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H. Julian Goldsmid

Introduction to Thermoelectricity

With 140 Figures

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Preface

This book has been written at a time when thermoelectric energy conversion is showing great promise. It was in 1953 that I first carried out the experiments on bismuth telluride that demonstrated the potential of thermoelectric refrigeration. The present-day thermoelectric modules are based on the work that was carried out during the late 1950s and the early 1960s on bismuth telluride and its alloys. Since that time, there have been significant advances in materials for thermoelectric generation, but at all temperatures the efficiency of energy conversion using thermocouples has fallen far short of that expected for an ideal thermodynamic machine. At last, with the advent of nanostructured thermoelements, there is the promise that substantial advances will be made.

The basic principles of thermoelectric devices have not changed over the years and the theory presented in the first few chapters will always be applicable as new materials are discovered. A review of existing thermoelectric materials is presented with a chapter devoted to bismuth telluride showing how improvements in its synthesis and composition have led to the present-day performance. It is not always appreciated that the behaviour of a specific alloy is strongly dependent on the manner in which it is prepared and a chapter is devoted to the production of materials, the stress being on principles rather than on experimental detail.

The assessment of the transport properties of thermoelectric materials presents special problems. The chapter on measurement techniques includes a discussion of the errors that can arise when the so-called figure of merit is determined for non-uniform specimens. Indeed, I myself was led astray in the interpretation of experimental observations on polycrystalline samples of anisotropic material before I realised the extent of the problem.

It is usual to make use of modules rather than simple thermocouples. There is an outline of the method of selecting commercial modules for any particular application and a discussion of the problems that arise from attempts to miniaturise the size of modules so as to economise on space and material. Throughout the book, I have tried to emphasise practical considerations.

A full understanding of the behaviour of nanostuctured thermoelectric materials requires the mastery of difficult theoretical concepts but it is hoped that the elementary treatment in this book will allow the reader to comprehend the basic principles. It is expected that the so-called bulk nanostructures will find their way into commercial production in the very near future.

It is only during the past 2 or 3 years that I have appreciated the potential of the synthetic transverse thermoelement and I have included a chapter that reviews this unusual configuration. I have also included discussions of energy conversion using the transverse thermomagnetic effects and the thermionic effects in solids and in vacuum. The latter, in particular, will lead to greatly improved efficiencies if they live up to their theoretical promise.

This book draws on my experience of thermoelectricity and its applications over the past 55 years. During that time I have been supported by many people and I acknowledge with gratitude the help that I have received from all of them.

In 1953, as a very junior scientist at the Research Laboratories of the General Electric Company, I was encouraged by my group leader, R.W. Douglas, to look into the possibility of using the Peltier effect in semiconductors as a practical means of refrigeration. He continued to support the project, in spite of scepticism from some of his senior colleagues, and the success of bismuth telluride as a thermoelectric material stems from his foresight. I received support from many others in the Solid Physics Group over the next few years and should mention particularly D.A. Wright, who supervised my Ph.D. studies, and Ray Drabble, who helped me to understand transport theory.

In my academic life between 1964 and 1988, first as Reader in Solid State Physics at the University of Bath and then as Professor of Physics at the University of New South Wales, I was fortunate to be working in institutions that had been founded to promote applied science. I was encouraged to continue my research on thermoelectricity and was joined by some excellent students. I am sure that I learned much more from them than they did from me.

I acknowledge the support that I have received over much of my career from Marlow Industries. Raymond Marlow enabled me to work closely with his company and kept me in touch with practical developments. In recent years, I have been stimulated by my contact with George Nolas and Ted Volckmann and I appreciate the fact that I am still able to work with Jeff Sharp and Jim Bierschenk.

Perhaps, my greatest inspiration has been the work of Abram Ioffe and I greatly valued the opportunity, in 2005, to join in the celebration of the 125th anniversary of his birth in the town of Romny in Ukraine. This was made possible through an invitation from Professor L.I. Anatychuk and I am most appreciative of his encouragement for me to continue with my research.

Over the whole of my career I have received enthusiastic support from my wife Joan and it is to her that I dedicate this book.

