Electronic Transports for Thermoelectric Applications on IV–VI Semiconductors

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Seebeck effect, Peltier effect, Thomson effect, electronic thermal conductivity, Hall effect, and Nernst effect are described on the basis of electronic conduction theory, taking account of effective mass anisotropy, nonparabolicity in E–$\mathbf{k}$ relation, and temperature dependent band gap. It is shown that the temperature dependence of the band gap does not modify the basic equations for the Seebeck coefficient, thermal conductivity, and Nernst coefficient. In narrow gap semiconductors, existence of minority carriers significantly enhances the electronic thermal conductivity, owing to the multiple carrier transport known as bipolar diffusion. Calibration coefficient γ for the Hall effect ($R_\mathrm{H} = -\gamma/en$) is increased by nonparabolicity in the E–$\mathbf{k}$ relation. Nernst coefficient gives useful information on scattering properties of the materials.
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1. Introduction

Developments of materials with high thermoelectric conversion efficiencies are important for energy and environmental issues. Dimensionless figure of merit $ZT = S^2 \sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, and κ the thermal conductivity, is used as indicators of the conversion efficiency. Among the parameters, thermal conductivity is an important parameter because the reduction of thermal conductivity increases the ZT and also reduces the necessary amount of the material for device fabrication. Seebeck coefficient is another important factor because it has the effect of second power on the efficiency. Narrow gap IV–VI semiconductors such as PbTe, PbS have been studied as high efficiency thermoelectric materials, because they have small lattice thermal conductivity, and relatively high Seebeck coefficient and electrical conductivity.[1–3] The narrow gap materials have a large nonparabolicity in E–$\mathbf{k}$ relation due to the narrow direct gap, and some of them have large anisotropies in effective masses at L-point of the Brillouin zone. In this paper, we describe theoretical electronic transports under electric and magnetic fields and under temperature gradient on the basis of Boltzmann equation, and derive the equations for Seebeck coefficient, Peltier coefficient, Thomson coefficient, and electronic thermal conductivity considering the nonparabolicity and anisotropy in the E–$\mathbf{k}$ relation, and also considering temperature dependent band gap. In the previous paper, we discussed the effect of temperature dependent band gap on the Seebeck effect.[4] However, more detailed discussion in this paper will show that no modification is necessary in the Seebeck coefficient calculation as omitted in subsequent paper.[5]

In narrow gap semiconductors, electronic thermal conductivity increases strongly at high temperature owing to a bipolar carrier transport, called as bipolar diffusion, where minority carrier flow strongly enhances the electronic thermal conductivity.[6–8] The detail mechanism is discussed here. Hall effect and Nernst effect under magnetic field is also discussed for anisotropic semiconductors with nonparabolic E–$\mathbf{k}$ relation. It is shown that a large calibration is necessary to obtain exact carrier concentration from Hall measurement in the nonparabolic semiconductors, and Nernst effect is useful to determine the scattering mechanism of carriers.[9]

2. Seebeck Effect, Peltier Effect and Electronic Thermal Conductivity

First, we consider the electronic conduction in crystalline solid under static electric and magnetic field. Electron velocity is given by $\boldsymbol{v} = (1/\hbar)\nabla_\mathbf{k} E(\mathbf{k})$, where $E(\mathbf{k})$ represents electron energy, and equation of electron motion under static electric and magnetic field is given by $\hbar \dot{\mathbf{k}} = -e(\mathbf{E} + \boldsymbol{v} \times \mathbf{B})$. The deviation of electron distribution from thermal equilibrium $f - f_0$, where $f_0(\mathbf{k}, \mathbf{r}) = 1/[1 + \exp\{(E(\mathbf{k}, \mathbf{r}) - E_\mathrm{F}(\mathbf{r}))/kT\}]$ is the electron distribution under thermal equilibrium, gives the current density by integrating all the electron contributions to the current. When $f - f_0$ is much smaller than f_0, the deviation is calculated from the Boltzmann equation under static condition:

$$(\dot{\mathbf{k}} \cdot \nabla_k f) + (\boldsymbol{v} \cdot \nabla f) + \frac{f - f_0}{\tau} = 0, \qquad (1)$$

where the first and second terms correspond to the changes of $f(\mathbf{k}, \mathbf{r})$ by electron flows in $\mathbf{k}$-space and real space, respectively, and the third term corresponding to relaxation with scattering time τ. Under static electric field along x-direction, constant temperature, and zero magnetic field, the electron distribution becomes

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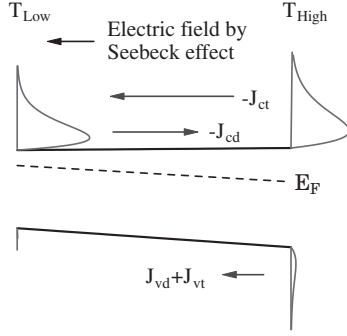*2Graduate Student, Japan Advanced Institute of Science and Technology

Fig. 1 Schematic band diagram, carrier distributions, and carrier flow under temperature gradient. Dependence of band gap on temperature for lead-salt IV–VI material is taken into account in the diagram.

