

Chapter 2: Metal materials - 2

What counts are the *specific* quantities:

- Conductivity σ (or the specific resistivity $\rho = 1/\sigma$).
- current density \underline{j} .
- (Electrical) field strength $\cdot \underline{E}$.

The basic equation for σ is:

n = concentration of carriers,

μ = mobility of carriers.

Ohm's law states:

It is valid for metals, but not for all materials.

$$\begin{aligned} [\rho] &= \Omega\text{m} \\ [\sigma] &= (\Omega\text{m})^{-1} = \text{S/m}; \\ \text{S} &= \text{"Siemens"} \end{aligned}$$

$$\sigma = |q| \cdot n \cdot \mu$$

$$\underline{j} = \sigma \cdot \underline{E}$$

σ (of conductors / metals) obeys (more or less) several rules; all understandable by looking at *n* and particularly *μ*.

- Matthiesen rule:

Reason: Scattering of electrons at defects (including phonons) decreases *μ*.

- "ρ(*T*) rule":

about **0,04 %** increase in resistivity per **K**

Reason: Scattering of electrons at phonons decreases *μ*.

- Nordheim's rule:

Reason: Scattering of electrons at **B** atoms decreases *μ*.

$$\rho = \rho_{\text{Lattice}}(T) + \rho_{\text{defect}}(N)$$

$$\Delta\rho = \alpha_{\rho} \cdot \rho \cdot \Delta T \approx \frac{0,4\%}{^{\circ}\text{C}}$$

$$\rho \approx \rho_A + \text{const.} \cdot [\text{B}]$$

Non-metallic conductors are *extremely* important.

- Transparent conductors (TCO's) ("ITO", typically oxides).
- Ionic conductors (liquid and solid).
- Conductors for high temperature applications; corrosive environments, .. (Graphite, Silicides, Nitrides, ...).
- Organic conductors (and semiconductors).

No flat panels displays = no notebooks etc. without **ITO**!

Batteries, fuel cells, sensors, ...

Example: **MoSi₂** for heating elements in corrosive environments (dishwasher!).

The future High-Tech key materials?

General Applications

Normal Applications

A world without **conductors** is even harder to imagine than a world without **semiconductors**. Examples for applications include

- High-voltage free-air power transmission lines.
- High voltage wires for trains (getting "scratched" all the time).
- In-house wiring.
- Low-voltage wiring (car systems).
- High current wiring (machines).
- System on-board wiring.
- Bond wires for **IC's** (diameter $< 30\mu\text{m}$).
- Metallization on chips.
- Screening electrical or magnetic fields.
- Avoidance of electrostatic charging.
- Electrodes for batteries, chemical reactors etc.
- Antennas.

Each use has special requirements which should be met by the conducting material.

Some examples for requirements

- **Money** (Use of **Au**, **Ag**, **Pt** etc. may be critical).
- **Chemistry** (general stability and reactivity; essential excludes **Na**, **K**, **Hg** etc. for most applications; corrosion properties, ...).
- **Mechanical** properties (Pure metals are often too soft, but alloys have higher resistivity).
- **Thermal** properties (temperature coefficient; no metal usable beyond ca. **1000 K**).
- **Compatibility with other materials** (contact corrosion, solderability, thermoelectric and thermomechanical properties, general chip compatibility, ...).
- **Compatibility with production technologies** (e.g. thin film deposition methods, wire making (try this with a brittle superconductor!),...).

Whole families of conductors, fine-tuned for a specific applications, were developed; below are some examples.

Cu based conductors

There are many precisely specified **Cu**-based conductors for all kind of specific applications, [examples](#) are given in the link.

Al based conductors

This family is primarily used for high-voltage free-air cables (in combination with a steel core) because of best fitting in terms of conductivity - price - mech. **strength** - corrosion requirements; cf. the [illustration](#) in the link.

