Applications of THERMO-ELECTRICITY

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Preface

Although the principal thermoelectric effects have been known for well over a hundred years their practical application has, until recently, been extremely limited. However, as a result of the use of thermocouples consisting of semiconductors rather than metals, refrigeration by means of the Peltier effect, as well as reasonably efficient thermoelectric generation, has now become possible. There is, thus, a rapidly growing interest in research on thermoelectric materials. One of the aims of this book is the introduction of the subject to those who are entering the field for the first time. It is also hoped that it will prove useful in providing an elementary account of the applications of thermoelectricity for students and those working in other fields.

I must express my appreciation of the assistance which I have received from many of the staff of these Laboratories during the preparation of the book. I should mention particularly Dr D. A. Wright and Dr A. K. Jonscher who read the manuscript; I have made use of a number of their suggestions.

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Symbols

C (subscript)	Cold junction
$\mathbf{E}$, E	Electric field
F	$\mu_0(m^*/m)^{3/2}/\kappa_1$
F_r	$\int_0^\infty \xi^r f_0 \, d\xi$
G	$(2\pi mkT/h^2)^{3/2}$
H (subscript)	Hot junction
$\mathbf{I}$, I	Electric current
K	Thermal conductance
K_n	$\dfrac{16\sqrt{2}\pi m^{*1/2}}{3h^3}\int_0^\infty \tau(\varepsilon)\, \varepsilon^{n+1/2}\dfrac{\delta f_0}{\delta \varepsilon}\, d\varepsilon$
L	Latent heat of fusion per unit volume
N	Number of stages in a cascade
N_v	Number of valleys in a many-valley semi-conductor
$\mathbf{P}$, P	Crystal momentum
Q	Rate of heat generation or cooling
R	Electrical resistance
R_L	Resistance of generator load
S	Cross-section area
T	Absolute temperature
T_M	Mean temperature
ΔT	Temperature difference
ΔT_{max}	Maximum temperature difference
V	Potential difference
W	Power supplied or yielded
Z	Figure of merit of a thermocouple

c	Thermal capacity per unit volume
e	Electronic charge
f_0	Fermi distribution function
h	Planck's constant
$\mathbf{i}$, i	Electric current density
k	Boltzmann's constant
l	Length
l_t	Mean free path of phonons
m	Mass of a free electron
m^*	Density-of-states effective mass of a charge carrier
m_1	Inertial effective mass of a charge carrier
n	Carrier concentration
n (subscript)	*n*-type, electron or negative
p (subscript)	*p*-type, hole or positive
$\mathbf{q}$, q	Heat flux density
r	R_L/R
t	Time
v	Velocity of sound
x	Proportion of minority component in an alloy
z	Figure of merit of a thermoelement
α	Seebeck coefficient
α_l	Phonon component of the Seebeck coefficient
γ	Thomson coefficient
ε	Kinetic energy of a charge carrier
ε_{av}	Average kinetic energy
ε_g	Energy gap
$\varepsilon_g(0)$	Energy gap at 0°K
ζ	Fermi potential
η	Reduced Fermi potential
Θ	Debye temperature
κ	Thermal conductivity

κ_e	Electronic component of the thermal conductivity
κ_l	Lattice component of the thermal conductivity
λ	Exponent of energy in scattering law ($\tau \propto \varepsilon^\lambda$)
μ	Carrier mobility
μ_0	Mobility of a non-degenerate semiconductor
ξ	Reduced kinetic energy
π	Peltier coefficient
π_l	Phonon component of the Peltier coefficient
ρ	Electrical resistivity
σ	Electrical conductivity
τ_e	Relaxation time of charge carriers
τ_d	Relaxation time of low frequency phonons
τ_t	Relaxation time of heat conduction phonons
ϕ	Coefficient of performance of a refrigerator
ϕ_{max}	Maximum coefficient of performance
Φ	Coefficient of performance of one stage of a cascade
ϕ_N	Coefficient of performance of a cascade
ψ	Efficiency of a generator

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CHAPTER I

Introductory

In 1821 Seebeck reported some experiments to the Prussian Academy of Sciences which showed that he had observed the first of the thermoelectric effects. He had produced potential differences by heating the junctions between dissimilar conductors. In spite of the fact that he did not fully understand the meaning of his results, Seebeck was able to arrange his conductors in more or less the thermoelectric series which is recognized today.

