Thermoelectricité comme sonde de l'orgnisation électronique dans les solides

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Outline

I. Introduction : electric vs. thermoelectric conductance

II. From Kondo effect to heavy-electron metals

III. The Nernst effect

IV. Quantum limit and dilute metals

•J. M. Ziman, Electrons and phonons

•D. K. C. Macdonald, Thermoelectricity

Flow of heat and charge



In general, σ , α and κ are tensors !

Off-diagonal components emerge in presence of magnetic field:

- •Hall effect
- •Nernst effect
- •Righi-Leduc effect

Experimental access to thermoelectric coefficients

- Impose a thermal gradient!
- Impede charge flow (J_e=0)!

$$\sigma \vec{E} = \alpha \vec{\nabla} T$$

$$\vec{S} = \alpha \vec{\nabla} T$$

$$\vec{S} = \frac{\alpha}{\sigma} = \frac{E_x}{\nabla_x T}$$

$$\vec{V} = S_{xy} = \frac{E_y}{\nabla_x T}$$

$$[\nu = \frac{-E_y}{B_z \nabla_x T}]$$

The linearized Boltzmann equation $\frac{f_k(r) - f^0}{1 \rightarrow \tau} = v_k \cdot \left(\frac{\partial f^0}{\partial T} \nabla T + \frac{\partial f^0}{\partial \varepsilon_k} E\right)$ Scattering time velocity ^{1.00} **a** 0.75 $f^0 = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1}$ 0.50 0.25electric field 0.00 $\zeta_T / \mu =$ 1.00 b 0.2 0.75 f⁰(ε) 0.50 -0.25 temperature gradient 0.00 0.0 --1 0 20 0.0 0.5 1.0 1.5 ε/μ $\mu/3$

Electric and thermoelectric conductivity



$$\sigma = -e^2 \int \tau(k) (v_k)^2 \frac{\partial f^0}{\partial \epsilon_k} dk$$

Always positive

Dominant contributors: $\varepsilon = \mu$

$$\alpha = e \int \tau(k) (v_k)^2 \ \frac{\partial f^0}{\partial T} dk$$

Can be positive or negative Dominant contributors:

 $\varepsilon < \mu$ and $\varepsilon > \mu$

Electrons which carry charge and those which carry heat!



Transport distribution function (Mahan & Sofo, 1996)

$$\Xi(\varepsilon) = \frac{h}{2} N(\varepsilon) v_k^2(\varepsilon) \tau(\varepsilon) = \frac{h}{2} N(\varepsilon) v_k(\varepsilon) \ell(\varepsilon)$$

It depends on both the electronic structure and scattering mechanism. In the material.

In a bulk solid, it replaces the transmission probability introduced by Landauer in the case of 1D systems!

Electric and thermoelectric conductivity

Parabolic dispersion with constant mean-free-path



$$\alpha = 2 \frac{ek_B}{h} \int (-\frac{\partial f}{\partial \varepsilon}) \frac{(\varepsilon - \mu)}{k_B T} \Xi(\varepsilon) d\varepsilon$$



High-energy electrons are faster and denser

The free electron gas



The Seebeck coefficient becomes scattering-independent, if the mean-free-path is independent of energy.

In a degenerate Fermi liquid ($k_BT << \epsilon_F$)

The Wiedemann-Franz law:

 $\frac{\kappa\alpha}{T} = \frac{\pi^2}{3} \frac{k_B^2}{e^2}$

The Mott formula:



$$S = \frac{\alpha}{\sigma} = \frac{\pi^2}{3} \frac{k_B^2}{e} T \frac{\partial \ln \sigma}{\partial \varepsilon} \bigg|_{\varepsilon = \mu}$$

Thermoelectricity probes electronic states near ,but not exactly at, the chemical potential , !

The Kondo effect



1936: Mysterious upturn in resistivity of gold seen by de Haas1950s: Role of MAGNETIC impurities pinned down1960s: Giant Seebeck effect in thermopower in impure noble metals1964: Kondo offers a solution (and defines a new problem)!

The isolated magnetic moment couples to the Fermi sea Incoming electrons are spin-flipped and visit states of opposite spin!

