

# THEORY OF THERMOELECTRIC REFRIGERATION

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In this paper we develop a new method of calculating temperature distribution in the elements of thermoelectric refrigerator, especially taking into account of Thomson effect, which was disregarded in the earlier theories. The discrepancy between the experimental result and the calculated value can be removed by making use of our method. Our method leads to the result that the maximum temperature difference is smaller and the value of the optimum current larger than those predicted by the earlier theory.

Next we tried to find the condition to make the temperature difference as large as possible by changing the resistivity of the semiconducting elements along the direction of flowing current. Under some assumptions, a numerical calculation was made. If we apply to Bi-Te alloy, the temperature difference can be increased by the amount of 14%.

In the last part, we also examine the effect of changing cross sectional area of the elements along its current flow. However, it is found in this case that the increase of temperature difference is not so large.

## 1. Introduction

Many attempts to obtain low temperature by means of Peltier effect have been made by various investigators for a long time. Earlier experiments<sup>1)2)</sup> were not successful, because metal was used as the element and the Peltier coefficient of metal is generally very small. Recent progresses in semiconductor researches have opened new possibilities of producing practical thermoelectric refrigerator.<sup>3)</sup>

According to Altenkirch's theory,<sup>4)</sup> it is necessary to maximize the factor  $\theta = (-\eta_1 + \eta_2) / (\sqrt{\lambda_1 \rho_1} + \sqrt{\lambda_2 \rho_2})$  in order to make the temperature difference maximum, where  $\eta_1$  and  $\eta_2$  are the thermoelectric power per degree,  $\lambda_1$  and  $\lambda_2$  thermal conductivity and  $\rho_1$  and  $\rho_2$  electrical resistivity of *n*-type and *p*-type specimens respectively. In semiconductor, Peltier coefficient which is the product of thermoelectric power per degree and absolute temperature is large though their electrical resistivity is also large. Moreover, for a given value of  $\eta$ ,  $\lambda\rho$  changes from material to material in semiconductor. This is constant in metal as is well known as Wiedemann-Frantz law. Thus the application of proper semiconductor having proper impurity content makes the temperature difference as large as 30 degrees or higher.

On the other hand, the theory of the thermoelectric refrigerator was only made by Altenkirch in 1911.<sup>4)</sup> (Many problems such that how we determine the impurity content of the elements or how we design the thermoelectric refrigerator etc. were discussed by many authors, of course. These discussions were, however, mostly based upon Altenkirch's one). His theory based upon rather crude model, and Thomson effect was neglected.

We, therefore, discuss in this paper the effect of Thomson heat on the theoretical formula of the temperature difference. (For this problem, some considerations were made by Joffe.<sup>5)</sup>) Next we examine the effects of unhomogeneity of both physical properties and geometrical size. The possibility of increasing the temperature difference by these means is discussed.

## 2. Effect of Thomson Heat

An unit thermocouple of the thermoelectric refrigerator is illustrated schematically in Fig. 1. In this figure, 1 is *n*-type and 2 is *p*-type semiconductors respectively, 3 and 4 are metal. It is assumed that the semiconductors 1 and 2 are isolated thermally from the surrounding, so that there is no thermal current flowing into the semiconductor through the side planes. The metal 4 is maintained at constant temperature  $T_H$  and the heat  $W$  (watts) flows into this system only through the metal 3. We also assume that the metal 3 has infinit electrical and thermal conductivities.

The heat  $Q_1$  generated in the semiconductor 1 per unit length is shown as

$$Q_1 = \frac{d}{dx_1} \left( \lambda_1 S_1 \frac{dT_1}{dx_1} \right) - \mu_1 J_1 \frac{dT_1}{dx_1} + \rho_1 J_1^2 / S_1. \quad (1)$$

In this equation,  $S_1$  is sectional area,  $J_1$  electrical current,  $T_1$  absolute temperature and  $x_1$  variable taken as in Fig. 1. The similar equation can be derived for  $Q_2$  which is the heat generated in semiconductor 2 by exchanging the suffix 1 to 2. Here the suffix 1 or 2 refers to the semiconductor 1 or 2. In eq. (1), the first term on the right shows that due to heat conduction, the second Thomson heat and the third Joule heat.