Kingston Beach
Tasmania, Australia
June 2009

Julian Goldsmid

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Contents

List of Symbols

A	Cross-section area, mean atomic weight, parameter for point-defect scattering
A_{M}	Parameter for mass-defect scattering
A_0	Richardson constant
a	Lattice constant
a_{H}	Scattering law dependent parameter in Hall coefficient
B	Magnetic field, parameter for umklapp scattering
B_{K}	Parameter in Keyes relation
C	Parameter for scattering by normal processes, concentration
c	Diameter of defect
c_{V}	Specific heat per unit volume
D	Diffusion coefficient in liquid
D^*	Specific detectivity
d	Width, electrode spacing, barrier width
d_{t}	Tunneling width
E	Electric field
E_F	Fermi energy
E_{g}	Energy gap
e	Electron charge
F_{n}	Fermi–Dirac integral
F_{NE}	Function proportional to thermomagnetic figure of merit
f	Fermi distribution function, measure of reduction of lattice conductivity in calculations for Si–Ge
f_0	Equilibrium Fermi distribution function
$\mathbf{G}$	Reciprocal lattice vector
G	Bulk modulus
g	Density of electron states, ratio of space occupied by insulation to that of thermoelements
h	Planck's constant, $h/2\pi$
I	Electric current
I_{q}	Current for maximum cooling power
I_ϕ	Current for maximum COP
i	Electric current density

i_1	Electric current density in a thermionic device
j	Heat flux density
K	Thermal conductance
K_c	Thermal conductance of end plates
K_{s}	Transport integral
k	Boltzmann's constant, segregation coefficient
$\boldsymbol{k}$	Wave vector for charge carriers
k_0	Parameter in Callaway's theory
L	Length, Lorenz number, latent heat
$\boldsymbol{l}$	Vector parallel to temperature gradient
l_{e}	Mean free path of charge carriers
l_{t}	Mean free path of phonons
M	$(1 + ZT_{\mathrm{m}})^{1/2}$, mean atomic mass, Average mass of unit cell
m	Mass of free electron, slope of liquidus
$m*$	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 cells per unit volume, number of couples in a module
N_0	Bose–Einstein function
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
n_{L}	Number of vibrational modes per unit volume and frequency
P	Ettingshausen coefficient, Poisson's ratio
p	Porosity factor, proportion of specular reflection of phonons
p	Subscript for positive holes
$\boldsymbol{p}$	Phonon momentum
q	Rate of heat flow
$\boldsymbol{q}_{\mathrm{L}}$	Phonon wave vector
q_{max}	Maximum cooling power
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
r_{c}	Electrical contact resistance for unit area
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, difference between liquidus and solidus temperatures
ΔT^*	Temperature difference between sink and source
ΔT_{max}	Maximum temperature difference
t	Time
u	Velocity of carriers
V	Voltage, mean atomic volume
V_{q}	Voltage for maximum cooling power
v	Speed of sound, speed of zone
W	Energy in a mode of vibration, thermal resistance
w	Electrical power
x	$\hbar\omega/kT$
y	Parameter in Callaway's theory
Z	Thermoelectric figure of merit for couple
Z_{NE}	Thermomagnetic or Nernst–Ettingshausen figure of merit,
${Z_{\mathrm{NE}}}^{\mathrm{i}}$	Isothermal thermomagnetic figure of merit
Z_{ϕ}	Transverse figure of merit
z	Figure of merit for single material
z_{d}	Phonon drag figure of merit
z_{1D}	One-dimensional figure of merit
z_{2D}	Two-dimensional figure of merit
α	Seebeck coefficient
α_{d}	Phonon drag Seebeck coefficient
α_{I}	Thermionic parameter replacing Seebeck coefficient
α_{T}	Thermal expansion coefficient
β	Chasmar and Stratton's materials parameter
β^*	$\left(1-\rho\Delta\rho/R_H^2B^2\right)$
β'	Materials parameter for a 2D conductor
β''	Materials parameter for a 1D conductor
β_{I}	Materials parameter for a solid-state thermionic device
$\mathit{\Gamma}$	Gamma function
γ	Grüneisen's parameter
δ	Atomic diameter
ε	Energy, emissivity, surface roughness
ε_{m}	Parameter in melting rule
η	Efficiency, reduced Fermi energy
η_{g}	Reduced energy gap
η_{r}	Reduced efficiency
$\mathit{\Theta}_{\mathrm{D}}$	Debye temperature
κ	Thermal diffusivity
$\mathit{\Lambda}$	Wavelength of phonons
$\mathit{\Lambda}_0$	Smallest phonon wavelength
λ	Thermal conductivity
λ_{e}	Electronic thermal conductivity