Others

In **one IC** you may find the following conductor materials:

- Poly crystalline highly doped **Si**.
- Silicides; i.e. **Si** - metal compounds like **NiSi₂**.
- **Al** with $\leq 1\%$ of **Si** and **Cu** if the chip was made before, say, **2000**.
- **Cu** with some additions instead of **Al** if the chip was made after **2000**.
- **W**.
- **TiN**.

because one material simply does not meet the specific requirements for conductor on chips.

Contacts

Contacts, meaning **mechanical contacts** here, are a major part of most electronic products. Even if there is no mechanical switch anymore, you still have the contact between the plug and the outlet, and/or the contact springs for the batteries.

Contacts include the following items:

- Switches, **plugs**, relays, connections to removable parts (batteries, light bulbs, ...), **pantographs** (the thing on top of a locomotive), "brushes" (for motors), and so on.
- Contacts are also the components or materials that often cause **trouble**. Contacts or switches are often the first components to break, and thus a nuisance to consumers like you and me.

There are many specific requirements for **contact materials**:

- Small contact resistance (it is never zero).
- No sticking or welding under load.
- No **abrasion** under load.
- No intermixing of materials.
- No wearing and tearing.
- Suitable mechanical properties, e.g. good elasticity (forever) for switches.

There are specific materials and group of materials generally favored for contacts:

- C (graphite in many forms) for pantographs and whenever you want to draw a big current.
- Cu, Ag, Au.
- Ru, Rh, Pd, Os, Ir, Pt.
- Mo, W.
-

An example of [Ag-based contact materials](#) can be found in the link.

For contact applications we find *expensive* materials, because in many applications only small quantities are needed and the inertness of noble metals is what counts.

Resistors

Basic requirements for **resistors** (still one of the most numerous component in circuits) are:

- Large region of **R** values (= device resistance in Ω) within **one** production technology.
- Small (ideally vanishing) temperature coefficient .
- Minimal noise.
- Small dependence of ρ on production parameters (good repeatability).
- No Ageing.
- Small thermoelectrical coefficients to **Cu** (you want a resistor, not a thermoelement).

Materials of choice include

- **Ta, Ta** based alloys, and in particular "**Constantan**" (55% **Cu**, 44% **Ni**, 1% **Mn**), a resistor material with an especially small temperature coefficient α_ρ , but a large thermoelectric coefficient).
- Strange mixtures of conductors and insulators including "**Cermet**" (short for Ceramics - Metals), e.g. **Cr - SiO₂**.

Details and data in the [\(future\)](#) link.

Heating

Basic requirements for **heating elements** are:

- High melting point.
- Chemical stability at high temperatures and in potentially corrosive environments.
- Mechanical strength at high temperatures.

The choice of a materials depends significantly on the range of temperatures envisioned. We have:

- **FeNiCr, FeNiAl** alloys.
- **Pt, W, Ta, Mo** - stable elements with a high melting point.
- **MoSi₂** Among more industrial applications also used as heaters in dish washers - this is very aggressive environment!
- Graphite (up to **3000 K** in non-oxidizing gas).