The Kondo effect

Table 1.

| Specimen | Treatment time (h) | Fe concentration (ppm) | Resistivity $(n\Omega cm)$ | Thermopower $(\mu V K^{-1})$ |
|----------|-----------------------|------------------------|----------------------------|------------------------------|
| 1 | 0 | 13 | 14-4 | - 7.18 |
| 2 | 4.1 | 1 | 4.8 | -1.71 |
| 3 | 8.2 | 0.1 | 4.1 | -0.17 |
| 4 | 12.3 | 0.01 | 4.0 | +0.01 |
| 5 | 16.4 | 0.001 | 4.0 | +0.03 |



Magnitude of Seebeck peak in Au-Fe at 4.2 K



The instrinsic diffusive Seebeck coefficient of gold is only 24nV/K @4.2K!

•AuFe (0.0.3 %): the most sensitive thermocouple at low T !

Why the effect is so drastic?



A resonance peak in one side of the dividing line!

Kondo lattices

•Intermetallics with atoms hosting f electrons (CeAl₃, YbAl₃, UPt₃...)

•At high temperature, isolated magnetic moments in a Fermi sea

•At low temperature, no dichotomy between isolated spins and mobile charges. Both merge in to a sea of heavy electrons!

$$C_{e} = \frac{\pi^{2}}{3} k_{B}^{2} T N(\varepsilon_{F}) = \frac{\pi^{2}}{3} k_{B}^{2} T \frac{n}{T_{F}} \propto k_{B} T \frac{m^{*} n^{1/3}}{\hbar^{2}}$$

• An electronic specific heat several orders of magnitude larger than copper!

Large Seebeck coefficient in heavy-electron metals

Jaccard & Sierro 1982



Thermopower and specific heat

In a free electron gas :

$$S = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{N(\epsilon_F)}{n} \qquad \qquad C_{el} = \frac{\pi^2}{3} k_B^2 T N(\epsilon_F)$$

Thermopower is "specific heat per carrier" [Macdonald 1962, Ziman, 1961, …]

The dimensionless ratio:

$$q = eN_{Av} \frac{S}{C}$$

is equal to -1 (+1) for free electrons (holes).

In many heavy-fermion metals q is close to unity!



Behnia, Jaccard & Flouquet, JPCM 2004



See also Sakurai & Isikawa JSPJ 2005

Theory: Miyake & Kohno JPSJ 2005 Zlatic et al., PRB 2007

Heavy Fermi liquids

• Enhanced specific heat

• Enhanced Pauli Susceptibility

• Enhanced inelastic resistivity

• Enhanced Seebeck coefficient

$$\gamma = \frac{\pi^2}{3} k_B^2 N(\varepsilon_F)$$
$$\chi = \mu_B^2 N(\varepsilon_F)$$
$$\rho = \rho_0 + AT^2$$
$$A \propto \frac{1}{\tau} \propto N(\varepsilon_F)^2$$
$$\frac{S}{T} = \frac{\pi^2}{3} k_B^2 \frac{N(\varepsilon_F)}{n}$$

Fermi liquid ratios





Current research on thermoelectricity of heavy electrons

Main themes

- Quantum criticality
- •Metamagnetic transitions
- •Hidden electronic orders
- •Fermi surface reconstruction
- •Ferromagnetic superconductors

Principal actors

- Grenoble (Flouquet)
- Dresden (Steglich)
- Tokyo (Izawa)
- Ames (Canfield)
- Geneva (Jaccard)

Kohler et al., 2008 Dresden



Ferromagnetic superconductors



Reentrant superconductivity: Ferromagnetic fluctuations generate a SC dome!

S-shape $H_{c2}(T)$ in UCoGe



Thermoelectric Response Near a Quantum Critical Point of β-YbAlB₄ and YbRh₂Si₂: A Comparative Study

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The effective Fermi temperature



All would diverge if T_F vanishes!

Seebeck coefficient is the only intensive coefficient (no geometric factor)!