$$f(\mathbf{k}, \mathbf{r}) = f_0(\mathbf{k}, \mathbf{r}) - \tau \dot{\mathbf{k}} \cdot \nabla_k f$$

$$= f_0 + E_x \frac{e\tau}{\hbar} \frac{\partial E(k)}{\partial k_x} \frac{\partial f_0}{\partial E(k)}$$

$$= f_0 - E_x \frac{e\tau v_x}{kT} f_0(1 - f_0), \quad (2)$$

where we used the relation $\partial f_0 / \partial E = -f_0(1-f_0)/kT$ and neglected terms higher than 2nd order of infinitesimal in third expression. Thus, drift current density along x-direction under electric field is given by

$$J_x = \frac{1}{4\pi^3} \sum_V \int_V (-ev_x) f dk^3$$

$$= \left(\frac{e^2}{4\pi^3 kT}\right) E_x \sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k = \sigma E_x, \quad (3)$$

where the summation is taken for all the valleys related to the electrical conduction and σ is electric conductivity. Thus, electric conductivity σ is given by

$$\sigma = \left(\frac{e^2}{4\pi^3 kT}\right) \sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k. \quad (4)$$

Next, we describe the Seebeck coefficient taking temperature dependent band gap into account. Figure 1 shows a schematic band diagram and carrier distributions under temperature gradient. The Seebeck voltage is the voltage along temperature gradient, and the coefficient is given by $S = (1/e) dE_F/dT|_{J=0}$. When we treat with temperature dependent band gap, the equation $\hbar\dot{\mathbf{k}} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$ must be modified to

$$\hbar \dot{\mathbf{k}} = -\nabla E(\mathbf{k}) - e\mathbf{v} \times \mathbf{B}. \quad (5)$$

Then, electron distribution under temperature gradient in x-direction and under zero magnetic field is given by

$$f(\mathbf{k}, \mathbf{r}) = f_0(\mathbf{k}, \mathbf{r}) - \tau \dot{\mathbf{k}} \cdot \nabla_k f_0 - \tau \mathbf{v} \cdot \nabla f_0$$

$$= f_0(\mathbf{k}, \mathbf{r}) - \tau \dot{\mathbf{k}} \cdot \nabla_k f_0 - \tau \mathbf{v} \cdot (\nabla T) \frac{df_0}{dT}$$

$$= f_0 + \frac{\tau}{\hbar} \frac{dE(\mathbf{k})}{dx} \frac{\partial E(\mathbf{k})}{\partial k_x} \frac{\partial f_0}{\partial E(\mathbf{k})}$$

$$- \tau v_x \frac{dT}{dx} \left(\frac{\partial f_0}{\partial T} + \frac{dE_F}{dT}\bigg|_{x=Const.} \frac{\partial f_0}{\partial E_F}\right.$$

$$+ \left.\frac{\partial E(\mathbf{k})}{\partial T}\bigg|_{E_x=0} \frac{\partial f_0}{\partial E(\mathbf{k})}\right)$$

$$= f_0 - \frac{\tau v_x}{kT} \left(\frac{dT}{dx} \frac{\partial E(\mathbf{k})}{\partial T}\bigg|_{E_x=0} + eE_x\right) f_0(1-f_0)$$

$$- \frac{\tau v_x}{kT} \frac{dT}{dx} \left(\frac{E-E_F}{T} + \frac{dE_F}{dT}\bigg|_{x=Const.}\right.$$

$$- \left.\frac{\partial E(\mathbf{k})}{\partial T}\bigg|_{E_x=0}\right) f_0(1-f_0)$$

$$= f_0 - \frac{\tau v_x}{kT} \frac{dT}{dx} \left(\frac{E-E_F}{T} + \frac{dE_F}{dT}\right) f_0(1-f_0), \quad (6)$$

where we neglected terms higher than 2nd order of infinitesimal in second expression and took account of the derivative of energy level $E(\mathbf{k})$ with temperature. Effects of electric field, carrier concentration, and band gap deviation were included in the dE_F/dT as given by

$$\frac{dE_F(n, E_g, T)}{dT} = \frac{\partial E_F}{\partial T} + \frac{\partial n}{\partial T} \frac{\partial E_F}{\partial n} + \frac{\partial E_g}{\partial T} \frac{\partial E_F}{\partial E_g} + eE_x \frac{dx}{dT}. \quad (7)$$

Thus current density and Seebeck coefficient under the temperature gradient are given by

$$J = \frac{1}{4\pi^3} \sum_V \int_V (-ev_x) f dk^3$$

$$= \frac{e}{4\pi^3 kT} \frac{dT}{dx} \sum_V \int_V \tau v_x^2 f_0(1-f_0) \left(\frac{E-E_F}{T} + \frac{dE_F}{dT}\right) d^3k$$

$$= \frac{e}{4\pi^3 kT} \frac{dT}{dx} \left[\frac{1}{T} \sum_V \int_V \tau v_x^2 f_0(1-f_0)(E-E_F) d^3k\right.$$

$$+ \left.\frac{dE_F}{dT} \sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k\right] \quad (8)$$

and

$$S = \frac{1}{e} \frac{dE_F}{dT}\bigg|_{J=0}$$

$$= -\frac{1}{eT} \frac{\sum_V \int_V \tau v_x^2 f_0(1-f_0)(E-E_F) d^3k}{\sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k}. \quad (9)$$

This eq. (9) was modified in Ref. 4), taking account of temperature dependent band gap. However, it is understood that no modification is necessary in the eq. (9) if we use the exact relation $\hbar\dot{\mathbf{k}} = -\nabla E(\mathbf{k})$ in eq. (5).

