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The Physics of Thermoelectric Energy Conversion

H Julian Goldsmid

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H Julian Goldsmid
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Morgan & Claypool Publishers

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This book is dedicated to my wife, Joan.

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Preface

For many years after their discovery in the early part of the nineteenth century the thermoelectric effects were not much more than a scientific curiosity. They eventually found application in the measurement of temperature and in the detection of thermal radiation. However, thermoelectricity is now regarded as a serious means for the conversion of heat into electricity and for heat pumping and refrigeration. The present-day thriving thermoelectric industry has come about through the dedicated research of materials scientists from all disciplines with a major contribution coming from solid state physicists. Considerable advances have been made since the introduction of semiconductor thermoelements in the middle of the twentieth century but much more needs to be done and it is hoped that this book will encourage a new generation of experimental and theoretical physicists to use their talents in the study of thermoelectricity.

Julian Goldsmid
Kingston Beach, Tasmania, Australia
March 2017

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Author biography

H Julian Goldsmid

After graduating from Queen Mary College, University of London in 1949 Julian Goldsmid joined the scientific staff of the General Electric Company in their Wembley laboratories. In 1964 he was appointed Reader in Solid State Physics at the University of Bath and in 1969 he became Professor of Experimental Physics at the University of New South Wales in Sydney. After retiring from his chair in1988 he was appointed Emeritus Professor. From 1989 to 1995 he was Chairman of the Australian National Standards Commission.

Julian Goldsmid has been a Visiting Professor at the universities of Karlsruhe, Sussex, Southampton and the Southern Methodist University in Dallas. Until recently he was a consultant for Marlow Industries. He is a Fellow of the Institute of Physics and Honored Academician of the International Thermoelectric Academy. In 2002 he was awarded the Golden Prize of that organisation. In 2012 he received the Outstanding Achievement Award of the International Thermoelectric Society. He also received the Lightfoot Medal of the Institute of Refrigeration in 1959. He was awarded his PhD degree by the University of London in 1958 and his DSc in 1966. He has been author or joint author of about 200 publications. He is credited with many developments in the field of thermoelectricity, including the first demonstration in 1954 of practical refrigeration using the Peltier effect in bismuth telluride.

List of symbols

A	Cross-section area, mean atomic weight
a	Lattice constant
B	Magnetic field
C	Thermal capacity
c	Diameter of defect
c_V	Specific heat per unit volume
D^*	Detectivity
d	Width
E	Electric field, energy
E_F	Fermi energy
E_g	Energy gap
e	Electronic charge
F_n	Fermi–Dirac integral
f	Fermi distribution function
f_0	Equilibrium Fermi distribution function
g	Density of electron states
h	Planck's constant
$\hbar$	$h/2\pi$
I	Electric current
I_ϕ	Current for maximum COP
i	Electric current density
j	Heat flux density
K	Thermal conductance
K_c	Thermal conductance per unit area of end plates
K_s	Transport integral
k	Boltzmann's constant
L	Length, Lorenz number
l_e	Mean free path of charge carriers
l_t	Mean free path of phonons
M	$(1 + ZT_m)^{1/2}$
m	Mass of free electron
m^*	Density-of-states effective mass
m_I	Inertial mass
m_N	Density-of-states mass for a single valley
N	Nernst coefficient, total number of modes of vibration, number of unit cell per unit volume, number of couples in a module, number of stages in cascade
N_A	Avogadro's number
N_v	Number of valleys in an energy band
n	Subscript for electrons
n	Electron concentration, ratio of layer thicknesses in a synthetic transverse thermoelement
P	Ettingshausen coefficient, Poisson's ratio
p	Subscript for positive holes
$\boldsymbol{p}$	Phonon momentum
q	Rate of heat flow, phonon wave number
Q_1	Rate of heat flow from source
R	Electrical resistance, gas constant, responsivity

