A note on the electrochemical nature of the thermoelectric power

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Abstract. While thermoelectric transport theory is well established and widely applied, there remains some degree of confusion on the proper thermodynamic definition of the Seebeck coefficient (or thermoelectric power) which is a measure of the strength of the mutual interaction between electric charge transport and heat transport. Indeed, as one considers a thermoelectric system, it is not always clear whether the Seebeck coefficient is to be related to the gradient of the system’s chemical potential or to the gradient of its electrochemical potential. This pedagogical article aims to shed light on this confusion and clarify the thermodynamic definition of the thermoelectric coupling. First, we recall how the Seebeck coefficient is experimentally determined. We then turn to the analysis of the relationship between the thermoelectric power and the relevant potentials in the thermoelectric system: As the definitions of the chemical and electrochemical potentials are clarified, we show that, with a proper consideration of each potential, one may derive the Seebeck coefficient of a non-degenerate semiconductor without the need to introduce a contact potential as seen sometimes in the literature. Furthermore, we demonstrate that the phenomenological expression of the electrical current resulting from thermoelectric effects may be directly obtained from the drift-diffusion equation.

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1. Introduction

Thermoelectricity is a mature yet still very active area of research covering various fields of physics, physical chemistry, and engineering. The large interest in thermoelectric
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systems is mostly due to the promising applications in the field of electrical power production from waste heat as thermoelectric devices may be designed for specific purposes involving powers over a range spanning ten orders of magnitude: typically from microwatts to several kilowatts. Further, thermoelectricity also provides model systems that are extremely useful in the development of theories in irreversible thermodynamics [1, 2].

The discovery of the thermoelectric effect is usually attributed to Seebeck. In 1821, he published the results and analysis of his experiments aiming at establishing a magnetic polarisation in a metallic circuit simply by perturbing the thermal equilibrium across this latter [3]. More precisely, Seebeck described the appearance of a magnetic field within a closed electrical circuit made of two dissimilar materials as the junctions between these materials were maintained at different temperatures. While Seebeck interpreted the observed phenomenon as a thermomagnetic effect, Oersted soon reexamined Seebeck’s work and showed that in this case the magnetic field was an indirect effect as it originated in the presence of an electromotive force induced by the temperature difference [4]. The proportionality coefficient between this electromotive force and the temperature difference across the system is the thermoelectric power, which has also been coined as “Seebeck coefficient”.

The definition of the thermoelectric coupling has later been extended from that derived from the first experiments to both thermodynamic [5] and microscopic [6, 7, 8, 9] properties of materials. However, as of yet, there still is no clear consensus on its relationship with the various thermodynamic potentials and their variations (see, e.g., [10, 11, 12, 13, 14]). Indeed as the terminology and conventions may vary from a discipline to another, say, e.g., solid-state physics and electrochemistry, it is not always straightforward to establish a clear distinction or relevant associations between Fermi energy at zero or finite temperature, electrochemical potential, voltage, Fermi level relative either to the conduction band minimum or to the vacuum, and chemical potential.

In this article, we discuss the definition of the Seebeck coefficient focusing particularly on the distinction between chemical and electrochemical potentials. First, in Sec. 2 we address the experimental determination of the Seebeck coefficient in order to identify the quantities of interest. Next, the purpose of Sec. 3 is to demonstrate that a clear physical picture of thermoelectric phenomena at the microscopic scale may be obtained on the condition that the potentials are carefully introduced. For this purpose, we review the standard definitions given in the literature to remove any confusion between the chemical and electrochemical potentials before we present and discuss our derivation of the Seebeck coefficient for a non-degenerate semiconductor.

2. Experimental determination of the thermopower

The determination of the Seebeck coefficient traditionally involves components made of dissimilar materials, which we label A and B respectively. The two materials are
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Figure 1. Determination of the Seebeck coefficient for a circuit composed of two dissimilar materials.

combined to obtain two junctions as depicted in figure 1. These junctions are then brought to different temperatures $T_1$ and $T_2$. An isothermal voltage measurement at a temperature $T_3$, is performed between the free ends of the component B. The voltage thus measured is $V_2 - V_1$ (this notation allows to clearly define a direction for the voltage) and the Seebeck coefficient $\alpha_{AB}$ associated to the global system, i.e. the couple AB, is defined as the proportionality coefficient between the resulting voltage and the applied temperature difference:

$$\alpha_{AB} = \frac{V_2 - V_1}{T_2 - T_1}.$$  \hspace{1cm} (1)

The coefficient $\alpha_{AB}$, obtained for the whole circuit, is related to the Seebeck coefficient of each material through:

$$\alpha_{AB} = \alpha_B - \alpha_A,$$ \hspace{1cm} (2)

where $\alpha_A$ and $\alpha_B$ are the Seebeck coefficients of the materials A and B respectively.