At stationary state,  $Q_1$  and  $Q_2$  must be equal to zero. Here we assume that  $\lambda$ ,  $\mu$ ,  $\rho$  and  $S$  are independent of  $T$  and  $x$ . Then the differential equations  $Q_1 = 0$  and  $Q_2 = 0$  lead to

$$T_1 = A_1 \exp(\mu_1 J_1 x_1 / \lambda_1 S_1) + \rho_1 J_1 x_1 / S_1 \mu_1 + B_1 \quad (2.1)$$

and

$$T_2 = A_2 \exp(\mu_2 J_2 x_2 / \lambda_2 S_2) + \rho_2 J_2 x_2 / S_2 \mu_2 + B_2, \quad (2.2)$$

where  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$  are integral constants.

By taking into account of the preceding assumptions, boundary conditions to determine the integral constants  $A_1$  etc. are written as follows;

$$\text{at } x_1 = 0 \text{ and } x_2 = 0 \quad T_1 = T_2 (= T_L) \quad (3.1)$$

$$\lambda_1 S_1 \frac{dT_1}{dx_1} + \lambda_2 S_2 \frac{dT_2}{dx_2} + W = (\Pi_{13} + \Pi_{32}) J \quad (3.2)$$

$$\text{at } x_1 = L_1 \quad T_1 = T_H \quad (3.3)$$

$$\text{at } x_2 = L_2 \quad T_2 = T_H, \quad (3.4)$$

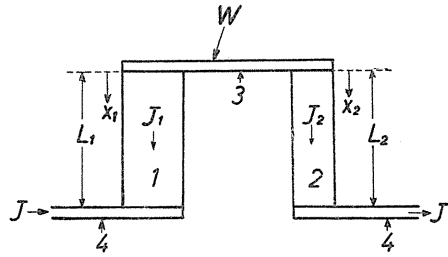


FIG. 1. Schematic diagram of an element of the thermoelectric refrigerator.

where  $-J_1 = J_2 = J > 0$ , and  $\Pi_{13}$  means Peltier coefficient when the electrical current flows from 1 to 3. The meaning of  $\Pi_{32}$  is also similar. In the latter parts of this paper, we will write  $\Pi_1$  and  $\Pi_2$  instead of  $\Pi_{13}$  and  $\Pi_{32}$ . In eq. (3.2),  $\lambda_1 S_1 (dT_1/dx_1)$  and  $\lambda_2 S_2 (dT_2/dx_2)$  are the conduction heats flow into the cold junction from the semiconductors,  $W$  is the heat flow into the cold junction from the metal 3 and  $(\Pi_1 + \Pi_2)J$  is the heat absorbed by Peltier effect. With eqs. (2) and (3), the integral constants can be determined as follows ;

$$A_1 = \frac{\{(\Pi_1 + \Pi_2)J - W - \sum_{i=1}^2 (\rho_i \lambda_i J_i / \mu_i)\} \{\exp(\mu_2 L_2 J_2 / \lambda_2 S_2) - 1\} + \mu_2 J^2 \sum_{i=1}^2 (\rho_i L_i / \mu_i S_i)}{\mu_1 J_1 \{\exp(\mu_2 L_2 J_2 / \lambda_2 S_2) - 1\} + \mu_2 J_2 \{\exp(\mu_1 L_1 J_1 / \lambda_1 S_1) - 1\}} \quad (4.1)$$

$$A_2 = \frac{\{(\Pi_1 + \Pi_2)J - W - \sum_{i=1}^2 (\rho_i \lambda_i J_i / \mu_i)\} \{\exp(\mu_1 L_1 J_1 / \lambda_1 S_1) - 1\} + \mu_1 J^2 \sum_{i=1}^2 (\rho_i L_i / \mu_i S_i)}{\mu_1 J_1 \{\exp(\mu_2 L_2 J_2 / \lambda_2 S_2) - 1\} + \mu_2 J_2 \{\exp(\mu_1 L_1 J_1 / \lambda_1 S_1) - 1\}} \quad (4.2)$$