Equation (9) shows that the Seebeck coefficient is given by an average value of electron energy divided by $-eT$. Thus the Seebeck coefficient and Peltier effect is related each other. Peltier effect is the thermal absorption or generation at the interface of materials by current. On the other hand, the Seebeck effect is the voltage generated by temperature gradient inside the material. Though the interface effect and bulk effect look like completely different, they have a relation each other as described many textbooks.[10,11] Using eq. (4) as electrical conductivity and considering each electron carries the energy $E - E_F$, energy flow inside the material by current I is just given by TSI, where we used the eq. (9) for the Seebeck coefficient S. At the interface of materials, the discontinuity of the energy flow results in the absorption or generation of the heat corresponding to the value $(S_2 - S_1)TI$, where S_1 and S_2 are Seebeck coefficient of the materials. Thus Peltier coefficient Π of the material is defined as $\Pi = ST$, which is known as second Kelvin relation. In conventional

textbooks,[10] the Kelvin relations had been derived thermo-electrically, assuming Onsager's theorem,[12] and the Seebeck coefficient had been defined as $S = \mathbf{E}/\nabla T$. On the other hand, we defined the Seebeck coefficient differently as $S = (1/e)dE_F/dT$ because experimental Seebeck voltage important for device application does not come from the electric field in the bulk region, but from the Fermi level difference.

Thomson effect is a phenomenon of heating or cooling of a current-carrying material with a temperature gradient. If a current density J is passed through a homogeneous material, the heat production W per unit volume and unit time is written by:

$$W = \rho J^2 - \mu_T J \frac{dT}{dx} \qquad (10)$$

where ρ is the resistivity of the material, dT/dx is the temperature gradient along the current direction, and μ_T is the Thomson coefficient. The Thomson coefficient is calculated considering the difference of energies carried by unit charge at the temperature points $T_L = T$ and $T_H = T + \Delta T$ under infinitesimally small electric field or current density:

$$Q\Delta x = \frac{1}{e} \frac{\sum_V \int_V \tau v_x^2 f_H (1 - f_H)(E - E_{FH}) d^3 k}{\sum_V \int_V \tau v_x^2 f_H (1 - f_H) d^3 k}$$

$$- \frac{1}{e} \frac{\sum_V \int_V \tau v_x^2 f_0 (1 - f_L)(E - E_{FH}) d^3 k}{\sum_V \int_V \tau v_x^2 f_L (1 - f_L) d^3 k}$$

$$= T_L S_L - T_H S_H + S\Delta T = -T\Delta S - \Delta T \Delta S, \quad (11)$$

where Q is the heat generated per unit volume and Δx is the distance between the two points. We also used the relation $E_{FH} = E_{FL} + eS\Delta T$, and the Thomson coefficient is given by

$$\mu_T = -\frac{W}{J\frac{dT}{dx}} = -\frac{Q}{\frac{dT}{dx}} = T\frac{dS}{dT}. \qquad (12)$$

The eq. (12) is known as the second Kelvin relation.

The Seebeck coefficient is calculated from eq. (9), taking account of carriers in all valleys correctly. After integrations over the constant energy surfaces, the equation becomes the following energy integral:

$$S = -\frac{1}{eT} \frac{\sum_V \int \tau(E) \bar{v}_x^2(E) f_0 (1 - f_0)(E - E_F) D(E) dE}{\sum_V \int \tau(E) \bar{v}_x^2(E) f_0 (1 - f_0) D(E) dE}, \qquad (13)$$

where $D(E)$ is the density of states in the V-th valley and $\bar{v}_x^2(E)$ is the value given by

$$\bar{v}_x^2(E) = \frac{1}{S_k} \int_{S_k} v_x^2(\mathbf{k}) dS_k. \qquad (14)$$

Here, S_k represents the area of constant energy surface with energy E in the V-th valley. In semiconductors and semimetals, constant energy surface near the Fermi energy often becomes rotational ellipsoid with longitudinal effective mass m_l and transverse effective mass m_t, and $\bar{v}_x^2(E)$ is written as

$$\bar{v}_x^2(E) = \frac{2}{3}\left(\frac{\cos^2 \phi}{m_l} + \frac{\sin^2 \phi}{m_t}\right)E = \frac{2E}{3m_{xx}}, \qquad (15)$$

where E is measured from the band edge, and ϕ is the angle between the longitudinal direction and x-axis.