λ_I	Thermal conductivity of insulation, thermionic quantity replacing thermal conductivity
λ_L	Lattice conductivity
μ	Carrier mobility
ν	Frequency
ξ	Reduced energy
π	Peltier coefficient
π_d	Phonon drag Peltier coefficient
ρ	Electrical resistivity
ρ_d	Density
σ	Electrical conductivity, Stefan–Boltzmann constant
σ_I	Thermionic quantity replacing electrical conductivity
σ_0	Parameter that depends on mobility and effective mass
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	Work function
ϕ	Coefficient of performance, angle of transverse thermoelement to normal to layers
ϕ_q	Coefficient of performance at maximum cooling power
ϕ_s	Coefficient of performance of each stage of a cascade
ϕ_ϕ	Maximum coefficient of performance
χ	Compressibility
ω	Angular frequency
ω_D	Debye angular frequency

Chapter 1
The Thermoelectric and Related Effects

1.1 Introduction

The first of the thermoelectric effects was discovered, in 1821, by T. J. Seebeck. He showed that an electromotive force could be produced by heating the junction between two different electrical conductors. The Seebeck effect can be demonstrated by making a connection between wires of different metals (e.g., copper and iron). The other ends of the wires should be applied to the terminals of a galvanometer or sensitive voltmeter. If the junction between the wires is heated, it is found that the meter records a small voltage. The arrangement is shown in Fig. 1.1. The two wires are said to form a thermocouple. It is found that the magnitude of the thermoelectric voltage is proportional to the difference between the temperature at the thermocouple junction and that at the connections to the meter.

Thirteen years after Seebeck made his discovery, J. Peltier, a French watchmaker, observed the second of the thermoelectric effects. He found that the passage of an electric current through a thermocouple produces a small heating or cooling effect depending on its direction. The Peltier effect is quite difficult to demonstrate using metallic thermocouples since it is always accompanied by the Joule heating effect. Sometimes, one can do no better than show that there is less heating when the current is passed in one direction rather than the other. If one uses the arrangement shown in Fig. 1.1, the Peltier effect can be demonstrated, in principle, by replacing the meter with a direct current source and by placing a small thermometer on the thermocouple junction.

It seems that it was not immediately realised that the Seebeck and Peltier phenomena are dependent on one another. However, this interdependency was recognised by W. Thomson (who later became Lord Kelvin), in 1855. By applying the theory of thermodynamics to the problem, he was able to establish a relationship between the coefficients that describe the Seebeck and Peltier effects. His theory also showed that there must be a third thermoelectric effect, which exists in a homogeneous conductor. This effect, now known as the Thomson effect, consists of reversible heating or cooling when there is both a flow of electric current and a temperature gradient.

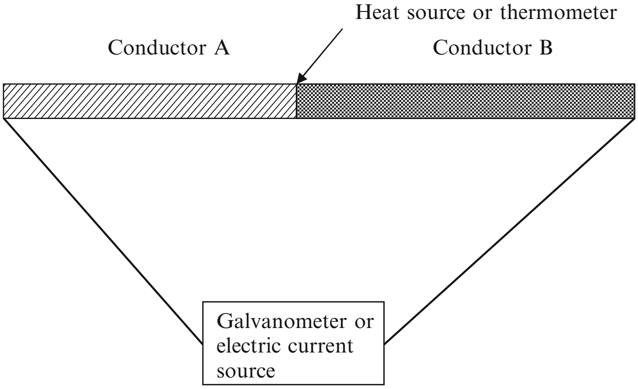

Fig. 1.1 Experiment to demonstrate the Seebeck and Peltier effects

The fact that the Seebeck and Peltier effects occur only at junctions between dissimilar conductors might suggest that they are interfacial phenomena but they are really dependent on the bulk properties of the materials involved. Nowadays, we understand that electric current is carried through a conductor by means of electrons that can possess different energies in different materials. When a current passes from one material to another, the energy transported by the electrons is altered, the difference appearing as heating or cooling at the junction, that is as the Peltier effect. Likewise, when the junction is heated, electrons are enabled to pass from the material in which the electrons have the lower energy into that in which their energy is higher, giving rise to an electromotive force.

Thomson's work showed that a thermocouple is a type of heat engine and that it might, in principle, be used either as a device for generating electricity from heat or, alternatively, as a heat pump or refrigerator. However, because the reversible thermoelectric effects are always accompanied by the irreversible phenomena of Joule heating and thermal conduction, thermocouples are generally rather inefficient.