The Nernst effect

$$\vec{J}_{e} = \sigma \vec{E} - \alpha \vec{\nabla} T$$

$$\vec{J}_{Q} = \alpha T \vec{E} - \kappa \vec{\nabla} T$$

 $\alpha \text{ is now a tensor}$

$$0 = \sigma \vec{E} - \alpha \vec{\nabla} T \quad \longrightarrow \quad \sigma_{xx} E_x + \sigma_{xy} E_y = \alpha_{xx} \nabla_x T + \alpha_{xy} \nabla_y T \\ - \sigma_{xy} E_x + \sigma_{yy} E_y = -\alpha_{xy} \nabla_x T + \alpha_{yy} \nabla_y T$$

$$\nabla_{y}T = 0 \quad \longrightarrow \quad [\sigma_{xy}^{2} + \sigma_{xx}\sigma_{yy}]E_{y} = [\sigma_{xy}\alpha_{xx} - \sigma_{xx}\alpha_{xy}]\nabla_{x}T$$

$$N = \frac{-E_{y}}{\nabla_{x}T} = \frac{\alpha_{xy}\sigma_{xx} - \alpha_{xx}\sigma_{xy}}{\sigma_{xx}\sigma_{yy} + \sigma_{xy}^{2}}$$

Nernst effect and Hall mobility

$$N = \frac{\alpha_{xy}\sigma_{xx} - \alpha_{xx}\sigma_{xy}}{\sigma_{xx}^{2} + \sigma_{xy}^{2}}$$

Extended Mott formula:

$$\alpha_{xx} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\partial \sigma_{xx}}{\partial \varepsilon} \qquad \qquad \alpha_{xy} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\partial \sigma_{xy}}{\partial \varepsilon}$$
$$N = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\partial \Theta_H}{\partial \varepsilon} |_{\varepsilon_F}$$

Nernst effect measures the change in the Hall mobility induced by shifting the Fermi level!

The Hall mobility

$$\Theta_{H} = \mu_{H} = \frac{e\tau}{m^{*}} = \frac{e}{\hbar} \frac{\ell}{k_{F}}$$
$$\Theta_{H}(\varepsilon) \propto \varepsilon^{\gamma} \qquad \frac{v}{T} = \frac{\pi^{2}}{3} \frac{k_{B}^{2}}{eB} \frac{\partial \Theta_{H}}{\partial \varepsilon} \bigg|_{\varepsilon_{F}} \Rightarrow \frac{v}{T} \approx \frac{\pi^{2}}{3} \frac{k_{B}^{2}}{e} \frac{\mu}{\varepsilon_{F}}$$



Quantum oscillations and the quantum limit

Landau quantization

B = 0

 $B \neq 0$



Electron energy spectrum is no more a continuum.

Fermi surface truncated by Landau tubes

Fig. 2.1. Schematic sketches of Landau tubes for (a) spherical surfaces of constant energy, (b) ellipsoidal surfaces of constant energy (direction of long axis shown by arrow). The FS is indicated by the broken curve and only the parts of the Landau tubes inside the FS are occupied at T = 0 (after Chambers 1956 and Gold 1968).



Shoenberg 1984



The magnetic field required to attain the quantum limit

When the magnetic length becomes shorter than the Fermi wave length!

$$\lambda_F \propto n^{-1/3}$$

$$l_B \propto B^{-1/2}$$

Particle (radius of curved trajectory)

The lower the carrier density, the lower B_{QL} !

| | Copper | bismuth |
|-------------------------------------|-----------|---------|
| Carrier density (cm ⁻³) | 8.5 10 22 | 3 10 17 |
| λ _F (nm) | 0.5 | 47 |
| $B_{QL}(T)$ | 30000 | 9 |

Giant quantum oscillations of the Nernst response The last expected peak @ 9 T b а 400 bismuth B// trigonal Nernst voltage (μV) 00 00 T= 320 mK MAMMAM 100 -80 60 40 0.2 10 0 3 4 $B^{-1}(T^{-1})$ B(T)

Giant Nernst quantum oscillations in graphite

Zhu et al., Nature Physics 2009





When a Landau level intersects the Fermi level, the Nernst response...





···vanishes in graphene!