In lead salt IV–VI semiconductors such as PbTe, PbSe, and PbS, the E–$\mathbf{k}$ relation is approximately represented by $E(1 + E/E_g) = \sum \hbar^2 k^2/2m_{ij}$ in two band flame work, and density of states $D(E)$ and $\bar{v}_x^2(E)$ are given by

$$D(E) = \frac{\sqrt{2m_t^2 m_l E\left(1 + \dfrac{E}{E_g}\right)\left(1 + \dfrac{2E}{E_g}\right)}}{\pi^2 \hbar^3}, \qquad (16)$$

and

$$\begin{aligned} \sum_V \bar{v}_x^2(E) &= \sum_V \frac{2}{3}\left(\frac{\cos^2 \phi}{m_l} + \frac{\sin^2 \phi}{m_t}\right)\frac{E(1 + E/E_g)}{(1 + 2E/E_g)^2} \\ &= \frac{2M}{3}\left(\frac{1}{3m_l} + \frac{2}{3m_t}\right)\frac{E(1 + E/E_g)}{(1 + 2E/E_g)^2} \\ &= \frac{2M}{3m_C}\frac{E(1 + E/E_g)}{(1 + 2E/E_g)^2}, \end{aligned} \qquad (17)$$

where $m_C = (1/3m_l + 2/3m_t)^{-1}$ is the conductivity effective mass, M is the number of equivalent valleys, and $M = 4$ in lead salt IV–VI semiconductors.

Thus Seebeck coefficient for single carrier conduction is given by

$$S = -\frac{1}{eT} \frac{\displaystyle\int_0^\infty \tau(E) f_0 (1 - f_0)\frac{(E - E_F)E^{3/2}(1 + E/E_g^{3/2})}{(1 + 2E/E_g)} dE}{\displaystyle\int_0^\infty \tau(E) f_0 (1 - f_0)\frac{E^{3/2}(1 + E/E_g)^{3/2}}{(1 + 2E/E_g)} dE}. \qquad (18)$$

In thermoelectric materials such as IV–VI semiconductors, lattice thermal conductivity is normally low, and electronic part becomes important especially at high temperature.

Energy flow along x-direction by carriers at $J = 0$ can be represented considering that each electron transfers the energy $E - E_F$ as

$$\begin{aligned} J_{Energy} &= \frac{1}{4\pi^3} \sum_V \int_V v_x (E - E_F) f dk^3 \\ &= -\frac{e}{4\pi^3 kT}\frac{dT}{dx}\left[\sum_V \int_V \tau v_x^2 f_0 (1 - f_0)\left(\frac{(E - E_F)^2}{eT} + S(E - E_F)\right)d^3 k\right] \end{aligned}$$

$$= -\frac{\mathrm{d}T}{\mathrm{d}x}\frac{\sigma}{e^2 T}\left[\frac{\sum_V \int_V \tau v_x^2 f_0(1-f_0)\frac{(E-E_F)^2}{eT}d^3k}{\sum_V \int_V \tau v_x^2 f_0(1-f_0)d^3k} - S^2 e^2 T^2\right], \tag{19}$$

where we used eqs. (4), (6) and (9). And electronic thermal conductivity K_E is given by

$$K_E = -\frac{J_{\text{Energy}}}{\mathrm{d}T/\mathrm{d}x} = \frac{\sigma}{e^2 T}\left[\frac{\sum_V \int_V \tau v_x^2 f_0(1-f_0)\frac{(E-E_F)^2}{eT}d^3k}{\sum_V \int_V \tau v_x^2 f_0(1-f_0)d^3k} - S^2 e^2 T^2\right]. \tag{20}$$

We discuss the meaning of the eq. (20) from the Fig. 1, where both electron and hole flows affect the current and the energy flows. From eqs. (8) and (9) with the condition $J = 0$, the current densities J_c and J_v in conduction and valence bands are written by

$$J_c = \left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)\frac{e^2}{4\pi^3 kT}\int_c \tau v_x^2 f_0(1-f_0)\left(\frac{E-E_F}{eT}+S\right)d^3k$$

$$= -\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)\frac{e^2}{4\pi^3 kT}\int_v \tau v_x^2 f_0(1-f_0)\left(\frac{E-E_F}{eT}+S\right)d^3k = -J_v. \tag{21}$$

Thus eq. (19) is transformed to the next equation using the eq. (21):

$$J_{\text{Energy}} = -\left(\frac{dT}{dx}\right)\frac{e^2}{4\pi^3 kT}\sum_{V=c,v}\int_V \tau v_x^2 f_0(1-f_0)\left(\frac{(E-E_F)}{eT}\frac{(E-E_{0V})}{e}+S\frac{(E-E_{0V})}{e}\right)d^3k$$

$$+\left(\frac{dT}{dx}\right)\frac{e^2}{4\pi^3 kT}\sum_{V=c,v}\frac{(E_F-E_{0V})}{e}\int_V \tau v_x^2 f_0(1-f_0)\left(\frac{(E-E_F)}{eT}+S\right)d^3k$$

$$= -\left(\frac{dT}{dx}\right)\frac{e^2}{4\pi^3 kT}\sum_{V=c,v}\int_V \tau v_x^2 f_0(1-f_0)\left(\frac{(E-E_F)}{eT}\frac{(E-E_{0V})}{e}+S\frac{(E-E_{0V})}{e}\right)d^3k$$

$$+\frac{(E_F-E_{0c})}{e}J_C + \frac{(E_F-E_{0v})}{e}J_v$$

$$= -\left(\frac{dT}{dx}\right)\frac{e^2}{4\pi^3 kT}\sum_{V=c,v}\int_V \tau v_x^2 f_0(1-f_0)\left(\frac{(E-E_F)}{eT}\frac{(E-E_{0V})}{e}+S\frac{(E-E_{0V})}{e}\right)d^3k$$