R_H	Hall coefficient
R_L	Load resistance
r	Scattering law parameter
S	Righi–Leduc coefficient
s	Compatibility factor
T	Temperature
T_1	Temperature of heat source
T_2	Temperature of heat sink
T_m	Mean temperature, melting point
ΔT	Temperature difference
ΔT^*	Temperature difference between sink and source
ΔT_{max}	Maximum temperature difference
t	Time
u	Velocity of carriers
V	Voltage, mean atomic volume
v	Speed of sound
w	Electrical power
x	$\hbar\omega/kT$
Z	Thermoelectric figure of merit for couple
Z_{NE}	Thermomagnetic or Nernst–Ettingshausen figure of merit
z	Figure of merit for single material
z_d	Phonon drag figure of merit
z_{trans}	Transverse figure of merit
α	Seebeck coefficient
α_d	Phonon drag Seebeck coefficient
α_T	Thermal expansion coefficient
β	Chasmar and Stratton's materials parameter, phase difference
Γ	Gamma function
γ	Grüneisen's parameter
ε	Emissivity
ε_m	Parameter in melting rule
η	Efficiency, reduced Fermi energy
η_g	Reduced energy gap
θ_D	Debye temperature
κ	Thermal diffusivity
λ	Thermal conductivity
λ_e	Electronic thermal conductivity
λ_I	Thermal conductivity of insulation
λ_L	Lattice conductivity
μ	Carrier mobility
ν	Frequency
ξ	Reduced energy
π	Peltier coefficient
π_d	Phonon drag Peltier coefficient
ρ	Electrical resistivity, density
σ	Electrical conductivity
τ	Thomson coefficient, relaxation time
τ_0	Scattering law constant
τ_d	Relaxation time for phonon drag
τ_e	Relaxation time for charge carriers
τ_{eff}	Effective relaxation time for charge carriers

τ_N	Relaxation time for normal processes
τ_R	Relaxation time for umklapp processes
ϕ	Coefficient of performance, angle of transverse thermoelement with normal to layers
ϕ_{max}	Maximum coefficient of performance
χ	Compressibility
ω	Angular frequency
ω_D	Debye angular frequency

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Chapter 1

The Seebeck and Peltier effects

1.1 Definition of the thermoelectric coefficients

In this book we shall review the physical aspects of an energy conversion process that does not require any mechanical movement. The thermoelectric phenomena in those solids that conduct electricity are a measure of the energy transported by the charge carriers. These effects are thermodynamically reversible but they are invariably accompanied by irreversible effects associated with electrical resistance and thermal conduction. One of our aims is to show how the reversible processes can be maximised and the irreversible processes minimised.

The effect that bears his name was discovered in 1821 by Thomas Seebeck. It is manifest as an electromotive force (EMF) or voltage, V, which appears when the junction between two dissimilar conductors (A and B) is heated. Strictly speaking, the effect depends on the temperature difference, ΔT, between the two junctions that are needed to complete the electrical circuit. The Seebeck coefficient is defined as

$$a_{\mathrm{AB}} = \frac{V}{\Delta T}. \tag{1.1}$$

Although the effect occurs only when there is a junction between two materials, the Seebeck effect is a characteristic of the bulk rather than surface properties.

The Seebeck effect is often used in the measurement of temperature. A thermocouple for this purpose typically consists of two metals or metallic alloys. For example, copper and constantan, with a differential Seebeck coefficient of about 40 μV K^{-1}, are commonly employed. Since a thermocouple measures the temperature difference between two junctions, the second junction must be placed in an enclosure at some known temperature, such as a bath of melting ice at 0 °C.

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A closely related effect was discovered in 1834 by Jean Peltier. Peltier heating or cooling occurs when an electric current, I, flows through the junction between two conductors. The Peltier coefficient, π_{AB}, is defined as

$$\pi_{AB} = \frac{q}{I}, \tag{1.2}$$

where q is the rate of heating or cooling.

It is rather more difficult to demonstrate the Peltier effect than the Seebeck effect. If the thermocouple branches are metallic, the reversible Peltier effect is usually overshadowed by irreversible Joule heating. Thus, unless the electric current is very small, the best that can be done is to show that the overall heating is less for the current flow in one direction rather than the other. Of course, with the semiconductor thermoelements that are now available, it is easy to show that water can be frozen with the current in one direction and boiled with the current in the opposite direction.