$$B_1 = T_H - A_1 \exp(\mu_1 L_1 J_1 / \lambda_1 S_1) - (\rho_1 L_1 J_1 / S_1 \mu_1) \quad (4.3)$$

$$B_2 = T_H - A_2 \exp(\mu_2 L_2 J_2 / \lambda_2 S_2) - (\rho_2 L_2 J_2 / S_2 \mu_2) \quad (4.4)$$

and the temperature difference  $\Delta T_1 = T_H - T_L$  is

$$\Delta T_1 = \frac{\{(\Pi_1 + \Pi_2)J - W + \left(\frac{\rho_1 \lambda_1}{\mu_1} - \frac{\rho_2 \lambda_2}{\mu_2}\right)J\}}{-\mu_1 J / \{\exp(-\mu_1 L_1 J / \lambda_1 S_1) - 1\} + \mu_2 J / \{\exp(\mu_2 L_2 J / \lambda_2 S_2) - 1\}} + \frac{\left(\frac{\rho_1 L_1}{S_1} J^2\right) / \{\exp(-\frac{\mu_1 L_1}{\lambda_1 S_1} J) - 1\} + \left(\frac{\rho_2 L_2}{S_2} J^2\right) / \{\exp(\frac{\mu_2 L_2}{\lambda_2 S_2} J) - 1\}}{-\mu_1 J / \{\exp(-\mu_1 L_1 J / \lambda_1 S_1) - 1\} + \mu_2 J / \{\exp(\mu_2 L_2 J / \lambda_2 S_2) - 1\}}. \quad (5)$$

This is the general formula of the temperature difference when we consider the effect of Thomson heat.

In order to compare this formula to Altenkirch's one, the exponential terms involved in eq. (5) are expanded in Maclaurin series under the assumption of  $|\mu_1 L_1 J / \lambda_1 S_1| < 1$  and  $|\mu_2 L_2 J / \lambda_2 S_2| < 1$ . The result is

$$\Delta T_1 \doteq \frac{-W + (\Pi_1 + \Pi_2)J - \frac{J^2}{2} \left(\frac{\rho_1 L_1}{S_1} + \frac{\rho_2 L_2}{S_2}\right)}{\left(\frac{\lambda_1 S_1}{L_1} + \frac{\lambda_2 S_2}{L_2}\right) + \frac{J}{2} \frac{S_1 S_2 \lambda_1 \lambda_2}{L_1 L_2} \left(-\frac{L_1^2}{S_1^2 \lambda_1^2} \mu_1 + \frac{L_2^2}{S_2^2 \lambda_2^2} \mu_2\right)} + \frac{\frac{J^2}{2} \left\{(\Pi_1 + \Pi_2) \left(-\frac{\mu_1 L_1}{\lambda_1 S_1} + \frac{\mu_2 L_2}{\lambda_2 S_2}\right) + \frac{J}{3} \left(\frac{\rho_1 L_1^2}{\lambda_1 S_1^2} \mu_1 - \frac{\rho_2 L_2^2}{\lambda_2 S_2^2} \mu_2\right) + \frac{J}{2} \frac{L_1 L_2 \rho_1 \rho_2}{S_1 S_2} \left(\frac{\mu_1}{\lambda_1 \rho_1} - \frac{\mu_2}{\lambda_2 \rho_2}\right)\right\}}{\left(\frac{\lambda_1 S_1}{L_1} + \frac{\lambda_2 S_2}{L_2}\right) + \frac{J}{2} \frac{S_1 S_2 \lambda_1 \lambda_2}{L_1 L_2} \left(-\frac{L_1^2}{S_1^2 \lambda_1^2} \mu_1 + \frac{L_2^2}{S_2^2 \lambda_2^2} \mu_2\right)}. \quad (6)$$

The value of the current  $J_e$  which makes the temperature difference  $\Delta T_1$  to be maximum is

$$J_e = J_0 (1 + \Delta J / J_0), \quad (7)$$

where  $J_0 = (\Pi_1 + \Pi_2) / \{(\rho_1 L_1 / S_1) + (\rho_2 L_2 / S_2)\}$  is the value for the case that we neglect