From an experimental viewpoint, the presence of the material B ($\neq A$) is mandatory as it is associated with the probe’s wires (see, e.g., [15]). However, if its Seebeck coefficient $\alpha_B$ is sufficiently small to be neglected, the measurement may be used to determine directly the Seebeck coefficient of material A. In this case, one gets:

$$\alpha_A = -\frac{V_2 - V_1}{T_2 - T_1}.$$ \hspace{1cm} (3)

Note the presence of a minus sign in the expression above: It is often overlooked in literature but, fortunately, that omission is most of the time compensated by the absence of a clear sign convention for the measured voltage.

Let us now turn to the analysis of the measured quantities. While the temperature is not subject to questionning, the voltage obtained from a voltmeter must be defined unambiguously. Indeed, it appears that its connection to the microscopic and thermodynamic properties of materials has remained unclear for quite some time, leading Riess to publish in 1997, hence fairly recently, an article untitled “What does a voltmeter measure?” [16]. In that paper, Riess demonstrated that the voltage between two points in a circuit is the difference of electrochemical potentials at the two considered
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points divided by the elementary electric charge \( e \), but not the difference between the electrostatic potentials alone. This result is recovered when one measures the voltage at the ends of a pn junction at equilibrium: While there is a built-in electric field associated to the depletion layer, the measured voltage remains zero. The Seebeck coefficient thus appears as a link between the applied temperature difference and the resulting difference of electrochemical potential between the two junctions.

The simple technique presented here is not the only one used to determine the thermopower of a given material. Indeed, since the measurement always involves a couple of materials, the absolute Seebeck coefficient of the second material has to be known accurately. To obtain this value, it is possible to use low temperature measurement to reach superconducting state where \( \alpha = 0 \) and then derive higher temperatures values using the Thomson coefficient that can be measured for a single material. For a detailed presentation of the Seebeck coefficient metrology, the reader may refer to the instructive review by Martin et al. [17].

3. Relationship between the thermoelectric power and the electrochemical potential

In order to better understand the influence of each potential, we identify the respective effects of temperature bias, concentration difference, and electric charge, and we discuss the relationship between chemical potential, electrochemical potential and the band diagram of materials. We then derive the Seebeck coefficient in the simple case of a non-degenerate semiconductor to illustrate the contribution of each potential.

3.1. Distinction between the potentials

Consider first the case of a volume that acts as a container of a given neutral species initially at thermodynamic equilibrium. Applying a thermal bias across the system yields a redistribution of the particles due to driven thermal motion ending up with a region of higher species concentration (cold end) and a region with lower concentration (hot end). If the system is characterized only by a concentration change in isothermal conditions, a particle current takes place from the region of higher concentration to that of lower concentration: this is the diffusion process associated to the variation of the species’ temperature- and density-dependent chemical potential across the system; it takes place until the diffusive equilibrium is reached. If the particles are electrically charged, say electrons in the vicinity of the junction of two different metals, this type of electrical current is referred to as the diffusion current. The inhomogeneous electron population on both sides of the junction thus generates an electric potential difference and hence an electric field which influences the electrons’ motion in such a fashion that it tends to curb the diffusion current. The electron motion driven by the electromotive force is the drift current, which, at thermal equilibrium, exactly cancels the diffusion current, in accordance with the principle of Le Chatelier and Braun.
In a typical thermoelectric solid-state device the physical processes are related to the coupled transport of electrons (or holes) and heat. Since each electron carries an electric charge \((-e)\), the chemical potential of an electron gas in a semiconductor cannot be equal to the variation of the free energy with respect to a change in electron concentration: the electric potential energy must be accounted for. Therefore as a thermal bias is applied across the thermoelectric system, a voltage appears, which induces an electromotive force such that the total electrical current results from both diffusion and drift and may be described by a drift-diffusion equation. The electromotive force derives from a potential, which is referred to as electrochemical potential. The total electrical current induced by thermal bias reflects the redistribution or flow of electrons in the system from the region with higher electrochemical potential to the region with lower electrochemical potential, thereby yielding (free) energy. As thermoelectric transport takes place, the system’s free energy varies, and the free energy per electron exchanged in the process corresponds to the electrochemical potential difference. Note that the quantities we just referred to as potentials are energies.