Thirteen years later, Peltier, a French watchmaker, published some results which showed that he had discovered a second thermoelectric effect. When a current is passed through a junction between two different conductors there is absorption or generation of heat depending on the direction of the current. This effect is superimposed upon, but quite distinct from, the Joule resistance-heating effect usually associated with the passage of an electric current. Peltier, like Seebeck, did not understand the true nature of his results but, in 1838, Lenz demonstrated that water could be frozen at a bismuth–antimony junction by the passage of a current; on reversing the current the ice could be melted.

Thomson, later Lord Kelvin, realized that a relation should exist between the Seebeck and Peltier effects and proceeded to derive this relation from thermodynamical arguments. These led him to the conclusion that there must be a third thermoelectric effect, now called the Thomson effect; this is a heating or cooling effect in a homogeneous conductor when an electric current passes in the direction of a temperature gradient.

In spite of the fact that the thermoelectric effects have been known for such a long time, practically the only devices based upon them, which have been employed until recently, are thermocouples for the measurement of temperature and thermopiles for the detection of radiant energy. Both applications utilize the Seebeck effect; in fact, they involve the thermoelectric generation of electricity from heat. In the past this process has been extremely inefficient but the high sensitivity of the associated instruments has enabled such devices to be employed satisfactorily. However, even inefficient thermoelectric refrigeration using the Peltier effect has been impossible up to the last few years.

The basic theory of thermoelectric generators and refrigerators was first derived satisfactorily by Altenkirch in 1909[1] and 1911.[2] He showed that, for both applications, materials were required with high thermoelectric coefficients, high electrical conductivities to minimize Joule heating, and low thermal conductivities to reduce heat transfer losses. However, it was quite a different matter knowing the favourable properties and obtaining materials embodying them, and so long as metallic thermocouples were employed no real progress was made. It is only since semiconductor thermocouples have been prepared that reasonably efficient thermoelectric generators and refrigerators have become possible.

The Kelvin Relations

Before proceeding to the theory of thermoelectric applications, the Kelvin relations and their derivation will be considered. The relation between the Seebeck and Peltier effects is particularly important since, whereas it is the Seebeck coefficient* (also known as the thermoelectric power, or thermal e.m.f. coefficient) which is most easily measured, it is the Peltier coefficient which determines the cooling capacity of a thermoelectric refrigerator.