Thomson effect, and  $\Delta J$  is the correction term due to Thomson effect. The exact expression of  $\Delta J$  will be given later, because the effect of  $\Delta J$  on  $\Delta T_1$  is very small. For geometrical condition, we use the result of Altenkirch which is

$$(L_2 S_1 / L_1 S_2) = \sqrt{\rho_1 \lambda_2 / \rho_2 \lambda_1}. \quad (8)$$

By means of these conditions, eq. (6) is transformed to

$$\Delta T_1 \doteq \frac{1}{2} \left( \frac{\Pi_1 + \Pi_2}{\sqrt{\rho_1 \lambda_1} + \sqrt{\rho_2 \lambda_2}} \right)^2 \left[ 1 + \frac{2}{3} \cdot \frac{(\Pi_1 + \Pi_2)(-\mu_1 + \mu_2)}{(\sqrt{\rho_1 \lambda_1} + \sqrt{\rho_2 \lambda_2})^2} \right]. \quad (6)$$

In this equation, the second term in angular bracket represents the effect of Thomson heat. Let  $\Delta T_0$  denote the temperature difference given by Altenkirch, then eq. (9) can be written in the form

$$(\Delta T_1 / \Delta T_0) - 1 = (4/3) \{ (-\mu_1 + \mu_2) / (-\eta_1 + \eta_2) \} (\Delta T_0 / T_L), \quad (10)$$

where

$$\Delta T_0 = (1/2) \{ (\Pi_1 + \Pi_2) / (\sqrt{\rho_1 \lambda_1} + \sqrt{\rho_2 \lambda_2}) \}^2.$$

In terms of these notations  $\Delta J$  is expressed as

$$(\Delta J / J_0) = (3/2) \{ (-\mu_1 + \mu_2) / (-\eta_1 + \eta_2) \} (\Delta T_0 / T_L). \quad (11)$$

Eqs. (10) and (11) might be able to explain the discrepancies between the experimental results and the earlier theory. It is indeed the case as far as  $\Delta J / J_0$  is concerned, but not the case as for  $\Delta T_1 / \Delta T_0$ . For instance (see Ref. 3 Fig. 4) the theoretical value of the  $(\Delta J / J_0)$  equals to about 14% whereas the experimental value is about 16%. But as for the temperature difference, eq. (10) is different from the experiment even in qualitatively. So that we must take into account of the effect of the heat  $W$ . The result is

$$\Delta T_1' \doteq \Delta T_1 \left\{ 1 - \left( \frac{W}{\Delta T_0} \right) / \left( \frac{\lambda_1 S_1}{L_1} + \frac{\lambda_2 S_2}{L_2} \right) \right\} \quad (12)$$

$$J_e' \doteq J_e \left\{ 1 - \frac{1}{2} \left( \frac{W}{T_L} \right) \left( \frac{-\mu_1 + \mu_2}{-\eta_1 + \eta_2} \right) / \left( \frac{\lambda_1 S_1}{L_1} + \frac{\lambda_2 S_2}{L_2} \right) \right\} \quad (13)$$

For previous example,  $(\Delta T_1' / \Delta T_1)$  is estimated to be 15%, and this corresponds to about  $W = 31 mW$ . The effect of  $W$  on  $J_e$  is smaller than 1% for this case. Thus by means of eqs. (10)–(13), we can explain the experimental results very well.

### 3. Effect of Changing Carrier Concentration

In this case,  $\lambda$  and  $\rho$  are the function of  $x$ . Eq. (1) does not hold now because of the presence of unhomogeneity, and we will try to derive an equation for  $Q$ . For the case of isotropic material even if it is not homogeneous, the heat produced per second in unit volume is given by<sup>6)</sup>

$$Q = JE - \partial w / \partial x,$$

since  $JE$  is the electrical energy supplied and  $\partial w / \partial x$  is the heat flowing out. If we express  $Q$  in terms of  $J$  and  $\partial T / \partial x$ , we find

$$Q = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + j \frac{T}{e} \cdot \frac{\partial \mathfrak{S}}{\partial x} + \rho j^2, \quad (14)$$

