

SEEBECK EFFECT

In 1821, early in the study of electromagnetic phenomena, Thomas Johann Seebeck discovered what is now termed the *Seebeck effect*. Seebeck had constructed a closed loop of two conductors by connecting the two ends of a copper wire to the two ends of a bismuth wire. As illustrated in Fig. 1, when the two junctions of the loop were held at different temperatures, Seebeck observed a magnetic field emanating from the loop. The strength of the magnetic field increased as the difference between the temperatures of the two junctions was increased.

Current flowing through the loop would induce the observed magnetic field. Thus, Seebeck could infer that having a temperature difference between the loop's two junctions induced electric-current flow around the loop. This electric-current flow implies the existence of an electromotive force (*emf*). The emf is the work per unit charge needed to drive charge flow through the circuit. In other words, the emf is the voltage associated with generating the electric current.

The Seebeck effect, depicted in Fig. 2, describes the emf produced by a closed loop of two dissimilar materials in the presence of a temperature difference between the two junctions. The emf is the sum of the emfs produced in each of the loop's two materials. The ratio of the emf induced in material A, $(emf)_A$, to the temperature differential across material A is defined as the absolute Seebeck coefficient of material A:

$$\alpha_A \equiv \frac{(emf)_A}{\Delta T} \quad (1)$$

The absolute Seebeck coefficient is defined to be positive when an emf drives current flow from a material's hot end to its cold end. With a closed loop, the current in one material flows from its hot end to its cold end while the current in the other material flows from its cold end to its hot end. Therefore, the emf of the loop as a whole is the difference of the emfs produced in each of the loop's two materials. The net Seebeck coefficient of the circuit is the difference of the absolute Seebeck coefficients of its two legs, $\alpha_A - \alpha_B$.

The absolute Seebeck coefficient of a material is often simply referred to as its Seebeck coefficient. The phrase *thermoelectric power*, the initials *TEP*, and the contraction *thermopower* are synonyms for a material's Seebeck coefficient. Common symbols for the Seebeck coefficient are α and S . Seebeck coefficients are measured in units of volts per kelvin. Seebeck coefficients of metals are typically small (several microvolts per kelvin, $\mu\text{V/K}$) and rise with increasing temperature. By contrast, insulating electrical behavior yields much larger Seebeck coefficients (millivolts per kelvin, mV/K) that fall with increasing temperature.

The practical utility of the Seebeck effect has been recognized for a very long time. In particular, Seebeck's discovery provides a means of converting heat into electric energy. Heat is supplied to maintain a temperature differential that in turn drives an electric current. Used in this manner, the Seebeck effect is the basis of thermoelectric energy conversion.

Thermoelectric generators are reliable and portable sources of electric power. They provide electricity in locations that lack connections to an electric-power grid. Thermoelectric-power generators are used extensively in rockets, in space probes, and sometimes in satellites. In these instances the heat required to operate the thermoelectric generators is obtained from radioisotopes. Such a thermoelectric generator is termed a

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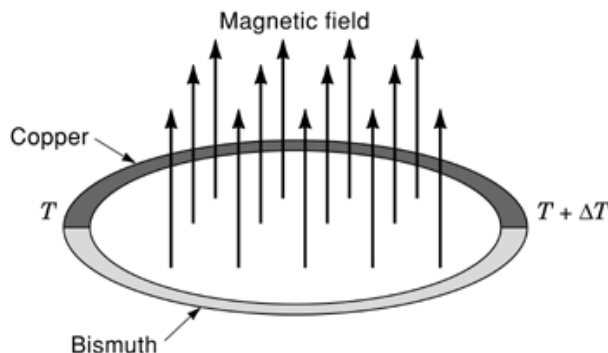


Fig. 1. Seebeck's experiment: A magnetic field is produced when a temperature difference ΔT is maintained between the two junctions of a closed loop composed of copper and bismuth segments.

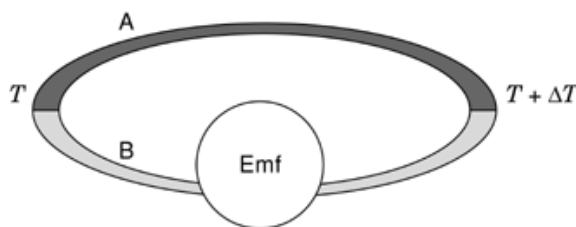


Fig. 2. The Seebeck effect: An electromotive force (emf) is produced when a temperature difference ΔT is maintained between the two junctions of a closed loop formed from segments of different materials (labeled A and B).

radioisotope thermoelectric generator (RTG). In remote terrestrial locations burning wood, kerosene, or propane can produce the heat needed to operate thermoelectric generators. Thermoelectric generators are also used to obtain electric power from heat that otherwise would be wasted. For example, thermoelectric generators can obtain electricity from the hot exhaust expelled from internal-combustion engines.

Thermoelectric generators generally utilize semiconductors. A semiconductor is an insulator whose electrical conductivity is enhanced through the addition of dopants. Dopants introduce additional charge carriers (electrons that are free to move through the solid) into an insulator. The addition of charge carriers augments a material's electrical conductivity. Common semiconductors (e.g., silicon, germanium, and semiconducting alloys of these two elements) have been employed in thermoelectric generators.

The Seebeck effect is also used in thermometry. It underlies the operation of a *thermocouple*. In particular, a thermocouple measures the net Seebeck emf of a couple composed of two materials whose Seebeck coefficients have been calibrated as functions of temperature. The absolute temperature can be determined when one junction of the couple is kept at a known reference temperature.

The materials used in thermocouples are typically metals and metallic alloys such as constantan (a copper–nickel alloy) and chromel (a nickel–chromium alloy). The Seebeck coefficient of a typical thermocouple is about $10 \mu\text{V/K}$. A commercial thermocouple is generally specified for use over a temperature range within which the net Seebeck coefficient of the thermocouple's two materials is nearly constant. The emf of the thermocouple is then simply proportional to the temperature difference.

Analysis of the Seebeck effect and other thermoelectric effects using basic principles of irreversible thermodynamics provides a very useful alternative definition of the Seebeck coefficient. In particular, the *absolute Seebeck coefficient of a material is the entropy transported with a charge carrier in isothermal flow divided by the carrier's charge*. This transported entropy can be thought of having two components. The first component

is the change in the entropy of the solid upon adding a charge carrier. The second component is the energy transfer associated with moving a carrier through the material divided by the product of the temperature and the carrier's charge. In most instances the first component predominates.

A prime contribution to the change of a solid's entropy upon the addition of a charge carrier is the change of the carriers' *entropy of mixing*. The carriers' entropy of mixing depends on the ratio of the carrier density to the density of accessible electronic states.

In semiconductors and insulators the carrier density is often much less than the density of thermally available states. In this circumstance, the addition of a charge carrier significantly affects the carriers' entropy of mixing. For this reason, the Seebeck coefficients of semiconductors and insulators are typically large. Specifically, the magnitude of an insulator's Seebeck coefficient is generally much greater than $\kappa/|e| = 86 \mu\text{V/K}$, where κ is the Boltzmann constant and $|e|$ is the absolute value of an electron's charge. Seebeck coefficients of insulators can be as much as 1 mV/K.

A contrasting situation exists in metals, where the carrier density is a significant fraction of the density of thermally available states. As a result, Seebeck coefficients of electric conductors are typically very small, that is, $\ll \kappa/|e|$. The Seebeck coefficients of metals are usually no more than $10 \mu\text{V/K}$.

Beyond the general contrast between the Seebeck coefficients of insulators and semiconductors and those of conductors, Seebeck coefficients depend upon how carriers move and interact with their surroundings. Both components of the Seebeck coefficient, the entropy change associated with the addition of a charge carrier and the energy transfer that accompanies charge transport, depend on the charge-transport mechanism.

Charge carriers' mobilities measure the ease with which they move. More precisely, the mobility is the velocity per unit electric field with which a carrier moves when driven by an electric field. Two complementary mechanisms of charge transport are important, depending on whether the carrier mobility is large or small. *Itinerant carriers* are viewed as moving freely except for occasional scattering events. The mobility of an itinerant carrier typically falls with increasing temperature and generally exceeds $1 \text{ cm}^2/\text{V}\cdot\text{s}$. By contrast, a carrier may move by *phonon-assisted hopping*. Hopping carriers are then viewed as usually being localized, confined to a specific location within a solid. All the while the solid's atoms vibrate about their equilibrium positions. Physicists describe atomic vibrations as due to excitations called *phonons*. Occasionally motion of surrounding atoms facilitates a localized carrier jumping from one location to another. The mobility of a carrier that moves by phonon-assisted hopping generally increases as the temperature rises, but generally remains $< 1 \text{ cm}^2/\text{V}\cdot\text{s}$.

There are several effects through which atomic vibrations can affect the Seebeck coefficients of itinerant carriers. In particular, the electronic energy levels occupied by carriers shift as the temperature is raised, and atoms vibrate more violently. Concomitantly, carriers' presence affects atomic vibrations. Thus, the addition of a charge carrier affects both electronic and atomic entropy. These entropy changes tend to cancel one another. As a result, the effect of electron-phonon interactions on the entropy-change contribution to the itinerant-carrier Seebeck coefficient can generally be ignored. However, atomic vibrations also scatter itinerant charge carriers. Momentum is thereby transferred from carriers to atoms. In some circumstances the energy flow associated with this carrier-induced atomic motion persists long enough to produce a significant energy-transfer contribution to the Seebeck coefficient. This effect, termed *phonon drag*, is observed at low temperatures in high-purity metals and semiconductors.

The Seebeck coefficients of hopping carriers depend upon the localized states between which the carriers hop and the means by which they do so. In particular, it is the density of thermally accessible localized states involved in hopping that enters into the entropy-of-mixing contribution to hopping carriers' Seebeck coefficients. Furthermore, since atomic vibrations are required to facilitate carriers' hopping between localized states, some vibratory energy can be transferred with a carrier as it hops. This energy transfer contributes to hopping carriers' Seebeck coefficients. Such energy-transfer contributions to the Seebeck coefficient can be distinguished from the entropy-of-mixing contribution because they are independent of the carrier density.

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Interactions among carriers also significantly affect the Seebeck coefficient. For example, entropy-of-mixing contributions are affected when Coulomb repulsion between hopping carriers often prevents more than one carrier from occupying a localized state. Furthermore, the entropy associated with unpaired carriers' spin orientations contributes to the carriers' entropy. These contributions are not often simple, since a carrier's spin is linked to other spins by exchange interactions.