The electrochemical potential \(\tilde{\mu}\) of a population of particles is the sum of a chemical contribution \(\mu\), the chemical potential, and of an electrical contribution \(\mu_e\): \(\tilde{\mu} = \mu + \mu_e\). \(\text{(4)}\)

The electrical contribution \(\mu_e\) may be expressed as a function of the electrostatic potential \(\varphi\) (a genuine potential contrary to \(\tilde{\mu}\) and \(\mu\)) so that the electrochemical potential reads: \(\tilde{\mu} = \mu + q\varphi\), \(\text{(5)}\)

where \(q\) is the electrical charge of the considered particle. When used in solid state physics, these quantities have to be related to an energy band diagram. This correspondence may be found for example in the book of Heikes and Ure [8]: Considering the example of an n-doped semiconductor, the electrochemical potential \(\tilde{\mu}\) corresponds to the Fermi level, the electrostatic energy \(-e\varphi\) corresponds to the energy level of the bottom of the conduction band while the chemical energy \(\mu\) corresponds to the difference between these two quantities and is often called Fermi energy. These notations are summarized on figure \(\text{[2]}\). The difference between Fermi level \((\tilde{\mu})\) and Fermi energy \((\mu)\) was already highlighted by Wood [9]: “The difference between the Fermi energy and the Fermi level should be noted. The Fermi energy is generally measured from the adjacent conducting band edge (valence or conduction band for holes or electrons, respectively), i.e. a reference level which may vary in energy, whereas the Fermi level is measured from some arbitrary fixed energy level”. This last remark stresses the importance of the choice of an energy reference, which is a key parameter: To express energies in a semiconductor, the bottom of the conduction band is often used as the reference [10]; however, for studies of non-equilibrium phenomena such as thermoelectricity, it is mandatory to define an arbitrary fixed energy reference independent of the position
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Figure 2. Energy levels in an n-type semiconductor highlighting the notations used in this article (adapted from [8]). The energy $E_G$ refers to the bandgap energy.

within the material since both $\tilde{\mu}$ and $\mu$ may vary along the system. It is the only way to correctly describe the relative displacement of these energies.

We take now the opportunity to discuss here a long-lasting confusion concerning the chemical and electrochemical potentials in solid-state physics, possibly resulting from the authoritative book by Ashcroft and Mermin [19]. Indeed, in this book, the relationship between these two potentials is given by equation (29.7) and reads:

$$\tilde{\mu}_{AM} = \mu_{AM} + e\varphi. \quad (6)$$

The subscript AM has been added to distinguish the quantities used in [19] from those used in the present article. When comparing the previous equation with (5), it appears that Ashcroft and Mermin swapped the chemical and electrochemical potentials defined in equation (4). This observation is further supported by the fact that for Ashcroft and Mermin, $\mu$ is considered to be the Fermi level. This inversion possibly originates in the confusion on the sign of the electrical charge of electrons, which can be denoted either as $-e$ with $e > 0$ or $e$ with $e < 0$. Furthermore, once the two potentials are interchanged, derivations shown in [19] become consistent with those in electrochemistry [20].

3.2. From potentials to thermopower: the illustrative case of a non-degenerate semiconductor

The Seebeck coefficient may be obtained from a microscopic analysis of the considered materials, with the local version of (3), in open-circuit condition, i.e., with a vanishing electrical current:

$$\alpha = \frac{\nabla \tilde{\mu}}{e\nabla T}, \quad (7)$$

where $\tilde{\mu}$ and $T$ are respectively the local electrochemical potential and temperature, defined at each point of the system. The notation $\nabla$ is associated to spatial the gradient of each quantity. For the sake of simplicity, we consider a unidimensional system so that
the spatial gradient reduces to its $x$-component: $\nabla_x$. The potential $V$ used in Sec. 2 is defined as $V = -\tilde{\mu}/e$.