where  $\mathfrak{S}$  is Seebeck coefficient,  $e$  electronic charge and  $j$  electric current density. In our case as unhomogeneity occurs along  $x$ , the second term which represents the thermoelectric heat is divided into two parts, and eq. (14) can be written in the form

$$Q = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) - \mu j \frac{\partial T}{\partial x} + \nu j \frac{\partial n}{\partial x} + \rho j^2, \quad (15)$$

where  $\mu = -(T/e)(\partial \mathfrak{S}/\partial T)$  is Thomson coefficient and  $\nu = (T/e)(\partial \mathfrak{S}/\partial n)$ , and  $n$  is the concentration of the charge carrier. For our model, the heat generated in unit length is given as

$$Q_i = \lambda_i S_i \frac{d^2 T_i}{dx_i^2} + \left( S_i \frac{d\lambda_i}{dx_i} - \mu_i J_i \right) \frac{dT_i}{dx_i} + \nu_i J_i \frac{dn_i}{dx_i} + \frac{\rho_i J_i^2}{S_i} \quad (i=1, 2). \quad (16)$$

Eq. (15) or (16) suggests that the presence of unhomogeneity produce an thermo-electric heat in addition to Thomson heat, which is proportional to the product of current density and the gradient of the carrier concentration.

For the sake of simplicity, we try to solve eq. (16) only for the case that the carrier concentration is expressed as the linear function of  $x_i$ , namely

$$n_i(x_i) = n_i(1 + \varepsilon_i x_i) \quad (17)$$

then  $\lambda_i(x_i) = \lambda_{li} + \lambda_{ei}(1 + \varepsilon_i x_i)$  and  $\sigma_i(x_i) = 1/\rho_i(x_i) = \sigma_i(1 + \varepsilon_i x_i)$ , ( $i=1, 2$ ) where  $\lambda_{li}$  and  $\lambda_{ei}$  are the lattice- and the electronic-thermal conductivities at  $x_i=0$  and  $\sigma_i$  (or  $\rho_i$ ) is the electrical conductivity (or resistivity) at  $x_i=0$ . For Seebeck coefficient, we use the theoretical expression for non-degenerated electron gas, i.e.,

$$\mathfrak{S}_i = \pm k \left\{ 2 + \ln \frac{n_i h^3}{2(2\pi m_i^* kT)^{3/2}} \right\}, \quad (18)$$

where  $k$  is Boltzmann's constant,  $h$  Plank's constant and  $m_i^*$  effective mass of electron or hole. From eq. (18)  $\nu_i$  is

$$\nu_1 = kT/en_1(x) \quad \text{and} \quad \nu_2 = -kT/en_2(x). \quad (19)$$

By means of eqs. (17), (18) and (19), eq. (16) is written as

$$\frac{d^2 T_i}{dx_i^2} + \frac{a_i}{1 + \varepsilon_i x_i} \cdot \frac{dT_i}{dx_i} = - \frac{c_i}{(1 + \varepsilon_i x_i)(1 + \gamma_i x_i)} \quad (i=1, 2), \quad (20)$$

where

$$a_i = \frac{\varepsilon_i \delta_i}{1 + \delta_i} - \frac{\mu_i J_i}{\lambda_i S_i} = \gamma_i - \frac{\mu_i J_i}{\lambda_i S_i} \quad \text{and} \quad c_i = (-1)^i \frac{\varepsilon_i J_i T_i}{\lambda_i S_i} \cdot \frac{k}{e} + \frac{\rho_i J_i^2}{\lambda_i S_i^2} \quad (21)$$

and  $\delta_i = \lambda_{ei}/\lambda_{li}$ .

The exact solution of eq. (20) can hardly be obtained, because  $c_i$  is the function of  $T_i$ . But the variation of  $T_i$  is considered to be small, and we neglect the dependence of  $c_i$  on  $x_i$ . (This order of variation on  $T_i$  exists in other constants, for example  $\rho_i \propto T_i^{3/2}$ .) Then the approximate solution of eq. (20) becomes as

$$T_i = -c_i \int_0^{x_i} (1 + \gamma_i u)^{-(a_i/\tau_i)} \int_0^u (1 + \gamma_i v)^{(a_i/\tau_i)-1} (1 + \varepsilon_i v)^{-1} dv du + A_i (1 + \gamma_i x_i)^{1-(a_i/\tau_i)} + B_i \quad (i = 1, 2) \quad (22)$$