1.2 The Kelvin relations

It is not surprising that the Seebeck and Peltier coefficients are inter-dependent. Kelvin established two laws that relate α_{AB} and π_{AB} to one another and to a third quantity, the Thomson coefficient, τ. The Thomson coefficient is the rate of heating per unit length when unit current passes along a conductor for unit temperature gradient. It may be expressed, therefore, as

$$\tau = \frac{\mathrm{d}q/\mathrm{d}x}{I\,\mathrm{d}T/\mathrm{d}x}. \tag{1.3}$$

Unlike the Peltier and Seebeck effects, the Thomson effect exists for a single conductor and is present for both branches of a thermocouple.

The relationships between the thermoelectric coefficients can be determined by the principles of irreversible thermodynamics. These relationships, which are known as Kelvin's laws, are

$$\pi_{AB} = a_{AB}T, \tag{1.4}$$

and

$$\tau_A - \tau_B = T\frac{\mathrm{d}\alpha_{AB}}{\mathrm{d}T}. \tag{1.5}$$

It would clearly be helpful if we could assign Seebeck and Peltier coefficients to each branch of a thermocouple so that α_{AB} and π_{AB} would be equal to $(\alpha_A - \alpha_B)$ and $(\pi_A - \pi_B)$ respectively. We note that the thermoelectric coefficients are equal to zero for all pairs of superconductors, so it is reasonable to suppose that the absolute values of α and π are zero for any superconductor. This being so, we can obtain the absolute values of α and π for any normal conductor by joining it to a superconductor. Of course, this procedure is effective only below the critical temperature of the superconductor. However, the absolute Seebeck coefficient of the normal conductor can be extrapolated to higher temperatures [1, 2] using the

second Kelvin relation, equation (1.5). This has actually been done for the metal lead, which can be used as a reference material in establishing the absolute Seebeck coefficients of other conductors.

The first of Kelvin's laws, equation (1.4), is useful in that it tells us that one does not need to specify both the Seebeck and Peltier coefficients. The Peltier coefficient is, in fact, rather difficult to determine, whereas the Seebeck coefficient is one of the easiest of physical properties to measure. Thus, it is common practice to develop the theory of thermoelectric energy conversion in terms of the Seebeck coefficient. If and when the Peltier coefficient is needed, it is replaced by αT.

1.3 Electrical resistance and thermal conductance

The Seebeck and Peltier effects are reversible and a thermoelectric energy convertor would have the characteristics of an ideal heat engine were it not for the presence of the irreversible effects of electrical resistance and heat conduction. If one attempts to reduce the Joule heating in a thermocouple by increasing the cross-section area and reducing the length one merely increases the heat conduction losses. In developing the theory of thermoelectric generation and refrigeration one needs to include terms that involve the electrical and thermal conductivities of the thermocouple materials.

The electrical conductivity, σ, is defined by the relation

$$\sigma = \frac{IL}{VA}, \tag{1.6}$$

where I is the electric current, V is the applied voltage, L is the length and A is the cross-section area. As we shall see later, it is important to specify that the voltage is that for isothermal conditions.

The other quantity of interest, the thermal conductivity, λ, is defined by

$$\lambda = \frac{qL}{A\Delta T}, \tag{1.7}$$

where q is the heat that is transported for a temperature difference ΔT over a length L.

It is obvious that the Seebeck and Peltier coefficients should be as high as possible and that the electrical conductivity should be large and the thermal conductivity small. However, as we shall see later, these requirements cannot all be met in a given material. Usually an increase in the thermoelectric coefficients is accompanied by a decrease in the electrical conductivity. In the next chapter we shall show the relative importance of the different properties and we shall introduce a quantity known as the figure of merit, z. We shall show how the performance of thermoelectric refrigerators and generators is related to z.