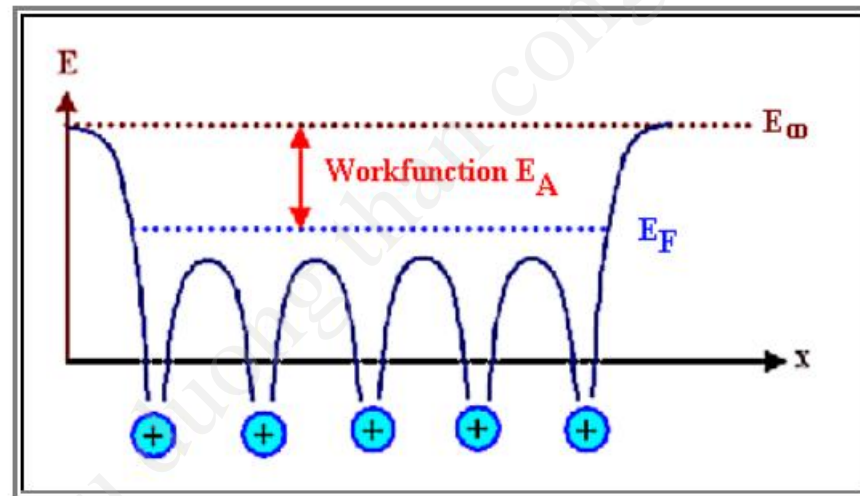
Special Applications

Thermionic Emission

Cathodes in **cathode ray tubes (CRT)**, in regular **electron tubes** (still used for special applications), but also in all electron beam tools as e.g. **electron microscopes** or **electron beam welding**, are one example of **special conductors**. We need to have free electrons in the material **and** we need to extract them from the material.

- For good cathodes we wish for some specific properties: First we want to extract lots of electrons **easily** and in **large quantities** (i.e. we want high current densities for little money).
- Second, we want to extract them from a very **small area** (for high brightness), so that we can consider the electron beam to come from a **point source** which makes (electron) optics a lot less complicated to handle!

Lets look at the free electron gas model and see how we can extract electrons in general.



For a metal, there are lots of electrons in the last band at all energies up to the Fermi energy, and at very low temperatures it takes at least the energy E_A to push an electron up the energy scale to E_∞ , where it would be free to go wherever it wants - it is no longer "bound" to the crystal. We call that particular energy the **work function** of the material.

The **work function** E_A of the material is thus the decisive quantity; it is the difference between the **Fermi energy** and the potential at infinity E_∞ .

$$E_A = E_F - E_\infty$$

If we let $E_\infty = 0$ and have the energy scale going "down", we simply have .

$$E_A = E_F$$

The current density for thermionic emission is given by the well-known **Richardson equation**, which we obtain by calculating how many electrons will have sufficient energy to overcome the energy barrier to the outside world from the energy distribution of electrons in a free electron gas model.

■ The Richardson equation for the current density j from a hot surface states:

$$j = A \cdot T^2 \cdot \exp - \frac{E_A}{kT}$$

- From measuring $j = j(T)$ we expect (almost) **Arrhenius** behavior; E_A then follows from the slope of the plot, the constant A from its intersection with the j - axis.

The pre-exponential factor **A** can be calculated from the free electron gas model, but than it is only a crude approximation for real materials. Its free-electron-gas value is:

$$A_{\text{theo}} = 120 \text{ A} \cdot \text{cm}^{-2} \cdot \text{K}^{-2}.$$

Lets compare that to some measured values (and bear in mind that **A** may depend on the Miller indices of the crystallographic plane from which we extract electrons, too - so numbers vary):

Material	Fe	Ni	Pt	Ta	W	Cs	LaB ₆
A [Acm ⁻² K ⁻²]	26	30	32	55	60	162	25
E_A [eV]	4,5 - 4,8	5,15 - 5,35	5,65	4,15 - 4,8	4,2	1,8 - 2,14	2,6
T_m [°C]	1 535	1 452	1 755	2 850	3 410	28,4	2 210

Cs has the lowest work function, but its melting point is so low that it is of no use. Optimizing everything, the winners are:

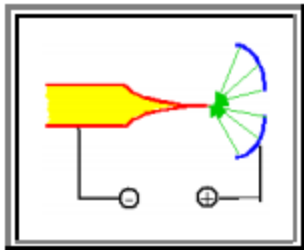
- W**, the workhorse for cathode materials.
- LaB₆**, a rather exotic material, because single crystals with very fine tips can be made that provide high current densities from a very small area. This is important whenever you want to focus the electron beam on a "point", e.g. in scanning electron microscopes. The focal point cannot be smaller than the area from where the electron beam was extracted from - *and you like it to be in the nm region*. The price one has to pay for this (besides for the **LaB₆** cathode, which is not cheap), is that the cathode has to be run in ultra high vacuum (**UHV**), because the fine tip would otherwise soon be damaged by ion bombardment resulting from ions extracted out of the residual gas atmosphere.