$$+\frac{(E_{0c}-E_{0v})}{e}J_v, \tag{22}$$

where we used the relation $(E-E_F) = (E-E_{0V}) + (E_{0V}-E_F)$, and E_{0c} and E_{0v} represent the average energies of electrons and holes, respectively, and $E_{0c}-E_{0v} \approx E_g + 3kT$, taking account of thermal energy as $(3/2)kT$. In the last expression of eq. (22), the first term corresponds to the energy transferred in conduction and valence bands without considering recombination. The last term corresponds to a bipolar carrier transport, known as bipolar diffusion, where the same amount of electrons and holes flow to low temperature side.[6,7] The thermal conductivity due to the bipolar carrier transport increases significantly with the minority carrier concentration thermally excited, even if the minority carrier concentration is much smaller than that of majority carriers.[8,13]

3. Hall and Nernst Effects

If we apply the magnetic field to z-direction under the current density along x-direction, an electric field appears along y-direction. This is known as Hall effect. If we replace the current density along x-direction to temperature gradient, an electric field also appears along y-direction. This is known as Nernst effect.
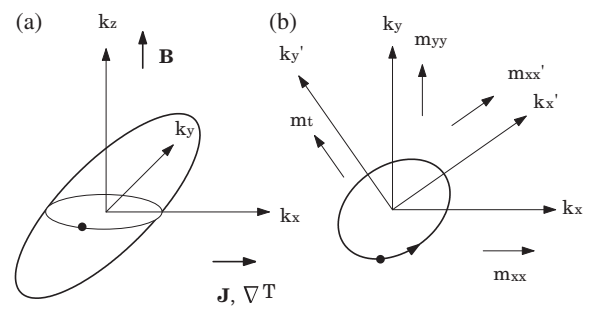

Fig. 2 (a) Constant energy surface and coordinate system. (b) Electron movement in **k**-space under magnetic field along z-direction, and definition of effective masses.

We consider the electron motion under magnetic field. The electron moves according to $\hbar\dot{\mathbf{k}} = -e\mathbf{v}\times\mathbf{B}$ in **k**-space under the magnetic field and zero electric field. In the valley with the anisotropic E–**k** relation shown in Fig. 2, where longitudinal effective mass is m_l and transverse mass is m_t, we assume the electron position (k_x, k_y, k_z) moves to $(k_{x''}, k_{y''}, k_{z''})$ after a small time τ without collision, then the following equation is satisfied:

$$
\begin{bmatrix} k_x'' \\ k_y'' \\ k_z'' \end{bmatrix} = \begin{bmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & -\frac{eB\tau}{m_t} & 0 \\ \frac{eB\tau}{m_{xx}'} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
$$

$$
\times \begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix}
$$

$$
= \begin{bmatrix} 1 & -\frac{eB\tau}{m_{yy}} & 0 \\ \frac{eB\tau}{m_{xx}} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} k_x \\ k_y \\ k_z \end{bmatrix}, \tag{23}
$$

where we took the major axis of the ellipsoid in *x*–*y* plane as k_x', the minor axis as k_y', and angle between k_x' and k_x axes as α. We neglected terms higher than $B^2\tau^2$ under weak magnetic field condition. In this case the electron velocity is transformed as

$$
\begin{bmatrix} v_x'' \\ v_y'' \\ v_z'' \end{bmatrix} = \begin{bmatrix} 1 & -\frac{eB\tau}{m_{xx}} & 0 \\ \frac{eB\tau}{m_{yy}} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} v_x \\ v_y \\ v_z \end{bmatrix}. \tag{24}
$$

Under current density along *x*-direction (J_x) and a constant temperature, Hall current ($J_{y,\text{Hall}}$) along y direction which balance with drift current is given by

$$
\begin{aligned}
J_{y,\text{Hall}} &= -\frac{1}{4\pi^3} \sum_V \int_V ev_y'' f dk^3 \\
&= \frac{1}{4\pi^3} \sum_V \int_V \left(-e\frac{eB\tau}{m_{yy}} v_x \right) f dk^3 \\
&= \left(\frac{e^2}{4\pi^3 kT} \right) eBE_x \sum_V \frac{1}{m_{yy}} \int_V \tau^2 v_x^2 f_0(1-f_0) d^3k \\
&= eBJ_x \frac{\sum_V \frac{1}{m_{yy}} \int_V \tau^2 v_x^2 f_0(1-f_0) d^3k}{\sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k} \\
&= -J_{y,\text{drift}} = -\left(\frac{e^2}{4\pi^3 kT} \right) E_y \sum_V \int_V \tau v_y^2 f_0(1-f_0) d^3k.
\end{aligned} \tag{25}
$$

where we used eqs. (2), (3), (4) and (24). Thus, Hall coefficient at weak magnetic field limit is given by

$$
\begin{aligned}
R_{\text{H}} &= \frac{E_y}{J_x B} = -\frac{kT}{en} \frac{\left(\sum_V \frac{1}{m_{yy}} \int_V \tau^2 v_x^2 f_0(1-f_0) d^3k \right)\left(\sum_V \int_V f_0 d^3k \right)}{\left(\sum_V \int_V \tau v_x^2 f_0(1-f_0) d^3k \right)\left(\sum_V \int_V \tau v_y^2 f_0(1-f_0) d^3k \right)} \\
&= -\frac{3kTm_{\text{C}}^2}{2enM} \sum_V \left(\frac{1}{m_{xx}m_{yy}} \right) \frac{\left(\int \tau^2(E) f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1} dE \right)\left(\int f_0 \Gamma^{1/2}\Gamma' dE \right)}{\left(\int \tau(E) f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1} dE \right)^2}
\end{aligned} \tag{26}
$$