Seebeck-coefficient measurements are valuable probes of a material's electronic transport. The sign of the Seebeck coefficient indicates the charge of the predominant carriers. The magnitude of the Seebeck coefficient indicates the ratio of the number of carriers to the number of thermally accessible electronic states. The temperature dependence of the Seebeck coefficient in simple semiconductors measures the characteristic energy, relative to the chemical potential, of the states associated with carrier's motion. Moreover, careful analysis of the Seebeck coefficient and its dependences on carrier concentration and temperature provide information about carriers' interactions with their surroundings and with other carriers. For these reasons, the science of the Seebeck coefficient remains an active area of study.

Active study of Seebeck coefficients also persists because the Seebeck effect underlies thermoelectric power generation and the operation of thermocouples. The Seebeck coefficients of novel materials are measured with the hope that they will better serve these applications.

Thermoelectric Effects in Irreversible Thermodynamics

Phenomena that link electrical and heat flows are generally termed thermoelectric effects. The Seebeck effect, Peltier effect, and Thomson effect are three thermoelectric phenomena. These three effects and the relationships between them can be readily described using general results of *irreversible thermodynamics* (1). Irreversible thermodynamics addresses flows of heat, particles, and charge. This approach elucidates the physical significance of the Seebeck coefficient. In particular, the Seebeck coefficient is seen to be the entropy per unit charge transported with a charge carrier.

Seebeck Coefficient. The electric current density is the charge per unit time passing through a unit cross-sectional area. When current is carried by particles of charge q , the electric current density is proportional to the current density from these particles' flow, J_N . The electric current density is

$$qJ_N = -(\sigma/q)\nabla\mu - \sigma\alpha\nabla T \quad (2)$$

where σ is the electrical conductivity and μ is the electrochemical potential. Thus, charge flow is driven by gradients of the electrochemical potential as well as by temperature gradients.

The electrochemical potential is the potential associated with applied fields plus the particles' chemical potential. Gradients of the chemical potential occur when the particle density is nonuniform. Gradients of the chemical potential drive particles to flow from regions of high density to regions of low density. As indicated by Eq. (2), applied fields, nonuniform particle densities, and thermal gradients can each drive current flow.

Measurements of the Seebeck coefficient are usually made in an open circuit where the net flow of charge carriers vanishes: $J_N = 0$. Then current flow driven by the temperature gradient is opposed and canceled by the current flow driven by the gradient of the electrochemical potential. In other words, the imposition of a temperature gradient induces a gradient of the electrochemical potential:

$$\nabla\mu = -q\alpha\nabla T \quad (3)$$

If the circuit is closed rather than open, the flow induced by the temperature gradient is unopposed. Then the temperature gradient itself produces current flow. The emf driving this current flow equals $(-\nabla\mu)/q$. This

driving force produces the Seebeck effect. Thus, irreversible thermodynamics yields a general formula for a material's Seebeck coefficient:

$$\alpha \equiv -\frac{1}{q} \frac{\nabla\mu}{\nabla T} \quad (4)$$

When the gradients used in measurements of Seebeck coefficients are small, the ratio of the gradients equals the ratio of the differentials, $\nabla\mu/\nabla T = \Delta\mu/\Delta T$. The definitions of the Seebeck coefficients contained in Eqs. (1) and (4) are then seen to be equivalent to one another.

Additional understanding of the physical significance of the Seebeck coefficient is obtained by using another result of irreversible thermodynamics. Namely, the heat current density is

$$\mathcal{J}_Q = T\alpha q \mathcal{J}_N - \kappa_T \nabla T \quad (5)$$

where κ_T is the thermal conductivity in the absence of particle flow ($\mathcal{J}_N = 0$). The entropy current density, \mathcal{J}_S , is obtained by expressing the heat flow in terms of the entropy flow $\mathcal{J}_Q = T\mathcal{J}_S$:

$$\mathcal{J}_S = \alpha q \mathcal{J}_N - (\kappa_T/T) \nabla T \quad (6)$$

In the absence of a temperature gradient this equation reduces to $\mathcal{J}_S = \alpha q \mathcal{J}_N$. The Seebeck coefficient α is then the entropy current density \mathcal{J}_S divided by the electric current density $q\mathcal{J}_N$. That is, with isothermal flow *the Seebeck coefficient is the entropy transported by a carrier divided by its charge*.

It is very useful to be able to relate the Seebeck coefficient to the entropy transported with a charge carrier. In particular, the third law of thermodynamics requires the vanishing of entropy at absolute zero. We can therefore infer that Seebeck coefficients must also vanish as the temperature approaches absolute zero.

Peltier Coefficient. The Seebeck effect is related to the Peltier effect, another thermoelectric phenomenon. The Peltier heat is the heat that must be supplied to a particle that passes through an isothermal junction between dissimilar materials in order to maintain the isothermal condition. That is, the Peltier coefficient for current passing through a junction between material A to material B, Π_{AB} , is the difference between the heat flow associated with carriers leaving the junction and that associated with carriers entering the junction, divided by the electric current passing through the junction, $q\mathcal{J}_N$. By using Eq. (6) the Peltier coefficient at a junction can be related to the Seebeck coefficients of the two materials that constitute the isothermal junction:

$$\Pi_{AB} \equiv \frac{\mathcal{J}_{Q,B} - \mathcal{J}_{Q,A}}{q\mathcal{J}_N} = T(\alpha_B - \alpha_A) \quad (7)$$

The Peltier coefficient of a junction is thus the product of the junction's temperature and the difference between the Seebeck coefficients of the junction's two materials. The relation, Eq. (7), between the Peltier coefficient of a junction and the absolute Seebeck coefficients of the joined materials is termed the *second Kelvin relation*, after Lord Kelvin, who observed the relationship between the Peltier and Seebeck coefficients.

The Peltier effect is a basis of cooling devices. In particular, Peltier cooling occurs as current passes through a junction between appropriate dissimilar materials. Commercial picnic coolers and coolers for electronics operate on this principle.

Thomson Coefficient. The Thomson effect is another thermoelectric effect. The *Thomson heat* Q_T is the heat exchange that results when an electric current flows through a temperature gradient. The *Thomson coefficient* τ is defined as the Thomson heat divided by the product of the electric current density and the

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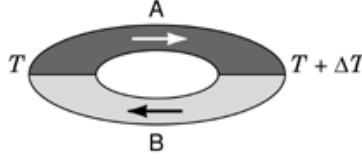


Fig. 3. A thermoelectric circuit comprising two materials whose junctions are at different temperatures. The arrows denoted the current-flow direction.

thermal gradient,

$$\tau \equiv \frac{Q_T}{qJ_N \nabla T} \quad (8)$$

The Thomson coefficient of a material is related to its Seebeck coefficient. This relationship may be inferred from the energy balance associated with slow steady-state flow through the idealized thermoelectric circuit of Fig. 3. That is, losses from Joule heating and to thermal diffusion are ignored. Then the three thermoelectric effects control absorption and dissipation of electric power. First, the Seebeck effect of the circuit's two legs produces a net power density of $(qJ_N)(\alpha_B - \alpha_A) \Delta T$. Second, the Thomson effect of the circuit's two legs reduces the power density by $(qJ_N)(\tau_A - \tau_B) \Delta T$. Finally, the Peltier effect causes a net loss of electric power density at junctions between dissimilar materials of $(qJ_N)[\Pi_{AB}(T + \Delta T) - \Pi_{AB}(T)] = (qJ_N)(d\Pi_{AB}/dT) \Delta T$. Equating the generated and dissipated powers of this ideal thermoelectric circuit yields

$$\alpha_B - \alpha_A = \tau_A - \tau_B + \frac{d\Pi_{AB}}{dT} \quad (9)$$

The derivative of the Peltier coefficient with respect to temperature may be evaluated using Eq. (7):

$$\frac{d\Pi_{AB}}{dT} = \alpha_B - \alpha_A + T \frac{d(\alpha_B - \alpha_A)}{dT} \quad (10)$$

Employing Eq. (10) in Eq. (9) then yields an expression for the difference of the Thomson coefficients in terms of the temperature dependences of the Seebeck coefficients:

$$\tau_B - \tau_A = T \frac{d(\alpha_B - \alpha_A)}{dT} \quad (11)$$

The Thomson coefficient of each material is related to its Seebeck coefficient by

$$\tau = T \frac{d\alpha}{dT} \quad (12)$$

The relations between the Thomson coefficients and the other thermoelectric coefficients [Eqs. (9), (11), and (12)] are each sometimes referred to as the *first Kelvin relation*.

In summary, three thermoelectric coefficients have been considered. The absolute Seebeck coefficient is the emf per unit temperature differential induced by maintaining a temperature differential across a material.

The Seebeck coefficient is also the entropy transported by a charge carrier in isothermal flow divided by the carrier's charge. The Peltier coefficient measures the heat that is absorbed or evolved as a charge passes through a junction. The Thomson coefficient measures the energy absorption resulting from a current flowing through a temperature gradient. The Peltier and Thomson coefficients are related to Seebeck coefficients through Eqs. (7) and (12).

Seebeck Effect for Itinerant Carriers

The Seebeck coefficient generally depends on carrier densities, the energies of states available to carriers, the interactions of the carriers with their environment, and the interactions of carriers with one another. For these reasons computation of a material's Seebeck coefficient is generally very complex. Fortunately, some general properties of Seebeck coefficients may be ascertained by studying simple models. Essential features of the electronic transport of many simple metals and semiconductors can be understood by regarding their charge carriers as freely moving.

General Formalism. A commonly employed approach considers electronic charge carriers as moving freely with their motion being occasionally interrupted by scattering events. These scattering events limit electronic motion, thereby producing electric resistance.

In thermodynamic equilibrium the states occupied by the charge carriers are such as to yield no net current flow. Applying potential and thermal gradients drives carriers toward state occupancies for which there is a net flow. Carriers' flow is opposed by their scattering, as scattering fosters carriers' return to equilibrium. This re-equilibration is characterized by the relaxation time τ .

The steady-state current for this simple model is obtained by solving the linearized Boltzmann equation. The particle current density for flow in the x direction under the combined influence of an electric field $-\partial V/\partial x$ and a thermal gradient $\partial T/\partial x$ is (See Ref. 2)

$$\begin{aligned} J_N &= \int dE \rho(E) f(E) [1 - f(E)] [v^2(E) \tau] \left[\left(\frac{-q}{\kappa T} \frac{\partial V}{\partial x} \right) - \left(\frac{E - \mu}{\kappa T^2} \frac{\partial T}{\partial x} \right) \right] \\ &\equiv \int dE \sigma(E) \left[\left(-\frac{\partial V}{\partial x} \right) - \left(\frac{E - \mu}{qT} \frac{\partial T}{\partial x} \right) \right] \end{aligned} \quad (13)$$

Here $\rho(E)$ is the density of electronic states, $v(E)$ is the carrier velocity, and $f(E)$ is the Fermi distribution function for carriers of energy E : $f(E) \equiv 1/\{\exp[(E-\mu)/\kappa T] + 1\}$. The electrical conductivity per unit energy, $\sigma(E)$, is defined in the second line of Eq. (13). The total electrical conductivity is given by the integral of $\sigma(E)$ over energy.