where  $A_i$  and  $B_i$  are integral constants. We define here constants  $F_i$ , and  $G_i$  as follows;

$$F_i \equiv - \int_0^{L_i} (1 + \gamma_i u)^{-(a_i/\tau_i)} \int_0^u (1 + \varepsilon_i v)^{-1} (1 + \gamma_i v)^{(a_i/\tau_i)-1} dv du \quad (23)$$

$$G_i \equiv (1 + \gamma_i L_i)^{-(a_i/\tau_i)+1} \quad (24)$$

then the integral constants  $A_i$  and  $B_i$  are determined by means of eqs. (3), (23) and (24) as

$$A_1 = \frac{\{(II_1 + II_2)J - W\}(G_2 - 1) - (c_1 F_1 - c_2 F_2) \lambda_1 S_1 (\tau_2 - a_2)}{(G_1 - 1) \lambda_2 S_2 (\tau_2 - a_2) + (G_2 - 1) \lambda_1 S_1 (\tau_1 - a_1)} \quad (25.1)$$

$$A_2 = \frac{\{(II_1 + II_2)J - W\}(G_1 - 1) - (c_2 F_2 - c_1 F_1) \lambda_2 S_2 (\tau_1 - a_1)}{(G_1 - 1) \lambda_2 S_2 (\tau_2 - a_2) + (G_2 - 1) \lambda_1 S_1 (\tau_1 - a_1)} \quad (25.2)$$

$$B_1 = T_H + c_1 F_1 + A_1 G_1 \quad (25.3)$$

$$B_2 = T_H + c_2 F_2 - A_2 G_2. \quad (25.4)$$

The temperature difference  $\Delta T_2$  is

$$\Delta T_2 = \frac{(II_1 + II_2)J - W + c_1 F_1 S_1 \lambda_1 (\tau_1 - a_1)/(G_1 - 1) + c_2 F_2 S_2 \lambda_2 (\tau_2 - a_2)/(G_2 - 1)}{\lambda_1 S_1 (\tau_1 - a_1)/(G_1 - 1) + \lambda_2 S_2 (\tau_2 - a_2)/(G_2 - 1)}. \quad (26)$$

This result can be calculated numerically or be expressed in the form of the sum of the power series if  $\varepsilon_i L_i < 1$  and  $\tau_i L_i < 1$ . But these calculations are so laborious that we will use some additional assumptions in order to simplify the calculation, namely we assume that the Thomson effect can be neglected. Then this result is compared to  $\Delta T_0$  instead of  $\Delta T_1$ . In this case eqs. (22)~(26) are not applicable because  $\tau_i = a_i$ . After some calculations we get the following result.

$$\Delta T_2^* = \frac{(II_1 + II_2)J - W + (\lambda_1 S_1 c_1 F_1^*/G_1^*) + (\lambda_2 S_2 c_2 F_2^*/G_2^*)}{(\lambda_1 S_1/G_1^*) + (\lambda_2 S_2/G_2^*)}, \quad (27)$$

where 
$$F_i^* = - (1/\varepsilon_i) \int_0^{L_i} (1 + \gamma_i x)^{-1} \ln(1 + \varepsilon_i x) dx \quad (28)$$

and 
$$G_i^* = (1/\gamma_i) \ln(1 + \gamma_i L_i). \quad (29)$$

Now we set  $\varepsilon_1 L_1 = \varepsilon_2 L_2 = \varepsilon L$ ,  $\gamma_1 L_1 = \gamma_2 L_2 = \gamma L$ , then  $F_1^* = F_2^* = F^*$  and  $G_1^* = G_2^* = G^*$ , and eq. (29) becomes

$$\Delta T_2^* = \frac{\{(II_1 + II_2) - (kT/e) \varepsilon L (2F^*/LG^*)\} J}{\{(\lambda_1 S_1/L_1) + (\lambda_2 S_2/L_2)\} (L/G^*)} - \frac{(1/2) \{(\rho_1 L_1/S_1) + (\rho_2 L_2/S_2)\} J^2 (2F^*/LG^*) - W}{\{(\lambda_1 S_1/L_1) + (\lambda_2 S_2/L_2)\} (L/G^*)} \quad (30)$$