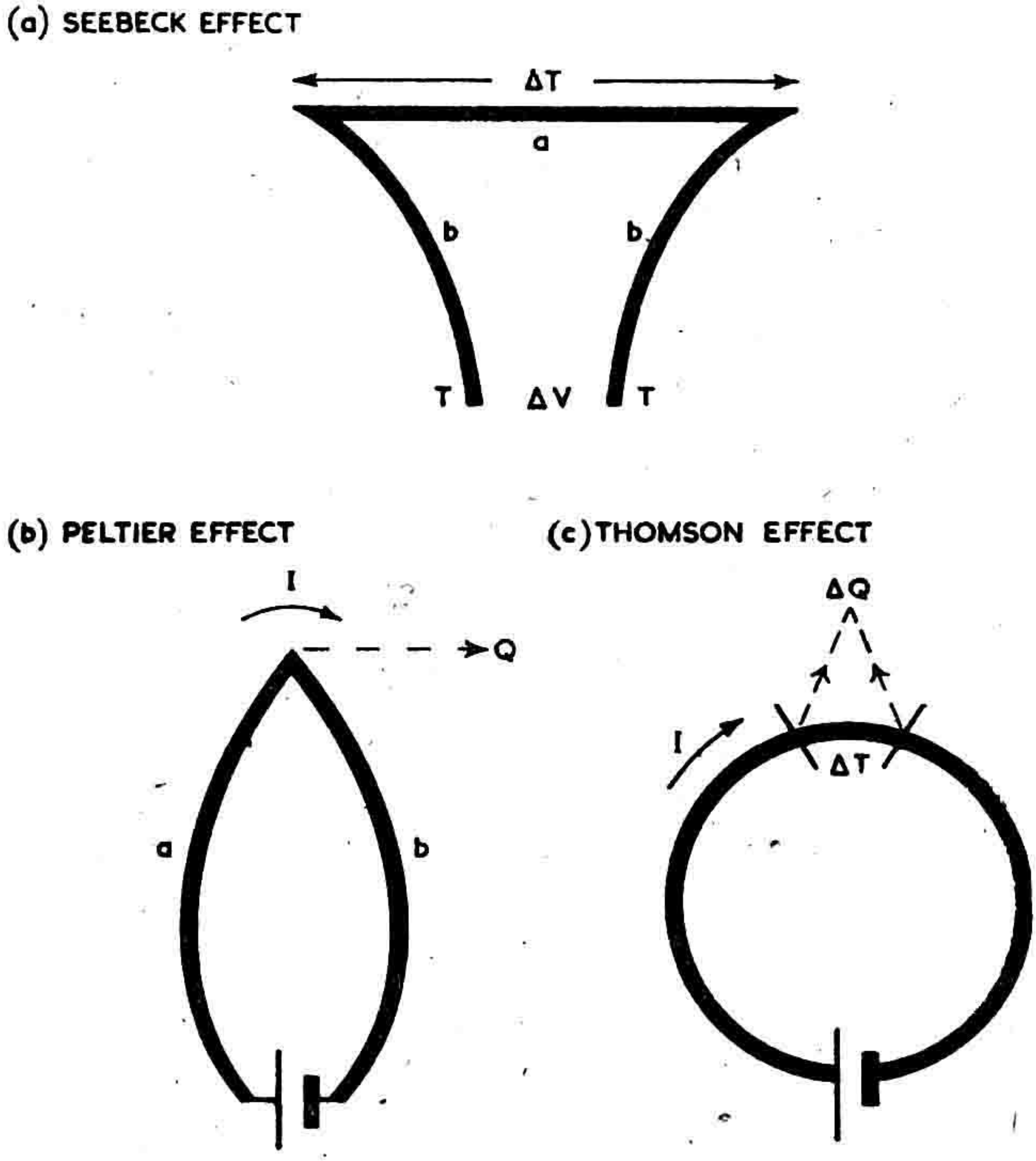

Fig. 1. The thermoelectric effects

* 'Seebeck coefficient' is used in preference to the other terms in accordance with the recommendations of a task group of the A.I.E.E. and I.R.E.

In order to define the thermoelectric coefficients, let us consider the circuits shown in figure 1. In figure 1(*a*) an open circuit potential difference ΔV is developed as a result of the temperature difference ΔT between the junctions of conductor *a* to conductor *b*. The differential Seebeck coefficient α_{ab} is defined by

$$\alpha_{ab} = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T} \tag{1}$$

In figure 1(*b*) there is a rate of reversible heat generation Q as a result of a current I passing through a junction between the conductors *a* and *b*. The Peltier coefficient π_{ab} is given by

$$\pi_{ab} = \frac{Q}{I} \tag{2}$$

Finally, figure 1(*c*) shows that the passage of a current I along a portion of a single homogeneous conductor, over which there is a temperature difference ΔT, leads to a rate of reversible heat generation ΔQ. The Thomson coefficient γ is defined by