The Seebeck coefficient is obtained by considering an open circuit in which no current is permitted to flow: $J_N = 0$. The Seebeck experiment entails measuring the potential difference that develops across this open circuit when a temperature gradient is maintained. Equation (13) indicates that the potential drop across the material, ΔV , in response to a thermal difference ΔT is

$$\begin{aligned} \Delta V &= \left(\frac{-1}{qT} \right) \frac{\int dE \sigma(E) [E - \mu]}{\int dE \sigma(E)} \Delta T \\ &\equiv \left(\frac{-1}{qT} \right) \langle [E - \mu] \rangle_{\sigma(E)} \Delta T \end{aligned} \quad (14)$$

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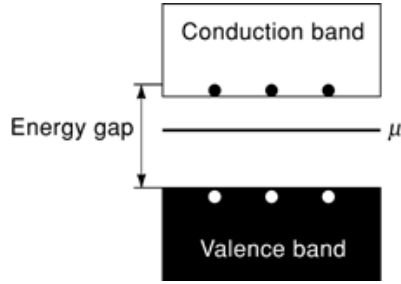


Fig. 4. The electronic states of an idealized insulator are illustrated schematically. An insulator is characterized by an energy gap between valence and conduction bands. Conduction-band states are almost empty but contain a few electrons (solid circles). Valence-band states are almost fully occupied by electrons but contain a few *holes* (open circles). The chemical potential μ lies between the valence and conduction bands.

As shown in the first line of Eq. (14), the Seebeck voltage ΔV is proportional to the average of $E - \mu$ with respect to $\sigma(E)$. The second line of Eq. (14) defines $\langle [E - \mu]_{\sigma(E)}$ as a symbol for this average. The primary contributions to this average come from terms with energies for which $\sigma(E)$ is relatively large. Thus, the carriers having energies that contribute most to the dc conductivity tend to contribute most to the Seebeck voltage.

Written in terms of this average, the Seebeck coefficient is

$$\alpha = -\frac{\Delta V}{\Delta T} = \frac{1}{qT} \langle [E - \mu]_{\sigma(E)} \rangle \quad (15)$$

This expression is consistent with that obtained from irreversible thermodynamics. In particular, the entropy of a system of N carriers is $(U - \mu N)/T$, where U is the system's internal energy. Adding a carrier to the system alters its entropy by $(\Delta U - \mu)/T$, where ΔU is the change in the internal energy. With noninteracting carriers, the change of the internal energy upon adding a carrier is just that carrier's energy: $\Delta U = E$. Thus, the expression of Eq. (15) denotes the average change of the entropy of the system upon the addition of a carrier of energy E weighted by that carrier's contributions to the dc conductivity divided by qT .

Seebeck Coefficients of Insulators and Metals. The Seebeck coefficients of insulators and metals differ significantly from one another. To readily appreciate these differences it is useful to first rewrite Eq. (15) as

$$\alpha = \left(\frac{\kappa}{q}\right) \frac{\langle [E - \mu]_{\sigma(E)} \rangle}{\kappa T} \quad (16)$$

where κ is the Boltzmann constant. When the Seebeck coefficient is expressed in this form, κ/q appears as the natural unit with which to measure the coefficient's magnitude. A Seebeck coefficient is generally regarded as small or large according as its magnitude is much smaller than or much larger than $\kappa/|e| = 86 \mu\text{V/K}$, where $|e|$ denotes the absolute value of the charge of an electron.

In an ideal intrinsic insulator, illustrated in Fig. 4, the chemical potential is near the center of the energy gap. Charge carriers are associated with electronic states that are partially filled. Most states lying below the chemical potential are filled. Carriers in these energy bands, the *valence bands*, are holes in otherwise filled levels. Analogously, most states lying above the chemical potential are empty. Carriers in these energy bands, the *conduction bands*, are electrons in otherwise empty levels. The Seebeck coefficient for an insulator is a

weighted average of that due to holes in the valence band and that due to electrons in the conduction band:

$$\alpha = \frac{\kappa}{|e|} \left[\left(\frac{\langle \mu - E \rangle_v}{\kappa T} \right) \left(\frac{\sigma_v}{\sigma_v + \sigma_c} \right) - \left(\frac{\langle E - \mu \rangle_c}{\kappa T} \right) \left(\frac{\sigma_c}{\sigma_v + \sigma_c} \right) \right] \quad (17)$$

where $|e|$ is the magnitude of an electron's charge, and the electrical conductivities of carriers in the valence and conduction bands are denoted by σ_v and σ_c , respectively. Holes in valence bands make a positive contribution to the Seebeck coefficient. By contrast, electrons in conduction bands make a negative contribution.

In addressing the Seebeck coefficients of insulators, it is customary to write the energies of valence-band and conduction-band states relative to their respective band edges, E_c and E_v : $E = E_v - \varepsilon_v$ and $E = E_c + \varepsilon_c$, respectively. Then the Seebeck coefficient takes the form

$$\alpha = \frac{\kappa}{|e|} \left[\left(\frac{\mu - E_v}{\kappa T} + A_v \right) \left(\frac{\sigma_v}{\sigma_v + \sigma_c} \right) - \left(\frac{E_c - \mu}{\kappa T} + A_c \right) \left(\frac{\sigma_c}{\sigma_v + \sigma_c} \right) \right] \quad (18)$$

where

$$A_v \equiv \frac{\langle \varepsilon_v \rangle_{\sigma_v(E)}}{\kappa T} \quad (19)$$

and

$$A_c \equiv \frac{\langle \varepsilon_c \rangle_{\sigma_c(E)}}{\kappa T} \quad (20)$$

The functions defined by Eqs. (19) and (20) are generally temperature-dependent. Nonetheless, in the common situation in which the widths of the insulator's valence and conduction bands greatly exceed the thermal energy κT , A_v and A_c are near constant with values of the order of unity. For this reason, A_v and A_c are often called the heat-of-transport "constants."

Often one of the two opposite-signed terms in the square brackets of Eq. (18) dominates the other. In these instances Eq. (18) becomes very simple. The magnitude of the Seebeck coefficient is then very large, $\gg \kappa/|e|$ (since $\mu - E_v$ and $E_c - \mu$ are typically much greater than κT), and it falls with increasing temperature in proportion to $1/\kappa T$ at high enough temperatures. The exception occurs if the two opposite-signed terms in the square brackets of Eq. (18) cancel one another. This situation is evident in that the Seebeck coefficient passes through zero as it changes sign.

Equation (18) also indicates that the Seebeck coefficient will become arbitrarily large as the temperature is lowered toward absolute zero. This feature of Eq. (18) violates the third law (Nernst postulate) of thermodynamics, which requires the entropy, and hence Seebeck coefficients, to vanish at absolute zero.

This dilemma is resolved by observing that low-temperature Seebeck coefficients are always dominated by transport among states with energies arbitrarily close to the chemical potential. The Seebeck coefficient for such transport, akin to that for metals (discussed below), vanishes as the temperature approaches absolute zero. Since such states are ignored in the model leading to Eq. (18), this formula is to be regarded as an approximation that fails at very low temperatures.

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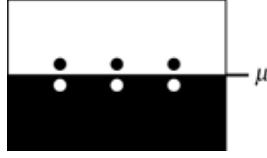


Fig. 5. The electronic states of an idealized metal are illustrated schematically. The chemical potential μ is the boundary between electronic levels that are mainly occupied and ones that are mainly empty. Solid circles indicate filled states above the chemical potential. Open circles indicate empty states below the chemical potential.

Metals are unlike insulators in that, as illustrated in Fig. 5, the chemical potential of a metal resides within the band of states occupied by electronic carriers. It is therefore convenient to measure a carrier's energy from the chemical potential, $E = \mu + \varepsilon$. In this situation the product of the factors that involve Fermi functions, $f(E)[1 - f(E)]$ of Eq. (14), may be approximated as a Gaussian function of ε that is peaked about $\varepsilon = 0$ with a width comparable to κT . The Seebeck coefficient then becomes

$$\alpha = \left(\frac{1}{qT} \right) \frac{\int d\varepsilon \rho(\mu + \varepsilon) \exp[-(\varepsilon/2\kappa T)^2] v^2(\mu + \varepsilon) \tau \varepsilon}{\int d\varepsilon \rho(\mu + \varepsilon) \exp[-(\varepsilon/2\kappa T)^2] v^2(\mu + \varepsilon) \tau} \quad (21)$$

Since the principal contributions to both integrals of Eq. (21) occur for $\varepsilon < \kappa T$, α must be small, $< \kappa/|e|$. Moreover, contributions to the numerator's integral from positive and negative values of ε tend to offset one another. As a result, evaluation of Eq. (21) shows that the magnitude of the Seebeck coefficient for a conventional metal (a) vanishes at absolute zero, (b) rises in proportion to the temperature, and (c) is very small:

$$\begin{aligned} |\alpha| &\approx \left(\frac{1}{|e|T} \right) \frac{\partial \ln[\rho(E)v^2(E)]}{\partial E} \Big|_{\mu} (\kappa T)^2 \\ &\approx \left(\frac{\kappa}{|e|} \right) \left(\frac{\kappa T}{\mu} \right) \end{aligned} \quad (22)$$

For a metal the chemical potential μ is typically at least 1 eV. By contrast, κT at room temperature (300 K) is about 0.025 eV. Thus, the magnitude of the Seebeck coefficient at room temperature is just a few microvolts per kelvin.

Seebeck Coefficients and Carrier Densities. It is instructive to treat the Seebeck coefficient of carriers in a single band in the (narrow-band) limit in which all N states of an energy band have the same energy E . In this limit the relation between the number of carriers, n , and the chemical potential μ is especially simple:

$$n = \frac{N}{e^{(E-\mu)/\kappa T} + 1} \quad (23)$$

Using Eq. (23), the expression for the single-band Seebeck coefficient, Eq. (16), may be rewritten as

$$\alpha = -\frac{\kappa}{|e|} \ln\left(\frac{1-c}{c}\right) \quad (24)$$

where $c \equiv n/N$ and the carriers are electrons, $q = -|e|$. In this limit, the relationship of the Seebeck coefficient to the carrier concentration becomes explicit. In particular, the Seebeck coefficient is large and negative when the number of electrons is much less than the number of available states ($c \ll 1$).