The current  $J_{e2}^*$  which makes the temperature difference  $\Delta T_2^*$  maximum is

$$J_{e2}^* = \{ (II_1 + II_2) - (kT/e) \varepsilon L (2F^*/LG^*) \} / \{ (\rho_1 L_1/S_1) + (\rho_2 L_2/S_2) \} (2F^*/LG^*), \quad (31)$$

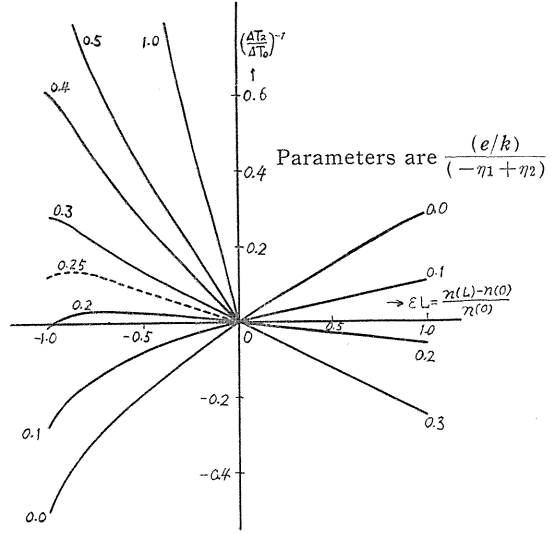
and this is substituted in eq. (30). The result is

$$\Delta T_2^* = \Delta T_0 \left\{ 1 - \frac{(k/e)\varepsilon L}{-\eta_1 + \eta_2} \left( \frac{2F}{LG} \right) \right\}^2 \left( \frac{G^{*2}}{2F^*} \right). \quad (32)$$

Numerical calculations of eq. (31) were carried out and the results for the case of  $\gamma_i=0$  are shown in Fig. 2, because the electronic contribution to the thermal conductivity seems to be small in semiconductor.

The maximum temperature difference obtained by Suge-Aoki<sup>7)</sup> for Bi-Te alloy is about 30° C, where  $-\eta_1 + \eta_2 = 320 \mu\text{V/deg.}$ , which correspond to  $(e/k)/(-\eta_1 + \eta_2) = 1/4$ . For this case it is found from Fig. 2 that the maximum of the increase in temperature difference occurs at about  $\varepsilon L = -0.9$  and its increments is about 14%.

FIG. 2. Increase of the temperature difference as the function of the gradient of the carrier concentration for the case of  $\mu=0$  and  $\gamma=0$ .



#### 4. Effect of Changing Sectional Area

Here we discuss only the case where sectional area  $S_i$  is represented by the linear function of  $x_i$ , i.e.,

$$S_i(x_i) = S_i(1 + a_i x_i). \quad (33)$$

Calculations were carried out as in 2. The result is

$$T_i = - (A_i/b_i) \{ S_i(1 + a_i x_i) \}^{-b_i} - c_i \ln S_i(1 + a_i x_i) + B_i, \quad (34)$$

where

$$A_1 = \frac{\{ (\Pi_1 + \Pi_2)J - W - \sum_{i=1}^2 (\lambda_i \rho_i J_i / \mu_i) \} \{ (1 + a_2 L_2)^{-b_2} - 1 \} / (S_1^{b_1} b_2)}{(\lambda_2 a_2 S_2 / b_1) \{ (1 + a_1 L_1)^{-b_1} - 1 \} + (\lambda_1 a_1 S_1 / b_2) \{ (1 + a_2 L_2)^{-b_2} - 1 \} - (\lambda_2 a_2 S_2 / S_1^{b_1}) \sum_{i=1}^2 c_i \ln (1 + a_i L_i)} \quad (35.1)$$