where we put $\Gamma = E(1 + E/E_g)$, $\Gamma' = d\Gamma/dE = (1 + 2E/E_g)$, the carrier concentration $n = (1/4\pi^3)\sum_V \int_V f_0 d^3k$, and used eqs. (15) and (16). The calibration coefficient γ in Hall coefficient ($R_{\text{H}} = -\gamma/en$) is given from eq. (26) as

$$
\gamma = -enR_{\text{H}} = \frac{3kTm_{\text{C}}^2}{2M} \sum_V \left(\frac{1}{m_{xx}m_{yy}} \right) \frac{\left(\int \tau^2(E) f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1} dE \right)\left(\int f_0 \Gamma^{1/2}\Gamma' dE \right)}{\left(\int \tau(E) f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1} dE \right)^2}. \tag{27}
$$

In Nernst effect with temperature gradient along *x* axis and magnetic field along *z* axis at $J = 0$, an electric field along *y* axis (E_y) appears. Electron distribution under the temperature gradient is given by eq. (6), and the distribution makes current density $J_{y,\text{Nernst}}$ in *y*-direction under the magnetic field B along *z*-direction as similar in eq. (25), where the $J_{y,\text{Nernst}}$ balance to the drift current density:

$$
J_{y,\text{Nernst}} = -\frac{1}{4\pi^3} \sum_V \int_V \left(\frac{e^2 B\tau v_x}{m_{yy}} \right) f d^3k = \frac{e^2}{4\pi^3 kT} \frac{dT}{dx} \sum_V \frac{eB}{m_{yy}} \int_V \tau^2 v_x^2 f_0(1-f_0)\left(\frac{E-E_{\text{F}}}{eT} + S \right) d^3k = -\sigma E_y. \tag{28}
$$

Here, we used eqs. (3), (4), (9), (17), and (24). Thus, the Nernst coefficient (A_{Ne}) is written by the following equation:[9]

$$
\begin{aligned}
A_{\text{Ne}} &= \frac{E_y}{B(dT/dx)} = -\frac{\sum_V \frac{e}{m_{yy}} \int_V \tau^2 v_x^2 f_0(1-f_0)\left(\frac{E-E_{\text{F}}}{eT} + S \right) d^3k}{\sum_V \int_V \tau^2 v_x^2 f_0(1-f_0) d^3k} \\
&= -\frac{em_{\text{C}}}{M} \sum_V \left(\frac{1}{m_{xx}m_{yy}} \right)\left(\frac{S \int \tau^2 f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1} dE + \frac{1}{eT}\int \tau^2 f_0(1-f_0)(E-E_{\text{F}})\Gamma^{3/2}\Gamma' dE}{\int \tau f_0(1-f_0)\Gamma^{3/2}\Gamma' dE} \right)
\end{aligned}
$$

$$= R_{\mathrm{H}}\sigma\left(S + \frac{1}{eT}\frac{\int \tau^2(E)f_0(1-f_0)(E-E_{\mathrm{F}})\Gamma^{3/2}\Gamma'^{-1}\mathrm{d}E}{\int \tau^2(E)f_0(1-f_0)\Gamma^{3/2}\Gamma'^{-1}\mathrm{d}E}\right),\qquad(29)$$

where we used eqs. (4), (15), (16), (17), (26), and (28).

4. Calculated Results

Figure 3 shows dependence of Seebeck coefficient of PbTe on electron concentration with the parameter of energy dependent scattering time calculated at room temperature from eq. (18). The absolute value of Seebeck coefficient strongly depends on the energy dependence of the scattering time. Normally, phonon scattering, where $\tau(E) \propto E^{-1/2}$, is dominant at or higher than room temperature. In nano-composite consisting of nanopowders, a filtering effect which enhances the scattering of low energy carriers can vary the energy dependence of scattering time.[14,15] Figure 4(a) shows the dependence of Seebeck coefficients of PbTe films, PbS films, and EuTe/PbTe superlattices on carrier concentration at 300 K, and corresponding theoretical values calculated assuming $\tau(E) \propto E^{-1/2}$. Figure 4(b) shows dependence of Seebeck coefficient on temperature for PbS and corresponding theoretical values. In these calculations, we used band-gap and effective-mass parameters shown in Table 1. Excellent agreements between experimental and theoretical values are obtained assuming $\tau(E) \propto E^{-1/2}$.

Figure 5 shows the electronic thermal conductivity calculated from eq. (20) for n-type PbTe, PbSe and PbS in the temperature range 300–800 K. In the calculation, we assumed room temperature electron mobilities 1500, 1000 and 600 cm²/Vs for PbTe, PbSe and PbS, respectively, and temperature dependence of the mobility $\mu \propto T^{-2.5}$ was assumed.[16] Band gap and effective mass data used in this calculation are listed in Table 1.[17,18] The strong enhancement in the thermal conductivity of PbTe and PbSe at low impurity concentration with temperature comes from the minority carrier effect in second term in eq. (22).