By contrast, when electrons occupy most states ($c \approx 1$), the vacant states are often regarded as the carriers. The Seebeck coefficient is large and positive when the number of these *holes* is much less than the number of available states ($c_h \equiv 1 - c \ll 1$):

$$\alpha = \frac{\kappa}{|e|} \ln\left(\frac{1-c_h}{c_h}\right) \quad (25)$$

The Seebeck coefficient changes sign when $c = c_h = \frac{1}{2}$.

Additional insight into the physical significance of the Seebeck coefficient can be obtained by considering the entropy of mixing associated with distributing n noninteracting carriers among N isoenergetic electronic states:

$$S_m = -N\kappa[c \ln c + (1-c) \ln(1-c)] \quad (26)$$

where again $c \equiv n/N$. Adding one more carrier changes the entropy of mixing by

$$\Delta S_m = \kappa \ln\left(\frac{1-c}{c}\right) \quad (27)$$

Thus, the Seebeck coefficient of Eq. (24) is just the change of the entropy of mixing due to the addition of an electron divided by the electron's charge, $q = -|e|$.

The Seebeck coefficient of conventional insulators and metals can be understood in terms of the effect that an additional carrier has on the carriers' entropy of mixing. The Seebeck coefficient of insulators is large because the carrier concentration is small. Thus, the addition of another carrier produces a fractionally large effect on the carrier concentration. In particular, the addition of the charge carrier greatly alters the entropy of mixing of an insulator's carriers. By contrast, the carrier density of a metal is relatively high. Therefore, the addition of a charge carrier has only a small effect on the entropy of mixing of a metal's carriers.

So far, this discussion of the relationship between the Seebeck coefficient and carrier densities has only considered the limit in which the relevant energy band is very narrow, $\ll \kappa T$. Nonetheless, the Seebeck coefficient of a wide-band insulator can also be expressed in terms of its carrier density. In these insulators, the densities of holes in the valence band and electrons in the conduction band are

$$n_v = N_v(T) \exp\left(-\frac{\mu - E_v}{\kappa T}\right) \quad (28)$$

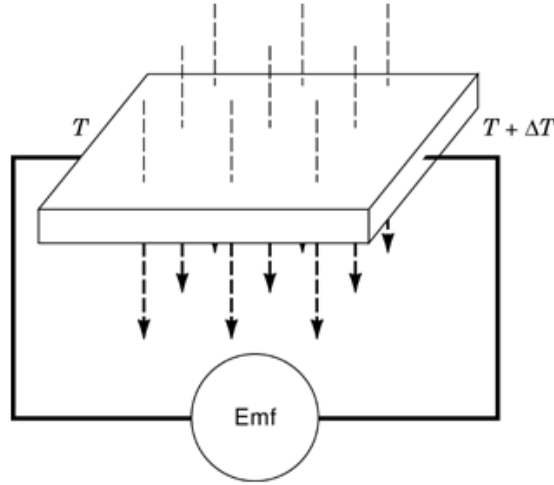


Fig. 6. The photo-Seebeck effect measures the Seebeck coefficient of a semiconductor while it is being illuminated.

and

$$n_c = N_c(T) \exp\left(-\frac{E_c - \mu}{\kappa T}\right) \quad (29)$$

where $N_v(T)$ and $N_c(T)$ are the densities of thermally accessible states at the top of the valence and bottom of the conduction band, respectively. Inserting these expressions into that for an insulator's Seebeck coefficient, Eq. (18), yields

$$\alpha = \frac{\kappa}{|e|} \left\{ \left[\ln\left(\frac{N_v(T)}{n_v}\right) + A_v \right] \left(\frac{\sigma_v}{\sigma_v + \sigma_c}\right) - \left[\ln\left(\frac{N_c(T)}{n_c}\right) + A_c \right] \left(\frac{\sigma_c}{\sigma_v + \sigma_c}\right) \right\} \quad (30)$$

Equation (30) indicates that the magnitudes of the valence-band and conduction-band contributions to the Seebeck coefficient each depend on the respective ratio of the density of thermally available states to the appropriate carrier density. Although electron and hole contributions tend to offset one another, the Seebeck coefficient is frequently dominated by the contribution from the carriers with the highest partial conductivity, σ_v or σ_c . In particular, if $\sigma_v \gg \sigma_c$, the Seebeck coefficient approaches that for holes in the valence band. Similarly, if $\sigma_v \ll \sigma_c$, the Seebeck coefficient becomes that for electrons in the conduction band. In either case only one of the two contributions to the expression in the large braces of Eq. (30) is of consequence.

Photo-Seebeck Effect. The photo-Seebeck effect is a variant of the Seebeck effect that can be used to probe the carrier density. In such an experiment, illustrated in Fig. 6, the Seebeck coefficient is measured as the material undergoes steady-state illumination. Photoexcitation increases the densities of electrons in the conduction band and holes in the valence band by Δn_c and Δn_v , respectively. Nonetheless, transport is often dominated by transport in just one band. If, for example, conduction-band transport dominates, the

photoinduced alteration of the Seebeck coefficient, $\Delta\alpha$, then becomes

$$\Delta\alpha = \frac{\kappa}{|e|} \ln\left(1 + \frac{\Delta n_c}{n_c}\right) \quad (31)$$

Thus, a photo-Seebeck experiment measures the photoinduced fractional change of the density of conduction-band electrons, $\Delta n_c/n_c$. This experiment complements a determination of $\Delta\sigma_c/\sigma_c$ from a photo-conductivity measurement.

Effects of Interactions on Itinerant Carrier's Seebeck Coefficients

Carriers' interactions with their surroundings and with one another will generally affect the Seebeck coefficient. These effects occur because such interactions usually modify the entropy change associated with adding a carrier to a solid. Furthermore, the transfer of energy and momentum from the carrier to its surroundings can induce a carrier-related heat (and therefore entropy) flow that contributes to the Seebeck coefficient.

Electron-Phonon Interaction: Temperature-Dependent Electronic Energies. The energy of an electron changes as the atoms surrounding it alter their positions. This effect is termed the *electron-phonon interaction*.

As a result of the electron-phonon interaction, atomic vibrations alter the energies of itinerant carriers in semiconductors and insulators. In particular, the electronic energy bands occupied by itinerant carriers are broadened by the electron-phonon interaction. Energy levels in the upper portion of an energy band rise, while energy levels in the lower portion fall. This broadening increases as atoms' vibrations become more violent. In particular, each electronic level shifts in proportion to the net phonon energy. Electronic levels shift by between 10^{-4} eV/K and 10^{-3} eV/K when the temperature is high enough for atoms' vibrations to be described with classical physics. These values typify the thermally induced shrinking of bandgaps observed in common semiconductors and insulators. In some materials, however, effects of thermal expansion mask this effect.

This coupling between itinerant carriers and the phonons is strong enough to significantly affect the Seebeck coefficient. In particular, semiconductors' band-edge energies typically shift by more than the thermal energy κT in the high-temperature regime where vibrations are classical. However, since energy shifts result from a carrier's coupling to atomic vibrations, calculating the Seebeck coefficient requires considering the phonons and a carrier's coupling to them (3).

Ignoring interactions between carriers and taking the Seebeck coefficient to be just the change of the solid's entropy upon addition of a charge carrier, we have

$$\alpha = \frac{1}{qT} \left(\left[\langle \varepsilon + E_p \rangle_1 - \langle E_p \rangle_0 \right] - \mu \right)_{\sigma(E)} \quad (32)$$

where the chemical potential μ is the change of the system's free energy that accompanies the addition of a charge carrier. The square-bracketed expression in Eq. (32) is the change of the internal energy induced by the addition of a charge carrier. In particular, $\langle \varepsilon + E_p \rangle_1$ denotes the thermal average over atomic vibrations of the carrier's energy ε plus the net phonon energy E_p , when one carrier is present. By contrast, $\langle E_p \rangle_0$ designates the thermal average of the phonon energy in the absence of any carriers. Equation (32) reverts to Eq. (16) in the absence of the electron-lattice interaction, since then $\langle E_p \rangle_1 = \langle E_p \rangle_0$ and $\langle \varepsilon \rangle_1 = E$.

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The net phonon energy is

$$E_p = \sum_{q=1}^N \hbar\omega_q(N_q + 1/2) \quad (33)$$

where ω_q and N_q denote the frequency and the excitation level of the q th of the N phonon modes, respectively. A carrier's interactions with phonons shifts its energy from E to

$$\varepsilon = E - \frac{1}{\kappa N} \sum_{q=1}^N \gamma_q(E) [\hbar\omega_q(N_q + 1/2)] \quad (34)$$

where $\gamma_q(E)$ characterizes the shift associated with the q th phonon mode.

Examination of Eq. (33) and Eq. (34) indicates that the addition of a charge carrier, adding ε to E_p , shift each phonon frequency by an infinitesimal amount ($\propto 1/N$ as $N \rightarrow \infty$) from ω_q to $\Omega_q \equiv \omega_q[1 - \gamma_q(E)/\kappa N]$. The averages in Eq. (32) are therefore seen to yield

$$\alpha = \frac{1}{qT} \left\langle E + \sum_{q=1}^N \left[\left(\frac{\hbar\Omega_q}{2} + \frac{\hbar\Omega_q}{e^{\hbar\Omega_q/\kappa T} - 1} \right) - \left(\frac{\hbar\omega_q}{2} + \frac{\hbar\omega_q}{e^{\hbar\omega_q/\kappa T} - 1} \right) \right] - \mu \right\rangle_{\sigma(E)} \quad (35)$$

Attention is now focused on the high-temperature regime where electronic levels shift most strongly with temperature:

$$\langle \varepsilon \rangle = E - T \left[\frac{1}{N} \sum_{q=1}^N \gamma_q(E) \right] \quad (36)$$

In this limit the Seebeck coefficient, Eq. (35), reverts to the form it has when the electron-phonon interaction is ignored, Eq. (16):

$$\alpha = \frac{1}{qT} \langle E - \mu \rangle_{\sigma(E)} \quad (37)$$

In particular, the electron-phonon interaction produces shifts of the electronic energy and vibrational energy that compensate one another. Thus, thermally induced shifts of the electronic levels that are observed with photospectroscopy do not affect the Seebeck coefficient.

Electron-Phonon Interaction: Phonon Drag. Scattering impedes the motion of itinerant carriers. In the case of carrier scattering by phonons (through the electron-phonon interaction), carriers' momentum is transferred to vibrating atoms. Most often this atomic momentum is then dissipated very rapidly. Thus, it is usually appropriate to assume that the energy flow associated with carriers' motion stops when the carrier is scattered.