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Chapter 2

The thermoelectric figure of merit

2.1 Coefficient of performance of thermoelectric heat pumps and refrigerators

The possibility of using the Peltier effect as a means of refrigeration was recognised in the nineteenth century. A refrigerator is a device for transporting heat from a source at a temperature T_1 to a sink at a higher temperature T_2. The ratio of the cooling power to the rate of working, i.e. the electrical power input, is known as the coefficient of performance, ϕ. The value of ϕ generally falls as $(T_2 - T_1)$ increases and there is a maximum temperature difference, ΔT_{max}, that can be achieved with any particular heat engine. It is desirable that both ϕ and ΔT_{max} should be large. It was shown by Altenkirch in 1911 [1] that these quantities can be related to the Seebeck coefficient and to the ratio of the electrical to thermal conductivity in each of the branches of a thermocouple that is used as a refrigerator. Altenkirch's theory is still useful though, at the time that it was presented, no thermoelectric materials were available that allowed worthwhile values of ΔT_{max} to be reached.

We discuss the performance of a thermoelectric refrigerator using the simple model shown in figure 2.1. The diagram shows a single thermocouple situated between a source of heat and a heat sink. The couple will generally consist of a positive and a negative branch though occasionally one of the branches may be a metal with a Seebeck coefficient that is close to zero. For example, a superconducting branch [2, 3] will not contribute to the thermoelectric effects but neither will it impair the performance of the other, active, branch. The branches are usually linked by metallic conductors.

When an electric current I flows through the couple there will be a Peltier cooling effect $I\pi_{AB}$, which will be of the order of a tenth of a watt per amp. Most practical refrigerators will require several watts of cooling and this is achieved by connecting many thermocouples thermally in parallel and electrically in series so as to avoid the use of excessively large currents. However, the theory for a single couple is equally valid for a multi-couple arrangement.

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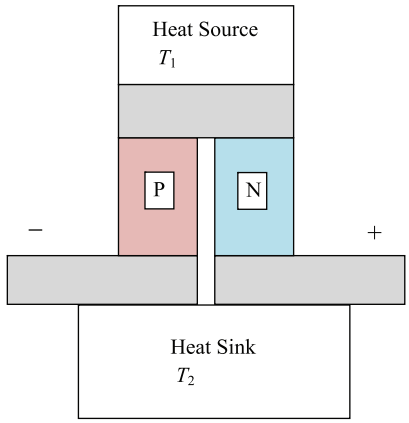

Figure 2.1. Basic thermoelectric refrigerator.

We shall suppose that the thermocouple makes perfect thermal contact with the source and sink and we shall ignore heat transport other than through the two branches. It will be necessary to take account of the relative ratios of length, L, to cross-section area, A, for the two arms. It will be supposed that the temperature dependence of the Seebeck coefficient and of the electrical and thermal conductivities can be ignored. This is a reasonable approximation for thermoelectric refrigerators since the temperature difference $(T_2 - T_1)$ is generally much less than the absolute temperature.

The Peltier cooling effect will be opposed by thermal conduction and by Joule heating, half of which will be delivered to the heat source and half to the sink. Thus, the overall rate of cooling is given by

$$q_1 = (\alpha_p - \alpha_n)T_1 I - I^2 R/2 - K(T_2 - T_1), \tag{2.1}$$

where R is the electrical resistance of the two branches in series and K is the thermal conductance of the branches in parallel. R and K are given by

$$R = \frac{L_p}{o_p A_p} + \frac{L_n}{o_n A_n}, \tag{2.2}$$

and

$$K = \frac{\lambda_p A_p}{L_p} + \frac{\lambda_n A_n}{L_n}. \tag{2.3}$$

The rate of expenditure of electrical energy, w, can be expressed as

$$w = (\alpha_p - \alpha_n)(T_2 - T_1)I + I^2 R. \tag{2.4}$$

Thence the coefficient of performance, ϕ, is given by

$$\phi = \frac{q_1}{w} = \frac{(\alpha_p - \alpha_n)T_1 I - I^2 R/2 - K(T_2 - T_1)}{(\alpha_p - \alpha_n)(T_2 - T_1)I + I^2 R}. \tag{2.5}$$