Field Enhanced Emission and Tunnelling Effects

If you run a **cathode**, emitting an electron beam, with **large** electrical fields between the cathode and the anode, you will find that your **workfunction** E_A seems to change to smaller values as the field strength increases.

This is called **Schottky effect**; it is observed at large field values of $(10^5 - 10^8) \text{V/cm}$.

If you apply even higher field strengths (and remember: $E = U/d$; you do not need high voltages U , only small dimensions d), E_A seems to vanish altogether.



- This effect is called **field emission**. It works even at room temperature and is barely temperature dependent, so it can not be a temperature activated process.
- Field emission is rather easy to obtain: all you have to do, is to make a very fine tip with a curvature of the tip in the **nm** - range as shown on the left.
- Field emission might then occur with a few Volts between the anode and the tip, because all the field lines will have to converge on the small tip.

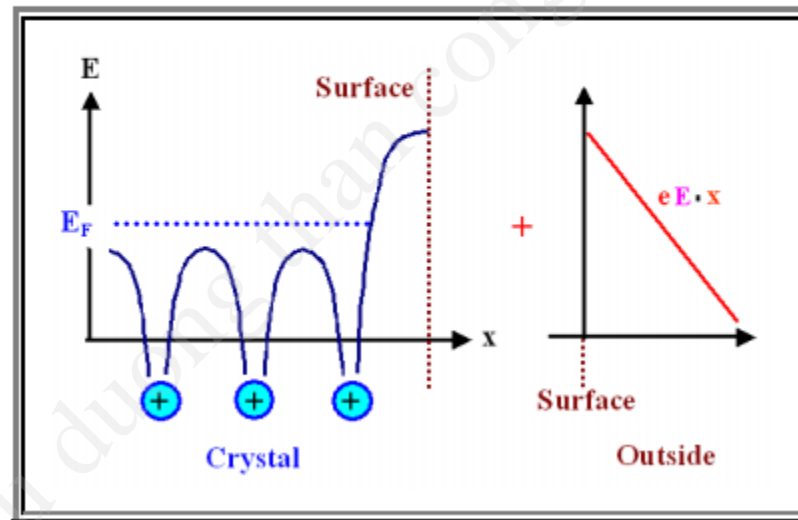
How can we understand these effects? Whereas the *Schottky effect* is relatively straight forward, *field emission* is a manifestation of the *tunnelling effect*, a purely quantum mechanical phenomenon.

Lets look at how the **free electron gas model** must be modified at high field strengths - and we will be able to account for *both* effects.

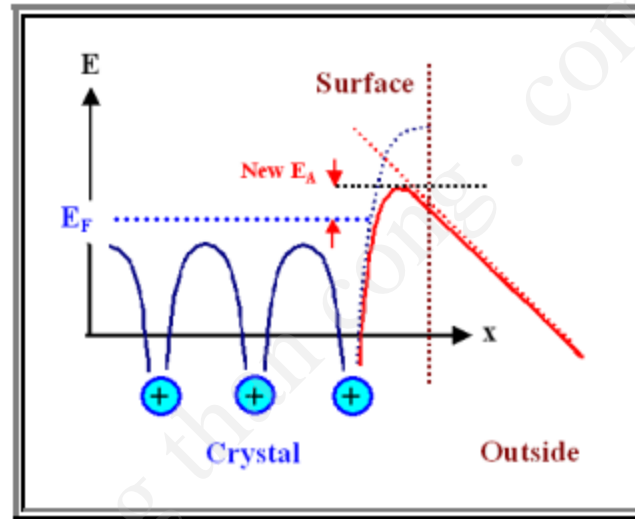
- The potential energy E outside of the material is such that electrons are to be extracted - it is not constant, but varies with the field strength E simply as

$$E = e \cdot E \cdot x$$

- E , the (constant) applied field strength (written in mauve to make sure that we do not mix it up with the energy E). We have the following situation:



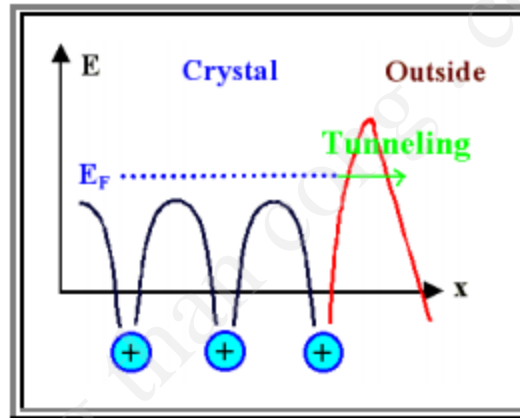
- Simply summing up the energies graphically yields the qualitative energy curve for an electron at the edge of a crystal as shown below.



- Whichever way you superimpose the potential energies, the potential barrier to the outside world will always be reduced. This explains qualitatively the *Schottky effect*.

The **field emission effect** requires a somewhat different consideration.

- Lets look at the **extremes** of the Schottky effect. For really high field strengths the potential barrier gets even lower and thinner, it may look somewhat like this:



Now the **tunneling effect** may occur. It is a phenomenon inherent in quantum mechanics and allows electron "waves" to "**tunnel**" through a potential barrier.

- In other words, the value of the **wave function** ψ for an electron does not go to zero abruptly at a potential barrier, but decays exponentially. There is then a finite amplitude for ψ **on the other side** of the potential barrier, an effect that is felt if the barrier is "thin" and low - as in the picture above. If the field strength is high enough, large quantities of electrons can directly tunnel to the outside world. More about tunnelling in the [link](https://fb.com/tailieudientucntt).

Field emission thus is a purely quantum mechanical effect; there is no classical counterpart whatsoever. It is used in a growing number of applications:

- **Electron microscopes** for special purposes (e.g. scanning electron microscopes with high resolution at low beam voltage, a must for the chip industry) are usually equipped with **field emission "guns"**.
- **"Scanning Tunnelling Microscopes" (STM)** which are used to view surfaces with atomic resolution, directly employ tunnelling effects.
- Large efforts are being made to construct flat panel displays with millions of miniature field emission cathodes - at least one per pixel.
- Some semiconductor devices (e.g. the **"tunnel diode"**) depend on tunnelling effects through space charge regions.

In other contexts, tunnelling is not useful, but may **limit** what you can do. Most notorious, perhaps, is the effect that **very thin** insulators - say **5 nm** and below - are insulating no more, a growing problem for the chip industry.

Thermoelectric Effects

So far we have only considered *one* conducting material; the unavoidable **contacts** between conductors, implicitly always required, were seemingly devoid of special properties.

● We know that this *is not true* for many other contacts; e.g. combinations of

- semiconductor - semiconductor.
- semiconductor - conductor.
- ionic conductor - conductor.

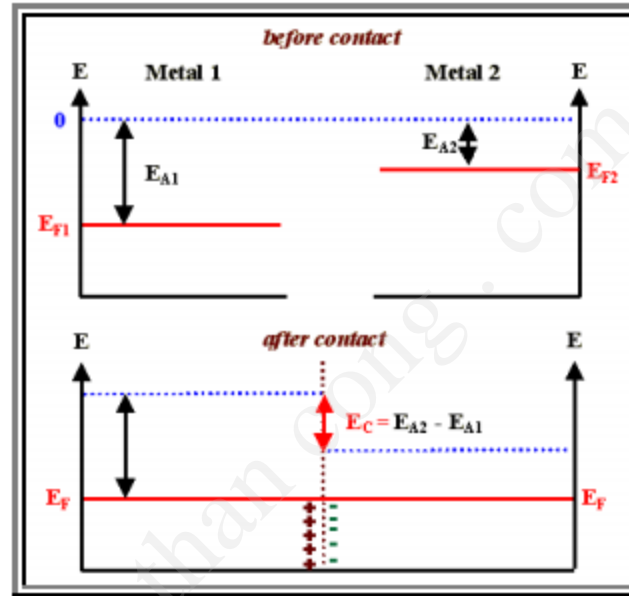
● What about *metal - metal contacts*?