Significant exceptions can occur at low temperatures in very pure semiconductors and metals. Dissipation of sound waves' momentum can then take an exceptionally long time (>1 ns). In these instances carrier-induced energy transport by sound waves (long-wavelength acoustic phonons) provides the dominant contribution to the Seebeck coefficient. This phenomenon is known as *phonon drag* (4). Phonon-drag contributions to the Seebeck coefficients of high-quality silicon, germanium, and diamond crystals with dopant density less than 10^{17} cm $^{-3}$ are about 4000 μ V/K at 50 K. Phonon-drag contributions to the Seebeck coefficients of metals are very much smaller.

A sound wave's momentum can be dissipated through its interaction with the atoms of the solid and through its interaction with electronic charge carriers. The net phonon-drag contribution to the Seebeck coefficient, α_d , is a combination of the phonon-drag contributions that result when one or the other of these dissipation mechanisms predominate. In particular,

$$\alpha_d = \frac{\alpha_a \alpha_c}{\alpha_a + \alpha_c} \quad (38)$$

where α_a and α_c represent the phonon-drag contribution in limiting cases in which sound waves' momenta are dissipated only through interactions with atoms and only through interactions with the charge carriers, respectively. When sound waves' interactions with carriers fail to limit the phonon-drag contribution ($\alpha_a \ll \alpha_c$), phonon drag is determined by atomic-dissipation processes: $\alpha_d \approx \alpha_a$. When sound waves' interactions with atoms are ineffective in limiting the phonon-drag contribution ($\alpha_a \gg \alpha_c$), carrier-related dissipation processes dominate: $\alpha_d \approx \alpha_c$.

The limit $\alpha_d = \alpha_a$ is addressed first. Carriers of charge q and density n garner momentum from an applied electric field E at the rate per unit volume of nqE . Presuming that a fraction f of carrier scattering occurs with sound waves, the momentum per unit volume carried by these sound waves is

$$P = nqEf\tau_s \quad (39)$$

where τ_s is the relaxation time for the dissipation of sound waves' momentum through their interactions with atoms. Specifically, sound waves disperse their momentum to the solid as a whole through interactions with high-energy phonons, point defects, and the sample's boundaries.

The heat current per unit cross-sectional area carried by the sound waves is Ps^2 , where s is the sound velocity. The ratio of the heat-current density to the particle-current density is the phonon-drag contribution to the Peltier heat:

$$\Pi_a = \left(\frac{qs^2\tau_s}{\mu_c} \right) f \quad (40)$$

where the particle-current density has been written in terms of the carrier mobility μ_c as $n\mu_c E$. The corresponding phonon-drag contribution to the Seebeck coefficient is

$$\alpha_a = \frac{\Pi_a}{qT} = \left(\frac{s^2\tau_s}{\mu_c T} \right) f = \frac{\kappa}{q} \left(\frac{s^2\tau_s}{D_c} \right) f \quad (41)$$

where the carrier mobility has been expressed in terms of carrier diffusion constant via the Einstein relation $\mu_c = qD_c/\kappa T$.

The complementary limit, $\alpha_d = \alpha_c$, is that in which sound waves and carriers only transfer momentum among themselves. In this limit carriers and sound waves move together with a common drift velocity v_D . The

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phonon-drag contribution to the Peltier heat is then

$$\Pi_c = \frac{N(T)\kappa T}{n} \quad (42)$$

where $N(T)$ is the density of long-wave phonons that interact strongly with the charge carriers. The phonon-drag contribution to the Seebeck coefficient is thus

$$\alpha_c = \frac{\kappa}{q} \left(\frac{N(T)}{n} \right) \quad (43)$$

Since phonons and carriers interact most strongly when they have comparable wavelengths, the density of phonon states with which carriers interact essentially equals the density of thermally accessible carrier states. These densities are those that appear in Eqs. (28) and (29): $N_v(T)$ and $N_c(T)$ for holes and electrons, respectively. These densities are proportional to $T^{3/2}$.

The transition from phonon drag associated with sound-wave dissipation through interaction with atoms to that through interaction with carriers occurs when $\alpha_a = \alpha_c$. As the temperature is lowered toward absolute zero, α_c falls below α_a . The phonon-drag contribution to the Seebeck coefficient, α_d , then approaches α_c as α_c tends toward zero in proportion to $T^{3/2}$. In contrast, if the temperature is raised high enough, α_a drops below α_c . The phonon-drag contribution to the Seebeck coefficient then approaches α_a and falls with rising temperature in proportion to τ_s . As a result, the phonon-drag contribution to the Seebeck coefficient is a peaked function of temperature.

All told, a significant phonon-drag contribution to the Seebeck coefficient requires carriers' momentum to be efficiently transmitted to sound waves that in turn dissipate this momentum very slowly. Thus, phonon drag tends to occur at low temperatures in high-quality material. Phonon drag introduces a low-temperature peak in a plot of the Seebeck coefficient against temperature.

Seebeck Coefficient for Phonon-Assisted Electronic Hopping

Electronic Localization, Carrier-Induced Atomic Displacements, and Phonon-Assisted Hopping. Even the best of crystals always contains some defects and impurities. For example, *vacancies*—missing atoms in an otherwise regular lattice—are common defects in ionic insulators such as alkali halides and oxides. In addition, all solids contain *impurities*—foreign atoms in low concentrations. Regions surrounding defects and impurities necessarily differ from regions that are free of them. Thus, electronic carriers may find it energetically preferable to remain close to defects and impurities. Defect and impurities that can bind electrons or holes are termed *traps*. Oxygen vacancies are examples of electron traps.

A trapped charge carrier generally induces displacements of the equilibrium positions of surrounding atoms. The forces that drive these atomic displacements are embodiments of electron–phonon interactions. In covalent materials strong short-range forces result when a static carrier disturbs the bonds that it contacts. In ionic materials even stronger long-range forces result from Coulomb interactions between the localized carrier and the ions that surround it.

As the atoms in the vicinity of a localized charge vibrate, they alter the potential well experienced by the electronic carrier. Since the electronic charge is much lighter and more agile than the relatively sluggish heavy vibrating atoms, it will readily adjust to such atomic vibrations. This electronic adjustment lowers the net energy associated with producing atomic deformations. A localized carrier thereby reduces the stiffness

constants that govern these atoms' vibrations. This carrier-induced softening lowers the frequencies of the vibrations.

Carrier-induced displacements of atoms' equilibrium positions and softening of their vibrations are both confined to a localized carrier's vicinity. Both effects tend to increase as the spatial extent of the localized carrier shrinks. However, as a carrier's spatial extent falls below an interatomic separation, carrier-induced displacements saturate and carrier-induced softening diminishes. In particular, as a localized carrier shrinks to a point, the forces between it and surrounding atoms approach limiting values. Furthermore, as a carrier shrinks to a point, it loses the property that drives carrier-induced softening, the ability to deform in response to atoms' displacements.

The forces between itinerant carriers and atoms are comparable to those between localized carriers and atoms. Although these forces are strong enough to induce significant atomic displacements, itinerant carriers often move so fast that surrounding atoms have insufficient time to adjust to their presence. Even then, effects that slow an itinerant carrier, such as the imposition of disorder, can trigger its collapse. The carrier then localizes and moves in concert with the pattern of atomic displacements that surround it.

The composite quasiparticle comprising the carrier and the pattern of atomic displacements that surround it is termed a *polaron* (5). A polaron bound to a defect or impurity is termed a *bound polaron*. Since a polaron's electronic carrier is confined by a pattern of displaced atoms, the carrier cannot move unless atoms move. A polaron cannot move faster than the appropriate sound velocity.

Polarons and even simple electronic carriers move by a succession of tunneling events. Each step is governed by a transfer energy that links two sites. The transfer energy (also called the resonance energy) results from overlap between the wave functions of initial and final states of the tunneling event. If the transfer energy is greater than the change of a carrier's energy as it moves between sites, *coherence* is maintained between successive transfers. Itinerant motion is coherent.

Conversely, a carrier loses its coherence if the change of its energy as it moves between sites exceeds its transfer energy. Disorder destroys electronic coherence when the difference between the electronic energies at initial and final sites exceeds the electronic transfer energy. Even a polaron moving between degenerate sites loses coherence if atomic motion associated with the transfer alters a carrier's energy by more than the transfer energy associated with its tunneling. Severely localized polarons, *small polarons*, typically move incoherently.

With loss of coherence successive transfers become independent of one another. Each transfer is then termed a *hop*. A carrier moves between sites in response to the motions of surrounding atoms. Such transport is termed *phonon-assisted hopping*.

The processes that govern a small polaron's phonon-assisted hopping are illustrated in Fig. 7. The left and right portions of this figure's bottom panel depict a carrier bound within a potential well produced by atomic displacements. The atomic displacements are shown beneath the potential well that they produce. The charge carrier, depicted by a black dot, occupies the potential well with the lowest-energy electronic state. Depending on the atomic displacements, the carrier can occupy either of two adjacent sites.

For a small polaron to move between these sites, the atoms must move in such a manner that the potential well confining the carrier shifts between the two locations (5). In the figure's depiction, the carrier moves between sites as the two atoms at the initially occupied site move closer together and the two atoms at the unoccupied site move further apart. This change of atomic configuration can occur by alternative routes.

The bottom panel of the figure depicts a low-energy charge-transfer process. In particular, the horizontal dashed double arrow indicates atoms' direct movement between initial and final configurations by quantum-mechanical tunneling. The electron tunnels between the two wells in concert with this atomic tunneling motion. Since atomic tunneling is difficult, such charge transfer is very slow.

The figure's middle panel depicts a higher-energy charge-transfer process. Increasing atoms' vibrational energy enables them to assume configurations that foster the atomic tunneling associated with charge transfer. In this excited vibrational state, the distance atoms must tunnel is reduced. A thickened dashed horizontal

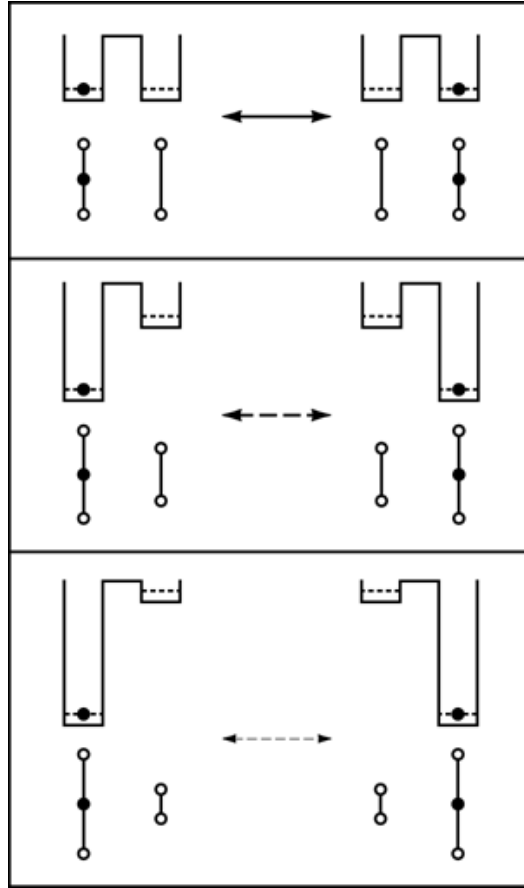


Fig. 7. Phonon-assisted hopping between adjacent sites is illustrated. The solid dots represent charge carriers, and the open circles atoms. The bottom, middle, and top panels indicate transfer processes that dominate at low, intermediate, and high temperatures, respectively. These processes are described in the text.

double arrow indicates enhanced atomic tunneling. Thus, increasing atoms' vibrational energy increases the charge-transfer rate.