Figure 6 shows calculated calibration coefficient γ in Hall coefficient for n-type PbTe at 300 K from eq. (27). In the calculation, current and magnetic field directions were assumed in [100] and [001], respectively, in which effective mass anisotropy do not affect the calibration coefficient. Generally, calibration coefficient depends on the current and magnetic field directions in the material with anisotropic effective masses, and the calibration values $(m_{\mathrm{C}}^2/M)\sum(1/m_{xx}m_{yy})$ for special current and magnetic field directions are shown in Table 2. In semiconductors with parabolic E–$\mathbf{k}$ relation and with no effective mass anisotropy, the calibration coefficient becomes 1.18 for phonon scattering with $\tau(E) \propto E^{-1/2}$, and 1.93 for ionized impurity scattering with $\tau(E) \propto E^{3/2}$ under nondegenerate condition. The value $\gamma = 1.65$ for n-type PbTe with $\tau(E) \propto E^{-1/2}$ is 40% larger than that for semiconductor with parabolic E–$\mathbf{k}$ relation comes from the nonparabolic effect.

Figure 7 shows Nernst coefficient of n-type PbTe calculated from eq. (29). If scattering time τ is independent of energy, Seebeck coefficient in the first term and second term in the parentheses cancel completely, and the sign of the
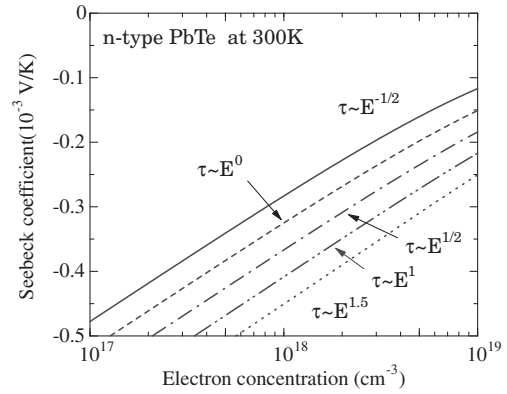

Fig. 3 Dependence of Seebeck coefficient for n-type PbTe on carrier concentration for various energy dependent scattering time. The Seebeck coefficient is strongly increased if the energy dependence of scattering time τ becomes positive.
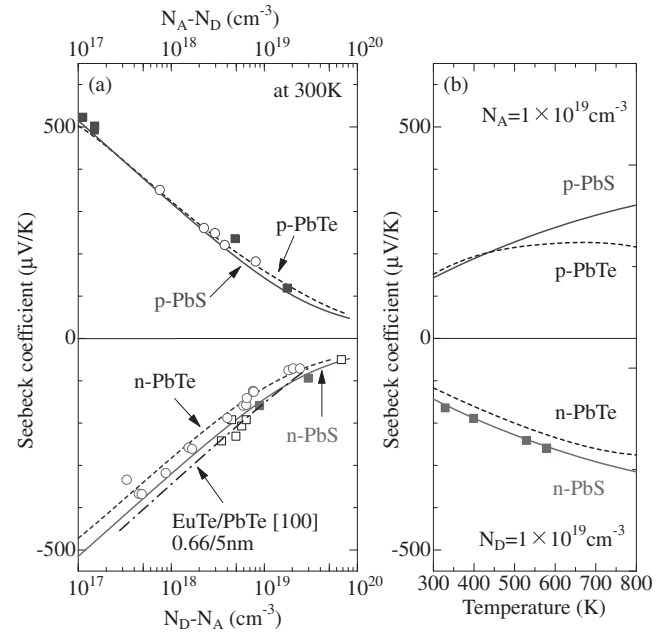

Fig. 4 (a) Experimental and theoretical dependence of Seebeck coefficient on impurity concentrations for PbTe films, PbS films, and EuTe/PbTe superlattices, and (b) Experimental and theoretical dependence of Seebeck coefficient on temperature for PbTe and PbS films.[4,5,8]

Nernst coefficient is changed by the scattering mechanism. Thus the Nernst coefficient is useful to determine the scattering mechanism of materials. In nanostructures consisting of nanopowders, a filtering effect which transport high energy carrier becomes important. In this case the sign of Nernst coefficient is inverted by the inverted energy dependence of collision time. The effect is useful to increase the Seebeck coefficient as discussed above.

Table 1   Band parameters used for the theoretical calculations of lead-salt IV–VI materials. PbTe has indirect valence band extrema near the L-point valence band tops with temperature independent band gap of 370 meV.[5]

