Material	ZT	Notes
oxide compounds ((SrTiO3)n(SrO)m with layered structure	~ 0.34 at 1000K	Very interesting for application at high temperature
Half Heusler alloys	~ 0.5-1.5 at 700K	relatively cheap - high power factor
Bismuth chalcogenides (Bi_2Te_3; Bi_2Se_3)	~ 0.8-1.0 at RT	Temperature independent ZT
Bismuth chalcogenides nanostructured (trylayersBi_2Te_3; Bi_2Se_3)	~ 2.4 at RT	Good electrical conductivity
Silicon-germanium alloys	~0.7 at RT	best thermoelectric materials around 1000 °C



Y. Qui, J. mater. Chem. A, 1, 6110, 2013

MAGENTA: ionic-liquid based ferrofluids; i.e., colloidal suspension of magnetic nanoparticles.
The aim is to create radically new thermoelectric materials that are versatile, cost-effective and non-toxic to assist the economically and environmentally sustainable energy transition in Europe