The problem of energy conversion using thermocouples was analysed by Altenkirch [1], in 1911. He showed that the performance of a thermocouple could be improved by increasing the magnitude of the differential Seebeck coefficient, by increasing the electrical conductivities of the two branches and by reducing their thermal conductivities. Unfortunately, at that time, there were no thermocouples available in which the combination of properties was good enough for reasonably efficient energy conversion, although the Seebeck effect has long been used for the measurement of temperature and for the detection of thermal radiation. It was only in the 1950s that the introduction of semiconductors as thermoelectric materials allowed practical Peltier refrigerators to be made. Work on semiconductor thermocouples also led to the construction of thermoelectric generators with a high enough efficiency for special applications. Nevertheless, the performance of thermoelectric energy convertors has always remained inferior to that of the best conventional machines.

In fact, there was little improvement in thermoelectric materials from the time of the introduction of semiconductor thermoelements until the end of the twentieth century. However, in recent years, several new ideas for the improvement of materials have been put forward and, at last, it seems that significant advances are being made, at least on a laboratory scale. It is reasonable to expect that this work will soon lead to much wider application of the thermoelectric effects.

1.2 Relations Between the Thermoelectric Coefficients

We now define the Seebeck and Peltier coefficients and show how they are related to one another. For the time being, we assume that the conductors are isotropic. We refer to the simple thermocouple shown in Fig. 1.2. Conductor A is joined at both ends to conductor B, the latter being divided into two parts so that, for example, a voltmeter can be inserted in the gap.

Suppose that a temperature difference ΔT is established between the two junctions and that the two free ends of conductor B are maintained at the same temperature, it will then generally be found that a potential difference V will appear between the free ends. The differential Seebeck coefficient, α_{AB}, is defined as the ratio of V to ΔT. Thus,

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

α_{AB} is deemed to be positive if the electromotive force tends to drive an electric current through conductor A from the hot junction to the cold junction. It is noted that, particularly in older texts, the quantity that is now known as the Seebeck coefficient has often been called the thermoelectric power or the thermal EMF coefficient.

We define the differential Peltier coefficient, π_{AB}, for the same thermocouple by supposing that a source of EMF is connected across the gap in conductor B so as to drive a current around the circuit in a clockwise direction. The Peltier coefficient is regarded as positive if the junction at which the current enters A is heated and the junction at which it leaves A is cooled. π_{AB} is equal to the ratio of the rate q of heating or cooling at each junction to the electric current I,

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

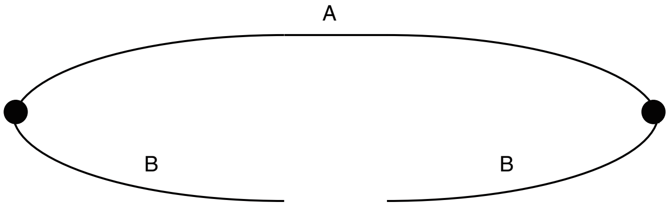

Fig. 1.2 Simple thermocouple

We note that it is much simpler to measure the Seebeck coefficient than the Peltier coefficient. Thus, while both quantities enter into the theory of thermoelectric energy conversion, it would be preferable if only one of them had to be specified. In fact, one of the Kelvin relations allows us express the Peltier coefficient in terms of the Seebeck coefficient. The relevant equation is

$$\pi_{\mathrm{AB}} = \alpha_{\mathrm{AB}} T. \tag{1.3}$$

The other Kelvin relation connects the Seebeck coefficient and the Thomson coefficient, τ, or, rather, the difference between the Thomson coefficients of the two conductors. The Thomson coefficient is defined as the rate of heating per unit length that results from the passage of unit current along a conductor in which there is unit temperature gradient. The appropriate Kelvin relation is

$$\tau_{\mathrm{A}} - \tau_{\mathrm{B}} = T \frac{\mathrm{d}\alpha_{\mathrm{AB}}}{\mathrm{d}T}. \tag{1.4}$$

The Seebeck and Peltier coefficients are defined above for a pair of conductors whereas it would be much more convenient if their values could be given for a single material. In fact, the absolute Seebeck or Peltier coefficient becomes equal to the differential coefficient if the second material can be regarded as having zero absolute coefficients. This concept can be realised, in practice, by using a superconductor as the second material. It is reasonable to assign zero Seebeck or Peltier coefficients to a superconductor since the differential coefficients between all pairs of superconductors are zero.