$$\gamma = \lim_{\Delta T \to 0} \frac{\Delta Q}{I \Delta T} \tag{3}$$

The Kelvin relations may be derived by applying the

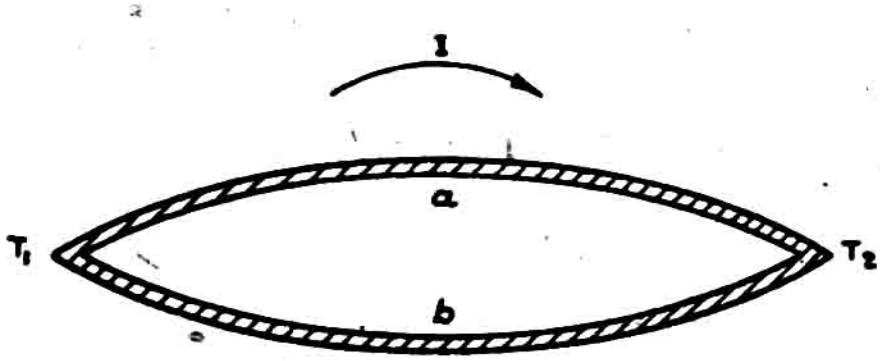

Fig. 2. A simple thermoelectric circuit

laws of thermodynamics to the simple circuit shown in figure 2. A current I passes round this circuit, which consists of conductors *a* and *b* with junctions at temperatures T_1 and T_2. From the principle of the conservation of energy, the heat generated must be equal to the consumption of electrical energy. If the current is small enough, Joule heating may be neglected. Thus,

$$\{(\pi_{ab})_2 - (\pi_{ab})_1\}I + \int_1^2 (\gamma_a - \gamma_b)IdT = \int_1^2 \alpha_{ab}I\,dT$$

Differentiating, one finds that

$$\frac{d\pi_{ab}}{dT} + \gamma_a - \gamma_b = \alpha_{ab} \tag{4}$$

In order to obtain a second relation between the coefficients it is necessary to apply the second law of thermodynamics. In order that this step should be valid it is essential that the process should be reversible. It is reasonable to suppose that the thermoelectric effects are reversible, but they are inevitably accompanied by the irreversible processes of Joule heating and heat conduction. Thus, the application of reversible thermodynamics is not strictly justified. However, the use of Onsager's reciprocal relations, which are based on irreversible thermodynamics, leads to the same conclusions,[3] so we shall assume that there is no overall change of entropy round the circuit of figure 2. Then,

$$\int^2 Id\left(\frac{\pi_{ab}}{T}\right) + \int_1^2 \frac{\gamma_a - \gamma_b}{T} I\,dT = 0$$

By differentiation it is found that

$$\frac{d\pi_{ab}}{dT} - \frac{\pi_{ab}}{T} + \gamma_a - \gamma_b = 0 \tag{5}$$

Combining equations (4) and (5)

$$\alpha_{ab} = \frac{\pi_{ab}}{T} \tag{6}$$

This, the first of the Kelvin relations, is the more important for our purposes since it relates the Seebeck and the Peltier coefficients. The second relation, which connects the Seebeck and Thomson coefficients, is

$$\frac{d\alpha_{ab}}{dT} = \frac{\gamma_a - \gamma_b}{T} \tag{7}$$

Both of Kelvin's laws have been confirmed, within experimental error, for a number of thermocouple materials.[4] However, it has been reported that equation (6) is not strictly obeyed for a germanium-copper couple.[5] In this case it appears that the value of the Peltier coefficient π is less than the product αT. In spite of this fact, it seems that the Kelvin relations are applicable to all the materials used in thermoelectric applications, and their validity will be assumed here.

The Seebeck and Peltier coefficients are both defined for junctions between two conductors but the Thomson coefficient is a property of a single conductor. Equation (7) suggests a way of defining the absolute Seebeck coefficient for a single material, namely by putting

$$\frac{d\alpha}{dT} = \frac{\gamma}{T}$$

It is established from the third law of thermodynamics that the Seebeck coefficient is zero for all junctions at the absolute zero of temperature; the absolute Seebeck coefficient of any material is, therefore, taken to be zero at this temperature. Then

$$\alpha = \int_0^T \frac{\gamma}{T} dT \tag{8}$$

The absolute Seebeck coefficient of a material at very low temperatures may be determined by joining it to a superconductor, the latter possessing zero thermoelectric coefficients. This procedure has been carried out for pure lead up to 18°K[6] and the Thomson coefficient for lead has been measured between 20°K and room temperature.[7] Its value in the range between 18°K and 20°K can be accurately extrapolated. Thus, by use of equation (8), the absolute Seebeck coefficient of lead has been established. The absolute Seebeck coefficient of any other conductor may be determined by joining it to lead.

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* Translations of most of the Russian journals to which reference is made in this book are published by the American Institute of Physics.