We emphasise the importance of the distinction between $\tilde{\mu}$ and $\mu$ on the derivation of the thermoelectric power using the example of a non-degenerate semiconductor doped with electrons. In this case, the expression of the carrier concentration $n$ is rather simple:

$$n(T) = N \exp\left(\frac{\tilde{\mu} - E_C}{k_BT}\right) = N \exp\left(\frac{\mu}{k_BT}\right), \quad (8)$$

with

$$N = 2 \left(\frac{2\pi m_{\text{eff}} k_BT}{\hbar^2}\right)^{3/2}, \quad (9)$$

and where $E_C$ is the energy level of the bottom of the conduction band, $m_{\text{eff}}$ is the electron effective mass, $k_B$ is the Boltzmann constant and $\hbar$ is the Planck constant. The Seebeck coefficient is associated to non-equilibrium phenomena, and, as such, it is tightly linked to transport properties of electrons inside the material. To take account of these properties, we build on the drift-diffusion equation used to obtain the net electrical current density $J_x$:

$$J_x = enM_n \mathcal{E}_x + eD_n \nabla_x n, \quad (10)$$

where $M_n$ and $D_n$ are the electron mobility and diffusivity, and where the electric field $\mathcal{E}_x$ is related to the energy level $E_C$ through:

$$\mathcal{E}_x = -\frac{\nabla_x E_C}{q} = \frac{\nabla_x E_C}{e}. \quad (11)$$

At first, we assume a situation where the electron diffusivity $D_n$ does not depend on the other parameters, including the position. The variation of $D_n$ will be discussed further below.

The Seebeck coefficient is obtained setting $J_x = 0$. However this current density should be related first to $\nabla_x T$ and $\nabla_x \tilde{\mu}$ rather than to $\mathcal{E}_x$ and $\nabla_x n$. To do so, we evaluate the gradient of the electron density given by (8) considering that $E_C$, $\tilde{\mu}$ and $T$ may vary along the material. This approach is seldom found in the literature as one often sets $E_C = 0$, thus considering the bottom of the conduction as the reference everywhere in the nonequilibrium system. As already stressed, this viewpoint is misleading for thermoelectric phenomena. In the framework of perturbation theory, the gradient of each parameter is considered to remain small compared to its average value, so the gradient of electron density reads:

$$\nabla_x n = \frac{3n}{2} \frac{\nabla_x T}{T} + \frac{n}{k_BT^2}[T (\nabla_x \tilde{\mu} - e\mathcal{E}_x) - \mu \nabla_x T]. \quad (12)$$

We then use this equality along with Einstein’s relation between the electron mobility $M_n$ to the electron diffusivity $D_n$:

$$\frac{M_n}{D_n} = \frac{e}{k_B T}. \quad (13)$$
to modify (10) as follows:

\[ J_x = enM_n \left( \frac{\nabla_x \tilde{\mu}}{e} + \frac{k_B}{e} \left[ \frac{3}{2} - \frac{\mu}{k_B T} \right] \nabla_x T \right). \]  

(14)

Now, setting \( J_x = 0 \) and using the definition given in Eq. (7), we find:

\[ \alpha = -\frac{k_B}{e} \left[ \frac{3}{2} - \frac{\mu}{k_B T} \right], \]  

(15)

with a constant electron diffusivity, which is the expected expression for a non-degenerate semiconductor.

Now, if we relax the assumption of the constance of \( D_n \), it becomes a function of the spatial coordinate \( x \) and we end up with the so-called Stratton’s equation [21]:

\[ J_x = enM_n \mathcal{E}_x + e \nabla_x (D_n n) \]
\[ = enM_n \mathcal{E}_x + e D_n \nabla_x (n) + en \nabla_x (D_n), \]  

(16)

It corresponds to a more general form of the drift-diffusion equation, which contains a third contribution to the carrier motion, directly linked to the gradient of diffusivity along the system. To evaluate its effect on the thermoelectric power, we may reexpress it as a function of the temperature gradient using the relation between the diffusivity \( D_n \) and the relaxation time of the carriers \( \tau \). Since \( M_n = e \tau / m_{\text{eff}} \), the Einstein relation reads:

\[ D_n = k_B T \frac{\tau}{m_{\text{eff}}}. \]  

(17)