Of course, there is no material that remains in the superconducting state at ordinary temperatures, so it might be thought that the absolute Seebeck coefficients of other materials can be obtained only at low temperatures. However, this is not the case. It is reasonable to write (1.4) in the form

$$\tau = T \frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{1.5}$$

for a single conductor. Thus, if the absolute Seebeck coefficient of a material at low temperatures is determined by connecting it to superconductor, one can then use (1.5) to find the value at higher temperatures after measuring the Thomson coefficient [2, 3]. This procedure has been carried out for the metal lead, which may be used as a reference material when determining the absolute coefficients for other substances.

In actual fact, most metals, like lead, have very small absolute values of the Seebeck coefficient compared with practical thermoelectric materials that are almost invariably semiconductors.

1.3 Effects in a Magnetic Field

Electric charges are subject to transverse forces when they travel in a magnetic field. Thus, the thermoelectric effects, like the other transport properties, become changed when a magnetic field is applied, and there also appear some new phenomena. We need to discuss these so-called thermogalvanomagnetic effects since they can affect the performance of thermoelectric devices and can even lead to new methods of energy conversion.

As we shall demonstrate in the next chapter, the electric and thermal conductivities are properties that are of importance when we are calculating the performance of devices based on the Seebeck and Peltier effects. Both quantities become less on the application of a magnetic field, though the changes are very small unless the field is very strong and the mobility of the charge carriers is high. The Seebeck and Peltier coefficients, too, will change under the influence of a magnetic field, B.

Usually, the value of the Seebeck coefficient will be the same when the direction of the magnetic field is reversed but this is not always the case. Any difference between the values of the Seebeck coefficient upon reversal of the field is called the Umkehr effect. The Umkehr effect has been shown [4] to be very large for certain orientations of the semimetal bismuth.

Another consequence of the action of a magnetic field [5] is the need to modify the Kelvin relation (1.3). The modified equation is

$$\pi(B) = T\alpha(-B). \tag{1.6}$$

When a transverse magnetic field is applied to a current carrying conductor, an electric field appears in a direction perpendicular to both the current and B. This is the well-known Hall effect. The Hall effect is not immediately relevant to energy conversion but is a useful tool in explaining the behaviour of the charge carriers. Of more direct significance for energy conversion are the transverse Nernst and Ettingshausen effects.

The Nernst effect, like the Hall effect, manifests itself as a transverse voltage in a magnetic field but it depends on the longitudinal temperature gradient or heat flow rather than on a longitudinal electric current. The Nernst coefficient, N, is defined by the relation

$$|N| = \frac{\mathrm{d}V/\mathrm{d}y}{B_z\,\mathrm{d}T/\mathrm{d}x}. \tag{1.7}$$

Here $\mathrm{d}V/\mathrm{d}y$ is the transverse electric field. The sign of the Nernst effect is given in Fig. 1.3, which illustrates all the transverse thermogalvanomagnetic phenomena. The sign of the Nernst effect does not depend on whether the charge carriers are positive or negative and, in this respect, it differs from the Hall effect.

The Ettingshausen and Nernst effects are related to one another in the same way as the Peltier and Seebeck effects. The Ettingshausen effect is a transverse temperature gradient that is the result of a transverse magnetic field and a longitudinal flow of electric current. The Ettingshausen coefficient, P, is defined by

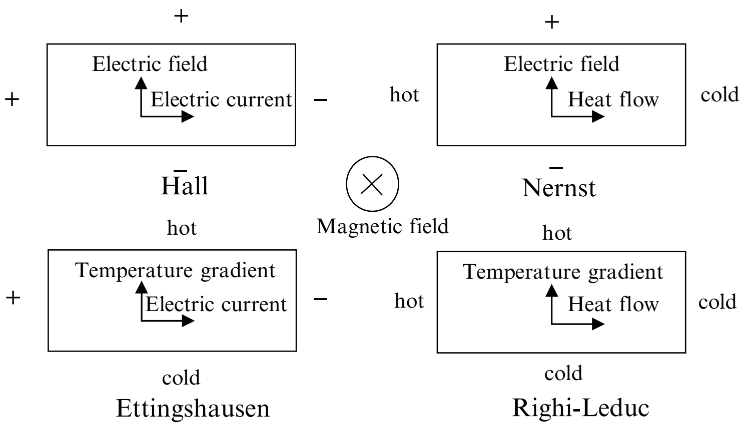

Fig. 1.3 The transverse thermogalvanomagnetic effects. When the effects are in the direction shown in the diagram, the coefficients are positive