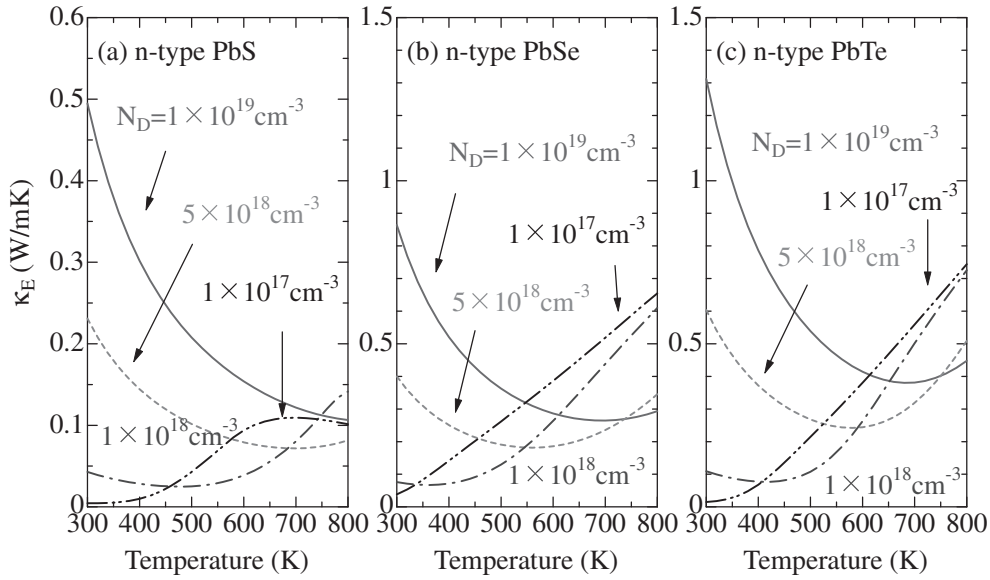|	E_g (T) [meV]	m_t (0) [m_0]	m_l (0) [m_0]	m_t (T) [m_0]	m_l (T) [m_0]
PbS	$263 + (400 + 0.256T^2)^{1/2}$	0.08	0.105	$\frac{E_{gL}(T)}{E_{gL}(0)}m_t(0)$	$\frac{E_{gL}(T)}{E_{gL}(0)}m_l(0)$
PbSe	$125 + (400 + 0.256T^2)^{1/2}$	0.04	0.07	$\frac{E_{gL}(T)}{E_{gL}(0)}m_t(0)$	$\frac{E_{gL}(T)}{E_{gL}(0)}m_l(0)$
PbTe	$167 + (400 + 0.256T^2)^{1/2}$	0.024	0.24	$\frac{E_{gL}(T)}{E_{gL}(0)}m_t(0)$	$\frac{E_{gL}(T)}{E_{gL}(0)}m_l(0)$

Fig. 5   Theoretical dependence of electronic thermal conductivities on temperature for (a) PbS, (b) PbSe, and (c) PbTe with various electron concentrations. The electronic thermal conductivity increases strongly with temperature owing to minority carrier effect.[8]
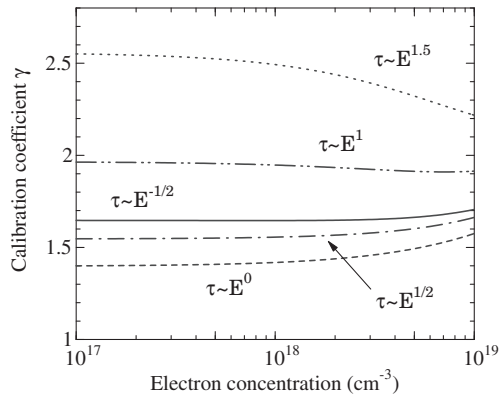

Fig. 6   Calibration coefficient γ in Hall coefficient ($R_H = -\gamma/en$) for n-type PbTe with current and magnetic field directions [100] and [001], respectively. Scattering mechanism affects the value γ strongly.
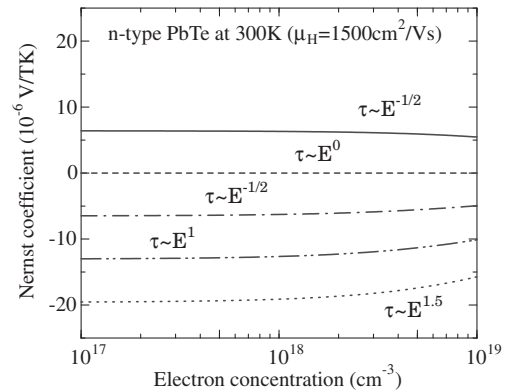

Fig. 7   Dependence of Nernst coefficient on carrier concentration of n-type PbTe for various energy dependent scattering time. The Nernst effect is useful to determine the scattering mechanism.

Table 2   Effect of effective-mass anisotropy on calibration coefficient in Hall effect for n-type PbTe.

Current direction	Magnetic field direction	$(m_C^2/M)\sum(1/m_{xx}m_{yy})$
[100]	[001]	1
[110]	[001]	0.82
[112]	[111]	0.94

5. Summary

In this paper, electronic conduction, Seebeck effect, Peltier effect, Thomson effect, electronic thermal conductivity, Hall effect, and Nernst effect important for thermoelectric applications were discussed taking account of effective mass anisotropy, nonparabolicity in *E*–**k** relation, and temperature

dependent band gap. It was shown that the temperature dependence of the band gap does not modify the basic equations for the Seebeck coefficient, thermal conductivity, and Nernst coefficient. In narrow gap semiconductors, existence of minority carriers enhances the electronic thermal conductivity. Calibration coefficient γ for the Hall effect ($R_{\mathrm{H}} = -\gamma/en$) increases by the nonparabolicity of the E–$\mathbf{k}$ relation. Nernst coefficient gives useful information on scattering properties of the materials.

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