Theory :2D (Girvin, Jonson PRB 1984)



Recent theory on Nernst quantum oscillations

PRL 104, 066601 (2010)

PHYSICAL REVIEW LETTERS

week ending 12 FEBRUARY 2010

Theory of Dissipationless Nernst Effects

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PHYSICAL REVIEW B 83, 085103 (2011)

Oscillations of the Nernst coefficient in bismuth

Yu. V. Sharlai and G. P. Mikitik

B. Verkin Institute for Low Temperature Physics & Engineering, Ukrainian Academy of Sciences, Kharkov 61103, Ukraine (Received 29 October 2010; published 9 February 2011)

| PRL 107, 016601 (2011) | PHYSICAL | REVIEW | LETTERS | week ending 1 JULY 2011 |
|------------------------|----------|--------|---------|----------------------------|
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Giant Nernst-Ettingshausen Oscillations in Semiclassically Strong Magnetic Fields

Igor A. Luk'yanchuk,¹ Andrei A. Varlamov,² and Alexey V. Kavokin³ ¹Laboratory of Condensed Matter Physics, University of Picardie Jules Verne, Amiens, 80039, France ²CNR-SPIN, Viale del Politecnico 1, I-00133 Rome, Italy ³Physics and Astronomy School, University of Southampton, Highfield, Southampton, SO171BJ, United Kingdom (Received 28 November 2010; published 29 June 2011)



Angle-resolved Landau spectrum in bismuth (experiment and theory)





Symbols: experimental data; Lines: theory

Agreement is very good for holes, but only fair for electrons

Zhu et al., PNAS (2012)

The band picture of metals and insulators!



How does an isulator become a metal?



Fermiology of doped semi-conductors

•Self-doped Bi_2Se_3 believed to be a bulk topological insulator with non-trivial surface states.

•**SrTiO**_{3- δ} discovered in 1964 as the first case of a "semiconducting superconductor"

•Many others to be explored: PbTe, InSb, ...)



Topological insulators in Bi₂Se₃, Bi₂Te₃ and Sb₂Te₃ with a single Dirac cone on the surface



Toplogical? Sure! Insulator? Hum...

Figure 2 | **Band structure, Brillouin zone and parity eigenvalues. a,b**, Band structure for Bi₂Se₃ without (**a**) and with (**b**) SOC. The dashed line indicates the Fermi level. **c**, Brillouin zone for Bi₂Se₃ with space group $R\overline{3}m$. The four inequivalent time-reversal-invariant points are $\Gamma(0,0,0)$, $L(\pi,0,0)$, $F(\pi,\pi,0)$ and $Z(\pi,\pi,\pi)$. The blue hexagon shows the 2D Brillouin zone of the projected (**1**, **1**, **1**) surface, in which the high-symmetry **k** points $\overline{\Gamma}$, \overline{K} and \overline{M} are labelled. **d**, The parity of the band at the Γ point for the four materials Sb₂Te₃, Sb₂Se₃, Bi₂Se₃ and Bi₂Te₃. Here, we show the parities of fourteen occupied bands, including five *s* bands and nine *p* bands, and the lowest unoccupied band. The product of the parities for the fourteen occupied bands is given in brackets on the right of each row.

Which side of the metal-insulator transition?

Critical density for metal-insulator transition



Quantum oscillations of the Nernst effect in Bi₂Se₃



Two routes towards Fermi temperature

Thermopower

Quantum oscillations:



n- doped SrTiO₃





carrier density (cm⁻³)













The lowest concentration has a single frequency



Two ways to estimate the Fermi energy



Dilute superconductors



SrTiO_{3- δ} [With $\delta \approx 10^{-5}$] is the most dilute superconductor!

SUMMARY

•Thermoelectricity is poorly understood and barely explored in many solids! Often, it opens another window to electronic properties.

•At the boundary between metals and insulators, a large entropy is shared by few carriers with a remarkable thermoelectric response.

•In dilute metals, when few landau tubes survive, the exit of each of them generates a large Nernst oscillation.

•Many interesting thermoelectric materials are on the metalic side of metal-insulator transition and have a Fermi surface.

Neville Mott on metals and non-metals

Dear Poler 1'00 thought a hot about a work is a more!" think one can only the question of Tro. a wind conducts, + a hun-more closen". Yam Hert



Dear Peter, I've thought a lot about 'What is a metal?' and I think one can only answer the question at T = 0 [the absolute zero of temperature]. There a metal conducts, and a non-metal doesn't.

(Edwards 1998)

Edwards, Phil. Trans. R. Soc. A 368, 941-965 (2010)

"Everyone knows what a metal is and can describe many of its characteristics. It is safe to say, however, that few people would define a metal as a 'solid with a Fermi surface'. This may nevertheless be the most meaningful definition of a metal...and provides a precise explanation of the main physical properties ..."

A. R. Mackintosh

Scientific American 1963

First-principle calculations for Bi₂Te₃