The figure's top panel depicts a still higher-energy charge-transfer process. If atoms' vibrational energy is sufficiently large, they can assume configurations in which charge transfer does not require atomic tunneling. The atoms then produce a double-well electronic potential in which the energies that a carrier would have in either well (dashed line) are equal. The solid horizontal double arrow indicates that the ensuing charge transfer occurs without atomic tunneling. Thus, sufficient increase in atoms' vibrational energy enables a carrier to move between sites without being slowed by atomic tunneling.

Figure 8 plots the rate for a small-polaron's phonon-assisted hopping against Θ/T , where $\Theta \equiv h\nu/\kappa$ is the temperature corresponding to the characteristic phonon frequency ν . At low temperatures hops that require atomic tunneling predominate. The corresponding rate rises with increasing temperature in a non-Arrhenius manner (6). At higher temperatures hops that occur without atomic tunneling dominate (7). The phonon-assisted hopping rate then assumes an Arrhenius form (see Ref. 5):

$$R = \left(\nu e^{-\varepsilon_a/\kappa T} \right) P \quad (44)$$

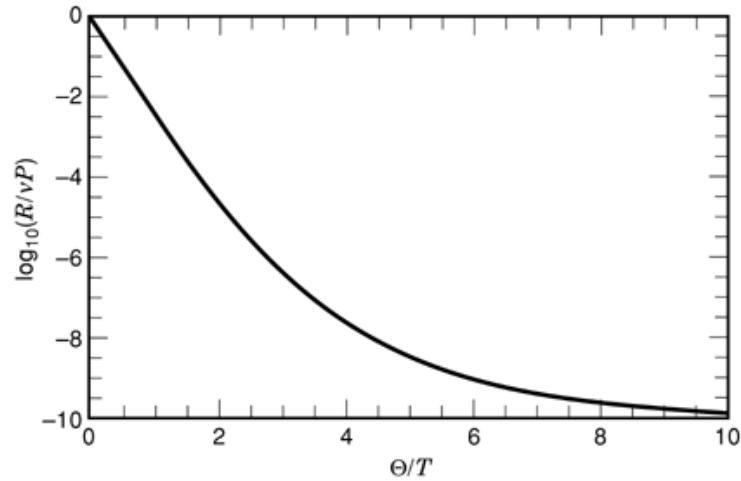


Fig. 8. A typical phonon-assisted hopping rate is plotted against Θ/T , where $\Theta \equiv h\nu/\kappa$ is the temperature corresponding to the phonon frequency ν .

The hopping activation energy ε_a is the minimum atomic displacement energy required to bring the electronic energy levels of a carrier's hop into coincidence with one another. P denotes the probability that a carrier will move between sites when a coincidence is established. This probability depends on the electronic transfer energy associated with moving between the double well's two sites. This transfer energy is often large enough for the carrier to readily adjust to atoms' motion and occupy the state with the lowest electronic energy. Then $P \approx 1$, and the hop is termed *adiabatic*.

Jumps between electronic states with radii comparable to interatomic separations manifest small-polaron hopping. The temperature dependence of the electrical conductivity resembles that of the elemental jump rate shown in Fig. 8. At high enough temperatures the carrier mobility is thermally activated with an activation energy that exceeds a substantial fraction of the characteristic phonon energy. This activated behavior reverts to non-Arrhenius behavior when the thermal energy κT falls below a fraction of this representative phonon energy.

This prototypical behavior is commonly observed for electronic hopping transport in crystals and glasses. For example, small-polaron hopping has been established for hopping between the S_8 molecules of the molecular crystal orthorhombic sulfur. Such hopping is also observed for hopping between Mn sites of the transition-metal oxide MnO. Electronic hopping is also observed in most amorphous semiconductors. These noncrystalline solids include amorphous silicon, germanium, and arsenic as well as transition-metal oxide glasses and chalcogenide glasses (e.g., As_2Te_3).

Seebeck Coefficient for Hopping. Hopping carriers' Seebeck coefficient can be treated as the sum of two contributions: $\alpha = \alpha_p + \alpha_v$ (see Refs. 8,9). The first contribution is the entropy change associated with adding a carrier to a collection of localized states, divided by the carrier's charge q . The second contribution is the vibrational energy transferred with a carrier as it executes phonon-assisted hops between localized states, divided by qT .

The entropy change resulting from the addition of a charge carrier to an assembly of localized states often may be regarded as having two components: $\Delta S_p = \Delta S_m + \Delta S_i$. The first component is the change of the entropy of mixing that results from adding a carrier, ΔS_m . The second component arises from the added carrier's interactions with its surroundings, ΔS_i .

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The change of the entropy of mixing associated with the addition of a carrier depends on which localized states carriers occupy. The mutual Coulomb repulsion between localized carriers is frequently strong enough to preclude carriers' double occupancy of a localized state. By contrast, the energy lowering associated with carrier-induced changes of atoms' motion may sometimes drive carriers to pair on a common localized state. Such bound pairs are called *bipolarons*.

To address carriers' entropy of mixing, first consider n carriers distributed among N_s equivalent sites. If these carriers' mutual repulsion constrains the carriers to only occupy sites singly, the entropy-of-mixing contribution to the Seebeck coefficient is (see Ref. 10)

$$\alpha_m = \frac{\Delta S_m}{q} = \frac{\kappa}{q} \ln \left(\frac{1 - c_1}{c_1} \right) + \frac{\kappa}{q} \ln 2 \quad (45)$$

for $c \equiv n/N_s \leq 1$. Here the concentration of singly occupied sites, defined as c_1 , equals c and the concentration of vacant sites is $1 - c_1$. The second contribution in Eq. (45) manifests an added carrier's two-fold spin degeneracy. This degeneracy factor causes the entropy-of-mixing contribution to the Seebeck coefficient to change sign at $c_1 = 2/3$.

When a net attractive interaction between carriers forces them to pair on c_2 doubly occupied sites, the entropy-of-mixing contribution becomes (see Ref. 10)

$$\alpha_m = \frac{\kappa}{2q} \ln \left(\frac{1 - c_2}{c_2} \right) \quad (46)$$

Equation (46) indicates that paired carriers behave like spinless particles having a charge of $2q$. Since the attraction that fosters carriers' pairing is finite, an increasing fraction of pairs will break apart as the temperature is raised. Pair breaking is increasingly supported by entropy considerations as the carrier concentration approaches its limiting values, $c_2 \ll 1$ or $c_2 \approx 1$.

The Seebeck coefficient described by Eqs. (45) and (46) remains finite as the temperature approaches absolute zero. However, thermodynamic arguments imply that Seebeck coefficients will vanish at absolute zero. This disparity occurs because thermodynamic arguments assume a nondegenerate ground state while the model that produces Eqs. (45) and (46) considers N -fold degenerate states. In actuality the degeneracy will be lifted due to overlap between localized states, disorder, and interactions between carriers. Nonetheless, the Seebeck formulae (45) and (46) become valid when the thermal energy κT exceeds the spread of localized-state energies associated with lifting their degeneracy.

Seebeck Effect with Carrier-Induced Softening of Atomic Vibrations. Adding a charge carrier to a localized state generally alters the entropy of its environment. In particular, a localized carrier reduces the stiffness constants that govern the vibrations of the surrounding atoms with which it interacts. The concomitant reduction of phonon frequencies $\Delta\omega_j$ produces an interaction-related contribution to the Seebeck coefficient (11). For $|\Delta\omega_j/\omega| \ll 1$,

$$\alpha_i(T) = \frac{\Delta S_i}{q} = \frac{\kappa}{q} \sum_j \left(\frac{-\Delta\omega_j}{\omega_j} \right) F_i(T/\Theta_j) \quad (47)$$

where the phonon temperature is defined by $\Theta_j \equiv \omega_j/\kappa$ and

$$F_i(T/\Theta_j) \equiv \left(\frac{\Theta_j/2T}{\sinh(\Theta_j/2T)} \right)^2 \quad (48)$$

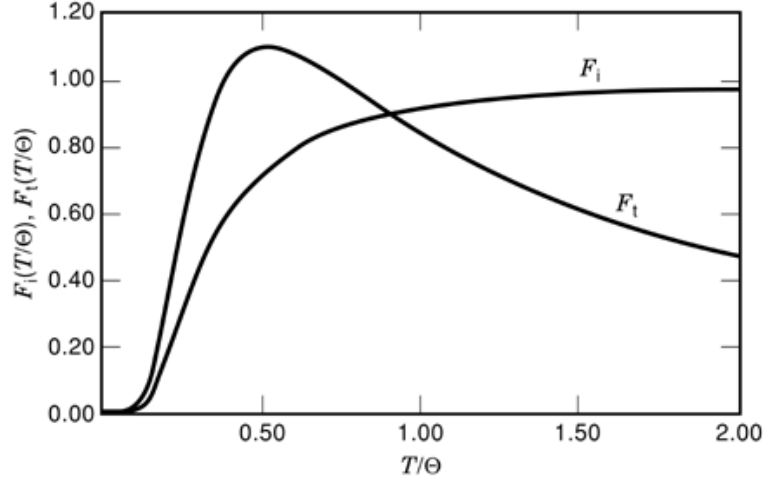


Fig. 9. $F_i(T/\Theta)$ and $F_t(T/\Theta)$ are plotted against T/Θ .

As depicted in Fig. 9, $F_i(T/\Theta)$ rises monotonically from zero to unity with increasing temperature.