$$|P| = \frac{\mathrm{d}T/\mathrm{d}y}{i_x B_z}, \tag{1.8}$$

where i_x is the longitudinal current density. As one might have expected, there is a thermodynamic relationship between the Nernst and Ettingshausen coefficients,

$$P\lambda = NT, \tag{1.9}$$

where λ is the thermal conductivity, which is included since the Ettingshausen coefficient is defined in terms of a temperature gradient rather than a heat flow.

To complete the transverse phenomena, there exists the Righi–Leduc effect, which is a transverse temperature gradient arising from a longitudinal heat flow. The Righi–Leduc coefficient, S, is given by

$$|S| = \frac{\mathrm{d}T/\mathrm{d}y}{B_z \mathrm{d}T/\mathrm{d}x}. \tag{1.10}$$

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Chapter 2
Theory of Thermoelectric Refrigeration and Generation

2.1 The Transport Effects

The thermoelectric phenomena are reversible in the sense that they do not of themselves give rise to thermodynamic losses. However, they are always, in practice, accompanied by the irreversible effects of electrical resistance and thermal conduction. It turns out that the performance of any thermocouple as an energy convertor can be expressed in terms of the differential Seebeck coefficient and the thermal and electrical resistances of the two branches. These resistances depend on the thermal and electrical resistivities and the ratios of length to cross-sectional area. Again we shall, in the first instance, assume that all the properties are independent of orientation.

The electrical resistivity, ρ, is the reciprocal of the electrical conductivity, σ, which is defined by the relation

$$I = \frac{\sigma V A}{L} \tag{2.1}$$

where I is the electric current through a specimen of constant cross-sectional area A and length L when a voltage V is applied. Likewise, the thermal conductivity, λ, is defined by the equation

$$q = -\frac{\lambda A\,\Delta T}{L} \tag{2.2}$$

where q is the rate of heat flow through a similar specimen that has a temperature difference ΔT between its two ends.

We shall refer to the thermoelectric coefficients and the electrical and thermal conductivities of a given material as its transport properties. All these properties will generally be temperature-dependent and this should be taken into account in any rigorous theory. The variation with temperature of the transport properties may not be too serious a matter in some applications of the Peltier effect when the temperature differences across the thermocouples are small but it can be very important in thermoelectric generation. However, in order to determine the relative importance of the different parameters we shall, for the time being, suppose that the conductivities and the Seebeck coefficient are all independent of temperature. The Kelvin relation (1.3) implies that, even when α is constant, π will be proportional to T.

In fact, we shall invariably express the Peltier coefficient, π, in terms of the more easily measured Seebeck coefficient, α.

2.2 Thermoelectric Refrigerators and Heat Pumps

We shall determine the performance of thermoelectric refrigerators and heat pumps using as our model the single thermocouple shown in Fig. 2.1. Practical devices usually make use of modules that contain a number of thermocouples connected electrically in series and thermally in parallel. This enables the cooler or heat pump to be operated from a power source that delivers a manageable current with a reasonable voltage drop. It is a simple matter to extend the equations for a single couple to a multi-couple arrangement.

In the elementary theory that is outlined in this chapter, it will be supposed that there is no thermal resistance between the thermocouple and the heat source or sink. It will also be assumed that all the heat flow between the source and sink takes place within the thermocouple. Thus, it will be supposed that thermal radiation and losses by conduction and convection through the surrounding medium are negligible. The two thermocouple branches in our model have constant cross-sectional areas. There have been suggestions [1] that tapered thermoelements might improve the performance but it is not difficult to show that they give no theoretical advantage. The thermoelements need not be of the same length but the ratio of length to cross-sectional area (the form factor) is of importance and, as we shall see, there is a preferred relationship between the form factors of the two branches.