● We routinely solder wires of different conductors together or join them in any way, and do not worry about the contacts. Besides, maybe, a certain (usually small) **contact resistance** which is a property of the interface and must be added to the resistance of the two materials, there seems to be no other specific property of the contact.

● But that is *only true* as long as *the temperature is constant* in the whole system of at least two conductors.

● The reason for this is that we always get a **contact voltage**, as in the case of semiconductors, but the extension of the charged layers at the interface (the Debye lengths) is so short that no specific phenomena result from this.

Consider the band diagrams before and after joining two metals



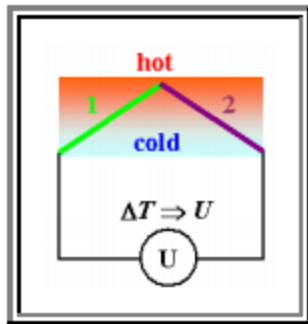
We have a dipole layer of charges at the interface which, owing to the large carrier density, is extremely thin and does not hinder current flow (it is easy for electrons to tunnel through the potential barrier).

We also have a *contact potential*, which is called the **Volta potential**. Since in any closed circuit (containing, e.g., the wires to the voltmeter), the *sum of the Volta potentials must be zero* in **thermal equilibrium**, it therefore can not be measured directly.

If, however, *one* of the at least two contacts needed for a closed circuit is at a temperature T_2 that is different from the temperature T_1 of the first contact, we have *non-equilibrium* and now a voltage may be measured. We observe the **Seebeck effect**, one of several **thermoelectric effects**.

Seebeck Effect

The Seebeck effect is the base for **thermoelements** or **thermocouples**, the standard device for measuring temperatures (the good old mercury thermometer is virtually nonexistent in technical applications, especially at high temperatures).



Lets look at a typical situation: We have a thermocouple mader with a material **1** and a material **2**. It's "contacted" by whatever (material **3**, black lines). The junction of material**1** and material **2** is hot, the rest is cold (and has the same temperature).

The voltmeter will show a **thermovoltage** that depends on ΔT and the two materials forming the thermocouple.

Generally, the thermovoltage should be larger for couples of conductors with very different Fermi energies or carrier densities, since then the Volta potential is larger.

Being more specific, the Volta potential should follow [Nernsts law](#). But here we are only interested in the practical aspects of thermocouples.

For technically important materials, it is convenient to construct a voltage scale for thermocouples given in **mV/100K**.

The voltage measured for a temperature difference of **100 K** is then the difference of the two values given on that scale for the two materials joined in a thermocouple. The zero point was arbitrarily chosen for **Pt**.

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Bi	Ni	Pd	Pt	Hg	PtRh	Cu	Mo	Fe	NiCr	Sb
-7,7	-1,5	-0,3	0	0	0,7	0,77	1,2	1,92	2,6	4,8

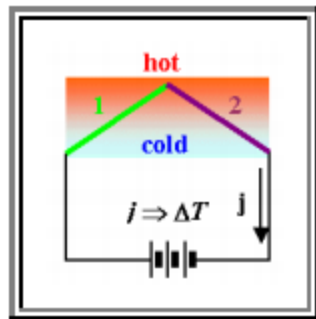
- Useful couples are, e.g. **Ni/NiCr**, with a thermovoltage of ca. **4 mV/100K** and a usable temperature range up to **1000 K**.

The Seebeck effect, for many years extensively used for measuring temperatures, can also be used to convert heat energy directly into electrical energy. **Thermoelectric generators** are becoming an exciting field of materials science, because optimized materials, based on a thorough understanding of the requirements for power generation and the concomitant requirements for the materials, are becoming available.