Carrier-induced softening also facilitates the transport of vibrational energy with a carrier as it hops (11). The mechanism for this energy transport is illustrated in Fig. 10. Namely, as a result of carrier-induced softening, the atomic displacements required for a phonon-assisted hop tend to occur at occupied sites. Thus, the energy required for a phonon-assisted hop is preferentially absorbed at the site the carrier initially occupies. Furthermore, the energy that is dissipated following a hop is preferentially emitted at the hop's final site. Therefore, carrier-induced softening results in a fraction of the hopping activation energy being transported with a carrier. Within the model of polaron hopping that yields the curve of Fig. 7, the contribution to the Seebeck coefficient from the transport of vibrational energy with a carrier is

$$\alpha_t \equiv \frac{E_t}{qT} = \frac{\kappa}{q} \sum_j \left(\frac{-\Delta\omega_j}{\omega_j} \right) \left(\frac{\varepsilon_a}{\kappa\Theta_j} \right) F_t(T/\Theta_j) \quad (49)$$

where ε_a is the activation energy in the high-temperature regime in which the hopping rate is Arrhenius, $|\Delta\omega_j/\omega| \ll 1$, and

$$F_t(T/\Theta_j) \equiv \frac{(\Theta_j/2T)^2}{\sinh(\Theta_j/2T)} \quad (50)$$

It is evident from Fig. 9 that $F_t(T/\Theta)$ is a peaked function of temperature that vanishes at $T=0$ and as $T \rightarrow \infty$.

All told, carrier-induced softening of atomic vibrations generates two contributions to the Seebeck coefficient. The two contributions result from (1) carrier-induced increase of atoms' vibrational entropy and (2) vibrational energy transport that accompanies a carrier's hop. These two effects can be distinguished from one another, since they manifest different temperature dependences. Furthermore, contributions to the See-

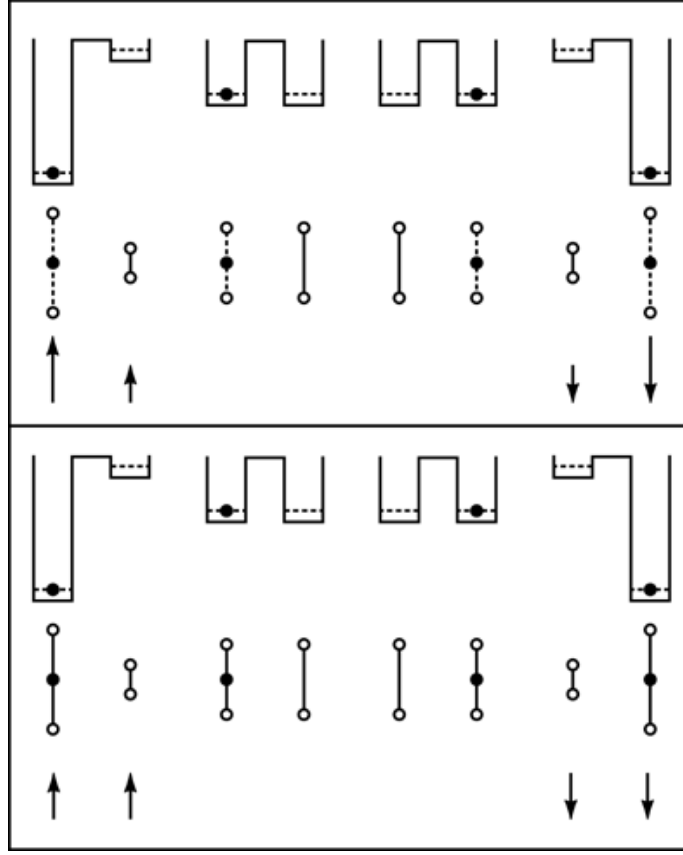


Fig. 10. The effect of carrier-induced softening is illustrated for a semiclassical hop. The lower panel schematically depicts the electronic potential wells, the atomic displacements, and the absorption and emission of vibrational energy (solid vertical arrows) in the four stages of a hop. The upper panel shows how carrier-induced softening (depicted with dashed lines) alters the hopping process. Carrier-induced softening leads to vibrational energy being transferred with the carrier.

beck coefficient from carrier-induced softening can be distinguished from entropy-of-mixing contributions. The former are independent of the carrier density.

Disorder-Induced Transport of Vibrational Energy. Phonon-assisted hopping frequently occurs between localized electronic states in disordered materials. Hops are then between states that generally differ in both energy and spatial extent. As shown in Ref. 9, the Seebeck coefficient associated with a hop from the i th site to the j th site is

$$\alpha_{i,j} = \frac{1}{qT} \left(\frac{E_i + E_j}{2} - \mu + E_t^{i,j} \right) \quad (51)$$

where E_i and E_j are the net energies associated with a carrier occupying the i th and j th sites, respectively, and $E_t^{i,j}$ is the vibrational energy transferred in the hop. Ignoring carrier-induced softening, the energy transported

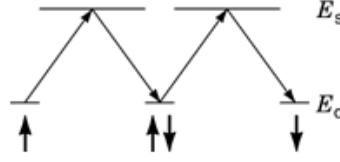


Fig. 11. Schematic illustration of the transport of vibrational energy as a carrier sequentially hops between small deep states of energy E_d and large shallow states of energy E_s . Upward- and downward-pointing bold arrows represent absorption and emission of vibrational energy, respectively.

with a carrier becomes

$$E_t^{i,j} = \frac{E_j - E_i}{2} \frac{\Gamma_i - \Gamma_j}{\Gamma_i + \Gamma_j} \quad (52)$$

where Γ_i and Γ_j measure the electron–phonon coupling associated with a carrier occupying the i th and j th sites, respectively. This transported energy evidently results from disorder. That is, $E_t^{i,j}$ vanishes when the hop is between equivalent sites ($E_i = E_j$ and $\Gamma_i = \Gamma_j$). Furthermore, it will become evident that $E_t^{i,j}$ does not generally average to zero with disorder, since the coupling constants Γ_i and Γ_j depend on the energies E_i and E_j .

The net electron–phonon coupling at a site depends upon the size of the localized electronic state. Severely localized states (e.g., deep defect and impurity states in semiconductors) generally have strong electron–phonon couplings. By contrast, the electron–phonon coupling is weak at mildly localized states (e.g., semiconductors’ shallow-impurity states). Simple models give the electron–phonon coupling at a localized state varying inversely with the state’s volume. Then $\Gamma_i/\Gamma_j = (R_j/R_i)^3$, where R_i and R_j are the characteristic radii of the i th and j th states, respectively.

The size of a localized state is also generally related to its energy. Localized states that are near an energy band tend to be larger than those whose energies are deep within a semiconductor’s intrinsic energy gap. Semiconductors’ deep states are small, while their shallow states are large.

Since the electron–phonon coupling strength of a state depends on its energy, vibrational energy will be transported with a carrier as it executes phonon-assisted hops. This feature is illustrated with an example in which a carrier hops alternately between small deep states of energy E_d and large shallow states of energy E_s . As illustrated in Fig. 11, vibrational energy is preferentially absorbed at the site of the small deep state when a carrier hops from it to a large shallow state. In addition vibrational energy is preferentially emitted at the small deep state when a carrier hops to it from a large shallow state. Thus, the carrier will carry the energy $E_t = (E_s - E_d)/2$ when $\Gamma_d \gg \Gamma_s$.

Upon adding the average energy of an occupied site, $(E_s + E_d)/2$, to the transport energy, the Seebeck coefficient for this example of disorder hopping becomes $\alpha = (E_s - \mu)/qT$. Thus, the vibrational energy transported with the carrier causes the characteristic energy in the Seebeck coefficient to be the energy of the upper state rather than the average of the upper-state and lower-state energies.

Magnetic Interactions and Hopping Carriers’ Seebeck Coefficient. Normal charge carriers (single electrons that can move) are imbued with a magnetic moment. In other words, each electron has a *spin*. Quantum-mechanical considerations ensure that an electron spin can be aligned in one of two directions. Thus an electron’s spin is said to be either up or down. The entropy associated with charge carriers’ spin alignments contributes to their Seebeck coefficient. For example, carriers’ twofold spin degeneracy contributes $(\kappa/|e|) \ln 2 \approx 60 \mu\text{V/K}$ to the Seebeck coefficient described in Eq. (45).

Application of a magnetic field constrains carriers’ spin alignments. In particular, it is energetically preferable for a spin to align with the magnetic field rather than against it. A magnetic field thereby removes

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the equivalence of opposite alignments of carriers' spins. In this manner, application of a magnetic field reduces the spin-entropy contribution to the Seebeck coefficient. The magnetic field dependence of this contribution is given by

$$\alpha_s(b) = \frac{\kappa}{q} [\ln(2 \cosh b) - b \tanh b] \quad (53)$$

Here $b \equiv \mu_m B / \kappa T$ denotes the ratio of the magnitude of a spin's Zeeman energy $\mu_m B$ to the thermal energy κT , where μ_m denotes the carrier's magnetic moment and B denotes the magnetic field strength. As b increases, α_s falls monotonically from $(\kappa/q) \ln 2$ toward zero. This fall will only be appreciable when the magnetic fields are large enough and the temperatures low enough for b to approach unity. For example, b approaches unity when B is about 10 T and T is about 10 K. Then the magnetic field dependence of the Seebeck coefficient provides a useful means to measure the carrier's magnetic moment.

Magnetic insulators are materials in which some atomic sites contain unpaired spins. Strong exchange interactions among a site's electrons (*intrasite* exchange), foster their behaving as a unified entity with a net spin $S_0 \neq 0$. A site's electrons also have relatively weak exchange interactions with electrons of surrounding sites. These *intersite* exchange interactions foster ordering of the net spins of a site with the net spins of surrounding sites. When the thermal energy falls well below the intersite exchange energy ($\kappa T \ll J$), a magnetic phase transition occurs. The net spins of sites then align with respect to one another. Most magnetic insulators order as *antiferromagnets*. There are then as many sites whose spins are aligned in one direction as in the opposite direction. However, some magnetic insulators (e.g., EuO) order as *ferromagnets*. In this situation, the spins at all sites align in a common direction.

In some magnetic semiconductors (e.g., MnO and UO₂), carriers hop among sites containing unpaired spins. The Seebeck coefficient then depends on the change of the spin entropy that results from placing a charge carrier on a site. Adding a carrier to a site changes its spin from S_0 to S_c . If both composite spins were free to align without regard to their interactions with spins on surrounding sites, the carrier-induced change in spin entropy would contribute $(\kappa/q) \ln[(2S_c + 1)/(2S_0 + 1)]$ to the Seebeck coefficient; see Refs. 12 and 13. However, changing a site's composite spin does alter its intersite exchange interactions. As a result, placing a carrier on a magnetic site affects the alignments of composite spins on surrounding sites (13). These two phenomena produce competing effects on the Seebeck coefficient. Studies of simple models of the Seebeck coefficient of magnetic materials when the temperature T exceeds the magnetic ordering temperature T_0 yield

$$\alpha_s(0) = \frac{\kappa}{q} \left\{ \ln \left(\frac{2S_c + 1}{2S_0 + 1} \right) \mp A \left(\frac{T_0}{T} \right)^2 \right\} \quad (54)$$

where the minus sign applies when $S_c > S_0$, the plus sign applies when $S_c < S_0$, and A is a numerical constant comparable to unity.