The quantity of greatest importance for a refrigerator is the coefficient of performance (COP), which is defined as the ratio of the heat extracted from the source to the expenditure of electrical energy. If the thermocouple were free of losses associated with heat conduction and electrical resistance, the COP would reach the ideal value; that is, the value for a Carnot cycle. The ideal COP can be much greater than

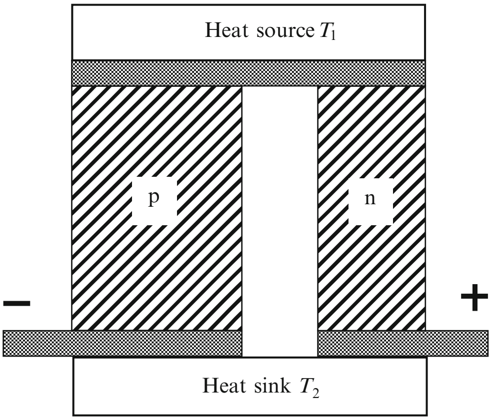

Fig. 2.1 Simple refrigerator or heat pump

unity as it is given by $T_1/(T_2 - T_1)$, where T_1 and T_2 are the absolute temperatures of the source and sink, respectively. We shall also be interested in the cooling power; i.e., the rate at which heat is extracted from the source.

A detailed derivation of the COP and cooling power may be found elsewhere [2]. Here, we shall outline the theory.

When a current, I, is passed through the couple, there is Peltier cooling at the source equal to $(\alpha_p - \alpha_n)IT_1$, where we have used the Kelvin relation (1.3) to eliminate the Peltier coefficient. α_p and α_n are the Seebeck coefficients of the two branches which, of course, should have opposite signs. This cooling effect is opposed by heat conduction at the rate $(T_2 - T_1)(K_p + K_n)$, where K_p and K_n are the thermal conductances of the branches. The cooling is also opposed by Joule heating within the thermoelements. It is easily shown that half of the Joule heating passes to the sink and half to the source, each half being equal to $I^2(R_p + R_n)/2$, where R_p and R_n are the thermal resistances of the branches.

The expression for the cooling power is

$$q_1 = (\alpha_p - \alpha_n)IT_1 - (T_2 - T_1)(K_p + K_n) - I^2(R_p + R_n)/2. \tag{2.3}$$

Also, the rate of expenditure of electrical energy is

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

where the first term is the rate of working to overcome the thermoelectric voltage whereas the second term is the resistive loss. The COP, ϕ, is then given by

$$\phi = \frac{(\alpha_p - \alpha_n)IT_1 - (T_2 - T_1)(K_p + K_n) - I^2(R_p + R_n)/2}{(\alpha_p - \alpha_n)I(T_2 - T_1) + I^2(R_p + R_n)}. \tag{2.5}$$

Equation (2.5) shows us that the COP depends on the current, as does the cooling power. As the current is increased, the Peltier cooling rises linearly but the Joule heating depends on I^2. Thus, a plot of cooling power against current has the parabolic form shown in Fig. 2.2. This plot represents, schematically, the situation in which T_1 is significantly smaller than T_2. Provided that the temperature difference is not too great, the cooling power will become positive at a certain value of the current. However, as the current is increased further, there will come a point at which the difference between the Peltier cooling and the Joule heating begins to diminish. In other words, there is a particular current at which the cooling power reaches its maximum value. Equation (2.3) shows that the maximum is reached when the Peltier cooling is twice that part of the Joule heating that reaches the cold junction.

There are two values of the current that are of special interest. The current, I_q, that yields the maximum cooling power is given by

$$I_q = (\alpha_p - \alpha_n)T_1/(R_p + R_n). \tag{2.6}$$

At this current, the COP is given by

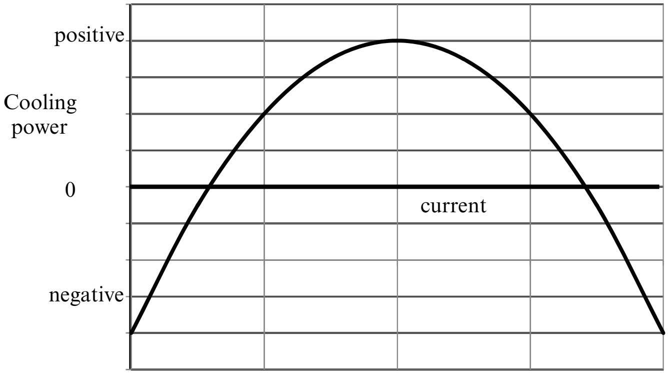

Fig. 2.2 Schematic plot of cooling power against current for a thermoelectric cooler. The cooling power is negative until the Peltier effect is great enough to counteract both heat conduction and Joule heating

$$\phi_q = \frac{ZT_1^2/2 - (T_2 - T_1)}{ZT_2T_1} \tag{2.7}$$

where Z is equal to $(\alpha_p - \alpha_n)^2/\{(K_p + K_n)(R_p + R_n)\}$. Equation (2.7) shows that the COP under the condition of maximum cooling power depends solely on Z and the temperatures of the source and sink. As we shall see, the optimum COP also depends only on these quantities and Z is therefore known as the figure of merit of the thermocouple. Z has the dimensions of inverse temperature and it is more usual nowadays to specify the dimensionless figure of merit, which is equal to ZT at a given temperature.