Other Thermoelectric Effects

There are several thermoelectrical effects which are deeply rooted in **non-equilibrium thermodynamics**. Essentially, there is a "*reciprocating*" coupling of *gradients in driving forces* and *currents of any kind* (not just electrical currents but also, e.g. particle currents, heat currents, or even entropy currents).

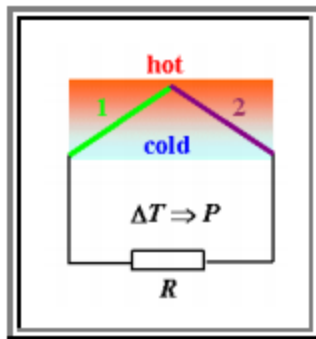
- Reciprocating* means, that if a *gradient* - e.g. in the *temperature* - induces an electric *current* across a junction (the Seebeck effect), than an electric current induced by *some other means* must produce a temperature gradient. And this does *not* address the heating simply due to ohmic heating!
- The "reversed" Seebeck effect does indeed exist, it is called the **Peltier effect**. In our schematic diagram it looks like this:



- An electrical current, in other words, that is driven through the system by a battery, would lead to a "heat" current, transporting thermal energy from one junction to the other one. One junction then goes down in temperature, the other one goes up.
 - This effect would also occur in hypothetical materials with zero resistivities (we do not mean superconductors here). If there is some resistance R , the current will always lead to some heating of the wires everywhere which is superimposed on the Peltier effect.
- The temperature difference ΔT between the two junctions due to the external current density j induced by the battery and the Peltier effect then is approximately given by

$$\Delta T \approx \text{const.} \cdot j$$

- The removal of heat or thermal energy thus is linear with the current density
- But there is always heating due to by ohmic losses, too. This is proportional to j^2 , so it may easily overwhelm the Peltier effect and no net cooling is observed in this case.
- ▶ The Peltier effect is not useful for *heating* - that is much easier done with resistance heating - but for *cooling*!
- With optimized materials, you can lower the temperature considerably at one junction by simply passing current through the device! The Peltier effect actually has been used for refrigerators, but now is mainly applied for controlling the temperature of specimens (e.g. chips) while measurements are being made.
- ▶ One can do a third thing with thermoelements: Generate power. You have a voltage coupled to a temperature difference, and that can drive a current through a load in the form of a resistor.



- Invariably the question of the efficiency η of power generation comes up. How much of the thermal energy in the system is converted to electrical energy?
- This is not easy to calculate. It is, however, easy to guess to what η will be proportional:
 - $\eta \propto K$.
 - $\eta \propto$
 - $\eta \propto K$

Thermionic emission provides electron beams.

The electron beam current (density) is given by the *Richardson equation*:

● $A_{\text{theo}} = 120 \text{ A} \cdot \text{cm}^{-2} \cdot \text{K}^{-2}$ for free electron gas model
 $A_{\text{exp}} \approx (20 - 160) \text{ A} \cdot \text{cm}^{-2} \cdot \text{K}^{-2}$

● E_A = work function $\approx (2 - >6) \text{ eV}$

● Materials of choice: **W**, **LaB₆** single crystal

High field effects (tunneling, barrier lowering) allow large currents at low T from small (nm) size emitter

$$j = A \cdot T^2 \cdot \exp - \frac{E_A}{kT}$$

Needs **UHV**!

There are several thermoelectric effects for metal junctions; always encountered in non-equilibrium.

Seebeck effect:

Thermovoltage develops if a metal A-metal B junction is at a temperature different from the "rest", i.e. if there is a temperature gradient

Peltier effect:

Electrical current I through a metal - metal (or metal - semiconductor) junction induces a temperature gradient $\propto I$, i.e. one of the junction may "cool down".

Essential for measuring (high) temperatures with a "thermoelement"
Future use for efficient conversion of heat to electricity ???

Used for electrical cooling of (relatively small) devices. Only big effect if electrical heating ($\propto I^2$) is small.