To keep the calculations on an analytical level, we assume that we deal with low-energy conduction electrons, and we express the relaxation time using a power law of the form: \( \tau \propto (E - E_C)^s \), where \( E \) is the total energy of the carrier and \( s \) is a characteristic exponent depending on the scattering mechanisms [21]. Note that the energy \( E - E_C \) corresponds to the thermal energy of the carriers in the conduction band and may thus be approximated by its average value, i.e., \( 3/2k_B T \). Replacing \( \tau \) in (17), we obtain:

\[ \nabla_x (D_n) = \frac{D_n}{T} (1 + s) \nabla_x (T). \]  

(18)

Finally, inserting (18) and (12) in (16) yields:

\[ J_x = enM_n \left( \frac{\nabla_x \tilde{\mu}}{e} + \frac{k_B}{e} \left[ \frac{5}{2} + s - \frac{\mu}{k_B T} \right] \nabla_x T \right), \]  

(19)

and consequently:

\[ \alpha = -\frac{k_B}{e} \left[ \frac{5}{2} + s - \frac{\mu}{k_B T} \right]. \]  

(20)

The contribution of the diffusivity gradient to the thermoelectric power is \(- (1 + s) k_B / e\) and hence depends only on the scattering parameter \( s \). This term has also been recovered
by Cai and Mahn \cite{12} using a Boltzmann equation. Note that this term was also introduced by Ioffe \cite{22} with the notation $\alpha_D$. However, Ioffe used a different power law: He assumed that the carrier’s mean free path $\bar{l}$ is proportional to $(E - E_C)^r$. He consequently found that $\alpha_D = -(1/2 + r)k_B/e$. This discrepancy is quite easy to understand since $\tau$ is proportional to $\bar{l}/\sqrt{E - E_C}$.

3.3. Discussion

While the result \cite{15} is well-known, its derivation presented here is quite original. Indeed, it was directly obtained from the drift-diffusion equation. Thus, the phenomenological equation associated to thermoelectric transport:

$$J_x = \sigma \frac{\nabla_x \tilde{\mu}}{e} - \sigma \alpha \nabla_x T,$$

where $\sigma = enM_n$ is the electrical conductivity, is identical to \cite{19} (or to \cite{14} depending on the hypothesis made). This latter appears as a modified form of the drift-diffusion equation, which accounts for the couple of variables $[\tilde{\mu}, T]$, or more precisely their gradients, rather than the traditional couple $[n, \varphi]$. This modification puts forth the fact that the first term of the right hand side of \cite{21} does not correspond any longer to the genuine local form of Ohm’s law since it does not involve the electrical field $E_x$. In this case, the true electromotive force is given by the gradient of the electrochemical potential as carriers experience both diffusion and effects of the electric field.

The simple derivation of \cite{19} has been allowed by the use as a reference of a fixed energy level, arbitrarily chosen but independent of the position along the material, rather than the bottom of the conduction band. This approach demonstrates that a particular knowledge of both $\nabla_x n$ and $E_x$ is not mandatory to determine the Seebeck coefficient. Indeed, these two contributions to the electrochemical gradient seems to always compensate each other in such a way that the resulting electromotive power is independent of specific assumptions, for example a constraint on the carrier concentration. Equation \cite{19} is thus valid for a wide range of temperatures: It is correct for the extrinsic regime, i.e., when the carrier concentration is fixed by the concentration of impurities, but it also remains valid in the freeze-out regime and in the intrinsic regime where additional carriers are thermally generated. However, in this latter regime, the electron hole contribution to thermoelectric power should also be considered as these minority carriers may no longer be negligible.

Let us now turn to the previous analysis of the thermoelectric power in non-degenerate semiconductor. In \cite{11}, Mahan introduces an effective Seebeck coefficient $\tilde{S}$, distinct from the genuine thermoelectric power \cite{3} obtained from measurements. In a subsequent article with Cai \cite{12}, this effective coefficient is presented as the ratio between the electric field and the temperature gradient. These two different Seebeck coefficients are related through the following relation \cite{12}:

$$\alpha = \tilde{S} + \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right)_n,$$  \tag{22}
A comparison of (16) with the equation (20) of [11] leads to identify the effective Seebeck coefficient to the contribution of the diffusivity gradient, i.e., $\alpha_D$. The second term of the right hand side of (22) should then be associated to the assumption of constant diffusivity, i.e., to (15). This expression is identical to the so-called Kelvin formula of the thermopower [13]. As discussed by Shastry [23], this contribution “captures the many body density of states enhancements, while missing velocity and relaxation contributions”. It thus justifies the introduction of the coefficient $\overline{S}$ to take into account dynamical effects. We believe however that this coefficient should not be presented as effective since it does not reflect the appearance of the electromotive force due to the temperature gradient. It represents only one of the possible contributions to this electromotive force. Furthermore, (19) shows that $\overline{S}$ is given by the ratio between the electric field and the temperature gradient only when the carrier density is constant, e.g., in a material with homogeneous doping in the extrinsic regime.

Finally, we want to point out two more publications discussing the definition of the thermoelectric power: In [22], Ioffe obtains (19); however he splits the Seebeck coefficient into three separate terms, one being $\alpha_D$ while the two others, $\alpha_n$ and $\alpha_\varphi$, are associated respectively to concentration gradient and to the “temperature dependence of the contact potential”. However, as demonstrated later by Chambers [24], contact potentials are irrelevant to thermoelectric effects. This latter term is thus introduced only to compensate the erroneous expression of $\alpha_n$ stemming from the confusion between $\varphi$ and $\tilde{\mu}/e$. One may also refer to [25] in which, the authors derive the Seebeck coefficient focusing only on potentials and the electric field rather than using a statistical approach.

4. Conclusion

In this article, we have discussed the definition of the thermoelectric power with a special emphasis on its relationship to the electrochemical potential. A proper consideration of all potentials inside the material has led to demonstrate that the phenomenological equation for the electrical current involving thermoelectric coefficients may be derived directly from the drift-diffusion equation. We also shed light on the physical interpretation of the effective Seebeck coefficient defined by Mahan, showing that it is actually related to the gradient of diffusivity along the system.

References

[1] de Groot S R 1958 Thermodynamics of Irreversible Processes (Interscience Publishers Inc., New York)
[2] Apertet Y, Ouerdane H, Goupil C and Lecoeur Ph (2012) Phys. Rev. E 85, 031116
[3] Seebeck T J 1821 Abh. K. Akad. Wiss. Berlin 289
[4] Oersted H C 1823 Annales de Chimie et de Physique 22 199
[5] Callen H B 1948 Phys. Rev. 73 1349
[6] Herring C 1954 Phys. Rev. 96 1163
[7] Price P J 1956 Phys. Rev. 104 1223
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[8] Heikes R R and Ure R W 1961 *Thermoelectricity: Science and Engineering* (Interscience Publishers).
[9] Wood C Reports on Progress in Physics 1988 51 459
[10] Kittel C 2005 *Introduction to Solid State Physics, 8th edition* (John Wiley & Sons, New York)
[11] Mahan G D 2000 J. Appl. Phys. 87 7326
[12] Cai J and Mahan G D 2006 Phys. Rev. B 74 075201
[13] Peterson M R and Shastry B S 2010 Phys. Rev. B 82 195105
[14] Varlamov A A and Kavokin A V 2013 EPL 103 47005
[15] Zhou Z and Uher C 2005 Rev. Sci. Instrum. 76 023901
[16] Riess I Solid State Ionics 1997 95 327
[17] Martin J, Tritt T and Uher C 2010 J. Appl. Phys. 108 121101, and references therein
[18] Callen H B 1985 *Thermodynamics and an introduction to Thermostatistics* (John Wiley & Sons, New York)
[19] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (Saunders, Philadelphia)
[20] Bard A J and Faulkner L R 2000 *Electrochemical Methods: Fundamentals and Applications, 2nd edition* (Wiley, New York)
[21] Lundstrom M 2009 *Fundamentals of carrier transport, second edition* (Cambridge University Press, Cambridge)
[22] Ioffe A F 1960 *Physics of Semiconductors* (Infosearch, Ltd., London)
[23] Shastry B S 2013 Thermopower in Correlated Systems, in *New Materials for Thermoelectric Applications: Theory and Experiment* (Springer Netherlands, Dordrecht)
[24] Chambers R G 1977 Physics Education 12 374
[25] Rose F W G Billig E and Parrott J E 1957 Journal of Electronics and Control 3 481