The other condition of particular interest is that of maximum COP. The current I_ϕ that satisfies this condition is specified by

$$I_\phi = \frac{(\alpha_p - \alpha_n)(T_2 - T_1)}{(R_p + R_n)\{(1 + ZT_m)^{1/2} - 1\}} \tag{2.8}$$

where T_m is the mean temperature. The optimum COP is

$$\phi_{max} = \frac{T_1\{(1 + ZT_m)^{1/2} - (T_2/T_1)\}}{(T_2 - T_1)\{(1 + ZT_m)^{1/2} + 1\}}. \tag{2.9}$$

It might be thought that one would wish to operate a thermoelectric refrigerator as close to the condition of optimum COP as possible. However, this is sometimes not practical. The cooling power under this condition can be much less than the maximum value, particularly, when the temperature difference between the source and sink is small. Thus, while the optimum COP condition may be economical in use of electrical energy, it may be uneconomical in the use of thermoelectric material. Generally speaking, the preferred current will lie somewhere between that for maximum cooling power and optimum COP.

The figure of merit Z itself may be optimised for a given pair of thermoelectric materials. The aim should be to make the product $(K_p + K_n)(R_p + R_n)$ as small as possible. This result is obtained when the form factors for the two branches satisfy the relation

$$\frac{L_n A_p}{L_p A_n} = \left(\frac{\rho_p \lambda_n}{\rho_n \lambda_p}\right)^{1/2}. \tag{2.10}$$

When (2.10) is satisfied the figure of merit is given by

$$Z = \frac{(\alpha_p - \alpha_n)^2}{\{(\lambda_p \rho_p)^{1/2} + (\lambda_n \rho_n)^{1/2}\}^2}. \tag{2.11}$$

It is usually the figure of merit defined by (2.11) that is meant when one discusses Z for a pair of materials.

In the search for improved thermocouples, it is uncommon to investigate a pair of substances at the same time. It would, therefore, be convenient if one could define a figure of merit for a single material. In practice, one makes use of the figure of merit z, which is given by $\alpha^2\sigma/\lambda$ or $\alpha^2/\lambda\rho$. The parameters used in defining z refer to the positive and negative thermoelements separately. It is important to realise that z cannot be used to calculate the performance of a thermocouple even if its value is known for both branches. For this purpose, the figure of merit Z must be used. However, it often turns out that Z lies close to the average of z_p and z_n so that it is meaningful to select materials on the basis of the single-material figure of merit.

One of the most important characteristics of a thermocouple is the maximum depression of temperature that can be reached through the Peltier effect using a single stage. This quantity, ΔT_{max}, can be calculated from (2.7). The maximum temperature depression is reached when the cooling power and, thus, the COP fall to zero. We see that this occurs when $(T_2 - T_1)$ becomes equal to $ZT_1^2/2$ so that

$$\Delta T_{max} = \frac{1}{2} Z T_1^2. \tag{2.12}$$

Figure 2.3 shows how ΔT_{max} varies with ZT_m when the heat sink is kept at 300 K. Practical thermoelectric refrigeration has stemmed from the development since the 1950s of thermocouples with ZT_m of the order of unity. Temperature depressions of 100° or more require values of ZT_m significantly greater than unity.

In Fig. 2.4, we show the optimum COP plotted against the dimensionless figure of merit for various heat source temperatures when the heat sink is at 300 K. It is noted that COPs that are considerably greater than unity can be achieved when ZT_m is equal to about 1 provided that the heat source is not at a too low temperature. For example, a COP value of 2 is reached when ZT_m is equal to 1, if the temperature difference between the source and sink is 20°. This is, of course, much smaller than the COP of an ideal refrigerator, which would be no less than 14 under the same conditions. A high COP is desirable, not only because it reduces the expenditure of electrical energy, but also because it allows a heat sink of smaller capacity to be