Small-polaron hopping describes the transfer of electrons between the Fe ions in Fe₃O₄. This material, commonly called lodestone or magnetite, is perhaps the oldest magnetic material known to man. Carriers introduced by intentional doping have been shown to move by small-polaron hopping between the magnetic ions of UO₂, MnO, and LaMnO₃.

Seebeck-Measurement Test for Hopping Transport. Seebeck-coefficient measurements are frequently used in conjunction with conductivity measurements to determine if carriers move by phonon-assisted hopping. With hopping, the rise of the carrier mobility μ_c with increasing temperature contributes significantly to the temperature dependence of the electrical conductivity, $\sigma = nq\mu_c$. By contrast, Seebeck coefficients, apart from contributions from vibrational softening and disorder effects, do not manifest the temperature dependences of carriers' hopping motion. Thus, comparisons of the temperature dependences of a material's

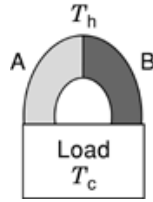


Fig. 12. A basic element of a thermoelectric generator is schematically represented. The hot junction between material A and material B is maintained at temperature T_h . The two legs of the thermocouple are connected to the circuit's load, which is at a lower temperature T_c .

conductivity and Seebeck coefficient can be used to determine if the carrier mobility shows the rapid rise with increasing temperature characteristic of small-polaron hopping.

A simple analysis is possible when the carrier density is thermally activated with the activation ε_n and the mobility is activated with the activation energy ε_a . The relevant equations for this analysis are then

$$\frac{\partial \ln \sigma}{\partial(1/\kappa T)} \approx -(\varepsilon_n + \varepsilon_a) \quad (55)$$

and

$$\frac{\partial \alpha}{\partial(1/\kappa T)} \approx -\varepsilon_n \quad (56)$$

Such analyses have been applied to demonstrate small-polaron hopping in transition-metal oxide glasses (e.g., glasses containing Fe and V), amorphous semiconductors (e.g., amorphous Si, Ge, and As), chalcogenide glasses (e.g., glasses based on As_2Te_3), and transition-metal oxides (e.g., *p*-type MnO and LaMnO_3). The activation energies of the mobility are thereby found to be about 1 eV for transition-metal oxide glasses. However, mobility activation energies between 0.1 eV and 0.3 eV are more common.

Efficiency of Thermoelectric Power Generation

The Seebeck effect is the basis of *thermoelectric power generation*. Electric power is thereby obtained from a heat source. The heat source is used to maintain a temperature difference between two portions of an electric circuit. The Seebeck effect is exploited to obtain an electric current from this temperature difference.

The heat source can be a nuclear reactor, a hot radioisotope, an engine's exhaust, a furnace, or a solar-energy collector. The idea of using the Seebeck effect to obtain electric power from the heat of a nuclear reactor was first advanced at the time of the Manhattan Project. Smaller-scale devices, termed *radioisotope thermoelectric generators (RTGs)*, simply use radioisotopes as heat sources. These devices are commonly employed in rockets and satellites to reliably obtain modest amounts of electric power. RTGs with long-lived radioisotopes have been used to provide electric power for spacecraft during extended missions to remote, inhospitable locations. Other thermoelectric devices utilize the heat of truck and automobile exhaust to satisfy the vehicle's ancillary electric power needs. Some of a furnace's heat can be used to generate electricity to power blowers that circulate hot air, thereby eliminating dependence on an external source of electric power. The Seebeck effect also provides a means to convert heat obtained in solar collectors into electricity. All told, thermoelectric energy conversion is widely used to marry a source of heat with a need for electric power.

The heart of a thermoelectric device is a thermoelectric couple. As illustrated in Fig. 12, the basic thermoelectric circuit is composed of two materials that are joined at a junction that is kept at an elevated temperature

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by a heat source. Current generated in the device flows through the two materials to the remainder of the circuit.

The couple's two materials are often chosen to maximize the efficiency of the conversion of heat to electricity. In addition, the device's two active materials and the junction between them must be able to survive and operate efficiently during prolonged exposure to high temperatures. When the heat is provided by a radioactive source, the thermoelectric materials also must be able to survive radiation-induced damage or be shielded from it. These concerns have motivated searches for materials for Seebeck devices among high-melting-point, radiation-tolerant solids.

The requirements for an efficient thermoelectric device can be ascertained by examining the operation of the single thermoelectric couple illustrated in Fig. 12. The efficiency of the couple is the power that is delivered to a load of resistance R_L divided by the heat flow Q that must be supplied to maintain the temperature gradient:

$$\eta \equiv \frac{I^2 R_L}{Q} \quad (57)$$

where I is the current flowing in the circuit. The current is just the Seebeck emf produced by the temperature difference ΔT divided by the total resistance of the circuit:

$$I = \frac{(\alpha_A - \alpha_B) \Delta T}{R_A + R_B + R_L} \quad (58)$$

where R_A and R_B are the resistances of the device's two legs.

It is usually adequate to approximate the Seebeck coefficient as being temperature-independent (14). Then, as shown by Eq. (12), the Thomson effect, defined by Eq. (8), can be ignored. In this case the heat flow that must be supplied to the hot junction to maintain its temperature is the sum of three terms:

$$Q = Q_T + Q_P - Q_J \quad (59)$$

The first term, Q_T , represents heat flow away from the hot junction through the thermoelectric materials:

$$Q_T \equiv (K_A + K_B) \Delta T \quad (60)$$

where K_A and K_B are the thermal conductances of the two legs. The second contribution is the Peltier heat current Q_P that is extracted from the hot-side electric junction, maintained at temperature T_h , as current passes through it:

$$Q_P \equiv T_h (\alpha_A - \alpha_B) I \quad (61)$$

The third contribution, Q_J , results because half of the Joule heating produced in the two legs, returns to the hot junction:

$$Q_J \equiv \frac{I^2 (R_A + R_B)}{2} \quad (62)$$

Combining these expressions, Eqs. (57) to (62), the efficiency is rewritten as

$$\eta = \frac{\Delta T}{T_h} \frac{1}{1 + \frac{1}{r} \left(\frac{\bar{T}}{T_h} \right) + \frac{(1+r)^2}{r T_h Z}} \quad (63)$$

where $\bar{T} \equiv (T_h + T_c)/2 = T_h - \Delta T/2$ is the average temperature of each leg of the couple. The six parameters that characterize the relevant electrical and thermal transport properties of the two materials have been combined in a single coefficient defined by

$$Z \equiv \frac{(\alpha_A - \alpha_B)^2}{(K_A + K_B)(R_A + R_B)} \quad (64)$$

The resistance of the load relative to the total resistance of the thermocouple is designated by

$$r \equiv \frac{R_L}{R_A + R_B} \quad (65)$$

It is evident from Eq. (63) that the efficiency is a peaked function of r . The maximum of the conversion efficiency occurs when r equals

$$r_m \equiv \sqrt{1 + Z\bar{T}} \quad (66)$$

The efficiency at this maximum can be written as

$$\eta_m \equiv \frac{\Delta T}{T_h} \left(\frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_c/T_h} \right) \quad (67)$$

The maximum efficiency is reduced from the Carnot efficiency, $\Delta T/T_h$, by the bracketed factor. The Carnot efficiency would only be regained were $Z\bar{T} \gg 1$. However, a more attainable regime is that in which $Z\bar{T} \ll 1$. Then

$$\eta_m \approx \frac{Z \Delta T}{4} \quad (68)$$

Schemes to maximize the value of Z usually begin by selecting materials with opposite-signed Seebeck coefficients in order to maximize $(\alpha_A - \alpha_B)^2$. Materials with low thermal conductivities are sought in order to minimize losses from thermal conduction along each of the thermocouple's legs. Difficult tradeoffs often occur because a material with a large Seebeck coefficient also usually has a high electrical resistivity.

It is, nonetheless, a simple matter to maximize the figure of merit given by Eq. (64) with respect to the relative cross-sectional area and thickness of a thermocouple's two legs. After performing this maximization

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the figure of merit becomes

$$Z_m \equiv \frac{(\alpha_A - \alpha_B)^2}{(\sqrt{\kappa_{TA}\rho_A} + \sqrt{\kappa_{TB}\rho_B})^2} \quad (69)$$

where κ_{TA} and ρ_A designate the thermal conductivity and electrical resistivity of material A, respectively. Similarly, κ_{TB} and ρ_B designate the thermal conductivity and electrical resistivity of material B, respectively.

It is common to focus attention on the properties of each of the couple's two materials. For this purpose a material's *thermoelectric figure of merit* has been defined as

$$z \equiv \frac{\alpha^2}{\kappa_T \rho} \quad (70)$$

where α is the material's Seebeck coefficient, κ_T is its thermal conductivity, and ρ is its electrical resistivity. The goal is to find robust materials that each have a large enough thermoelectric figure of merit for zT to approach and perhaps even exceed unity at the device's operating temperature.

Present-day thermoelectric devices use materials for which zT is comparable to unity. Bismuth telluride, antimony telluride, lead telluride, and silicon–germanium alloys are currently used in devices. However, many other materials are being studied with the hope that they will have higher zT values and will be the basis of improved devices. Extensive descriptions of these materials are contained among the 15 articles of Ref. 15 that address thermoelectric materials.

The difficulty in finding a material with an exceptionally large value of z is evident from Eq. (70). Namely, materials that have large Seebeck coefficients also tend to have high electrical resistivities, and materials with low electrical resistivities also tend to have high thermal conductivities. Thus, advantageous properties of a material tend to be offset by its disadvantageous properties. The goal is therefore to discover or create materials in which the usual compensatory relationships between the Seebeck coefficient, the electrical resistivity, and the thermal conductivity are relaxed.

Solids with unusual, albeit complex, structures sometimes possess unexpected combinations of transport coefficients. Clathrates are materials containing cagelike structures. For example, boron carbides are based on twelve-atom cagelike clusters, and skutterudites are based on even larger ones. These clathrates have exceptionally low thermal conductivities. Thus, they are being considered for use in thermoelectric devices. Indeed, boron carbides also have much larger Seebeck coefficients (about $300 \mu\text{V/K}$ at 300 K) than would be expected from their high carrier densities (16). However, their low carrier mobility keeps zT from rising above unity.

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