$$A_2 = \frac{\{ (\Pi_1 + \Pi_2)J - W - \sum_{i=1}^2 (\lambda_i \rho_i J_i / \mu_i) \} \{ (1 + a_1 L_1)^{-b_1} - 1 \} / (S_2^{b_2} b_1)}{(\lambda_2 a_2 S_2 / b_1) \{ (1 + a_1 L_1)^{-b_1} - 1 \} + (\lambda_1 a_1 S_1 / b_2) \{ (1 + a_2 L_2)^{-b_2} - 1 \} + (\lambda_1 a_1 S_1 / S_2^{b_2}) \sum_{i=1}^2 c_i \ln (1 + a_i L_i)} \quad (35.2)$$

$$B_1 = T_H + A_1[\{S_1(1 + a_1 L_1)\}^{-b_1/b_1}] + c_1 \ln S_1(1 + a_1 L_1), \quad (35.3)$$

$$B_2 = T_H + A_2[\{S_2(1 + a_2 L_2)\}^{-b_2/b_2}] + c_2 \ln S_2(1 + a_2 L_2), \quad (35.4)$$

$$\text{and} \quad b_1 = \mu_1 J / \lambda_1 a_1 S_1, \quad b_2 = -\mu_2 J / \lambda_2 a_2 S_2, \quad c_1 = \lambda_1 b_1 / \mu_1, \quad c_2 = \lambda_2 b_2 / \mu_2. \quad (35.5)$$

The temperature difference  $\Delta T_3$  is given as

$$\Delta T_3 = \frac{\{(I_1 + I_2)J - W - \sum_{i=1}^2 (\lambda_i \rho_i J_i / \mu_i)\}}{\sum_{i=1}^2 [a_i b_i \lambda_i S_i / \{1 + (1 + a_i L_i)^{-b_i}\}] - \frac{\sum_{i=1}^2 [\lambda_i a_i b_i c_i S_i \ln(1 + a_i L_i) / \{1 - (1 + a_i L_i)^{-b_i}\}]}{\sum_{i=1}^2 [a_i b_i \lambda_i S_i / \{1 - (1 + a_i L_i)^{-b_i}\}]} \quad (36)$$

If  $a_1 L_1 < 1$  and  $a_2 L_2 < 1$ , then the eq. (36) can be expanded and the final result is

$$\Delta T_3 = \Delta T_0 \left\{ 1 + \frac{4}{3} \left( \frac{-\mu_1 + \mu_2}{-\eta_1 + \eta_2} \right) \frac{\Delta T_0}{T_L} + \frac{2}{3} \left( \frac{-\mu_1 + \mu_2}{-\eta_1 + \eta_2} \right) \frac{\Delta T_0}{T_L} aL + O(\mu_i^2) \right\}. \quad (37)$$

In this we assume that  $a_1 L_1 = a_2 L_2 = aL$ . From this equation, it is found that the effect of changing the sectional area appears only through the effect of Thomson heat, so that this effect seems not to be serious. If we neglect the Thomson effect, we can easily see that  $\Delta T_3$  is exactly the same as the earlier theory.

## 5. Conclusion

In cooling experiments of the element of the thermoelectric refrigerator, there was differences between the earlier theory and experiments. These differences are interpreted as the effect of Thomson heat. Thomson effect causes the temperature difference to be large, but this becomes smaller by the heat  $W$  flowing into the cold junction. As the result, the temperature difference does not so largely differs from the earlier theory in spite of the presence of the heat  $W$ . On the other hand, the current corresponding to maximum temperature difference is little affected by the heat  $W$ , and the difference between the earlier theory and the experiment becomes appreciable. This difference well explained quantitatively by our theory.

It is found that the temperature difference can be increased by changing its carrier concentration along the current flow. The presence of the gradient of the carrier concentration lead to following two effects; the one is the thermoelectric heat (absorption or generation) which is proportional to the product of the current density and the gradient of the carrier concentration, the other is the change of Joule heat. As these two effects oppose each other, optimum gradient of the carrier concentration exists for certain given boundary conditions at the cold junction. But the presence of two opposing effects restrains the increase of the temperature difference for actual case. For example, this maximum increase would be 14% for Bi-Te alloy.

The effect of changing sectional area is summarized as follows. This effect does no appear directly, and appears only through the effect of Thomson heat. As the result this effect is not so serious, and it would be several per cent.



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