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The Effect of Thermally Produced Lattice Defects on the Electrical Properties of Tellurium*

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Synopsis

The electrical properties of tellurium crystals are re-investigated under the assumption of excess holes in the valence band owing to the trapping of electrons by the lattice defects generated by the thermal excitation of lattice atoms. From the observed data of the electrical conductivity and the Hall effect, and by applying the treatment of composite semiconductor in which the extrinsic acceptors and the thermally produced acceptors both generate holes other than the intrinsic pair excitations of electrons and holes, the width of the forbidden energy band ΔE, the effective masses of electrons and holes m_e and m_h, and the carrier mobilities due to the lattice scattering μ_{eL} and μ_{hL} are determined as $\Delta E = 0.32 + 1.9 \times 10^{-4} T$ eV, $m_e = 0.68\,m$, $m_h = 0.91\,m$ and $\mu_{eL} = 2.1\mu_{hL} = 6.1 \times 10^6 T^{-\frac{3}{2}}$ cm^2/volt·sec.

The sign reversals of Hall effect and thermoelectric power from minus at lower temperatures to plus at higher ones found in the pure intrinsic region are explained by the predominance of holes released from the lattice defects the concentration of which increases with the rise of temperature, and the optimum fit of the calculated characteristics to the observed one is obtained by assuming the activation energy to produce one lattice defect as 0.52 eV.

I. Introduction

Previously we measured the electrical properties of highly purified tellurium crystals and tried to deduce the electron characteristics on the basis of the semiconductor band scheme, that is, the value of the forbidden band width, the concentrations, the mobilities and the effective masses of electrons and holes, etc. in tellurium in terms of the resistivity, the Hall coefficient and the magnetoresistive coefficient of the purest specimen in a high temperature region by applying the theory of *intrinsic* semiconductor(1). Furthermore, using these quantities we could explain substancially the observed bahaviour of the thermoelectric power(2). These treatments have given fairly reasonable results throughout the temperature range, with the exception of one abnormal character that the effective mass of electrons m_e increases with temperature rise, in contrast to little change of the hole mass m_h, from $0.67\,m$ at low temperatures, via $m_e = m_h = 0.85m$ at 520°K to $0.93\,m$ at 600°K. This temperature dependence of the electron mass originated from the sign reversal of Hall coefficient at 520°K from minus at lower temperatures to plus at higher ones which is the proper behaviour to tellurium.

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* The 749th report of the Research Institute for Iron, Steel and Other Metals.

(1) T. Fukuroi, S. Tanuma, S. Tobisawa, Sci. Rep. RITU (A), **1** (1949), 373.

(2) T. Fukuroi, S. Tanuma, Sci. Rep. RITU (A), **4** (1952), 353.

We supposed at that time: if assuming a dual conduction band scheme consisting from one filled band and two overlapping conduction bands whose bottoms are slightly shifted each other and the lower one of them gives a smaller effective mass and the higher gives a larger one compared with the effective mass in the filled band, the above peculiar result on the electron mass might be understood. Furthermore the suggested band model also lends itself to account qualitatively for the disagreement of the temperatures of sign reversal of the Hall coefficient and the thermoelectric power, that is, the temperature of the former reversal (520°K) is higher than that of the latter (450°K).

On the other hand, such facts are reported lately that the lattice defects which rise in the crystal in thermal equilibrium may trap electrons hence generating positive holes in the filled band as in the cases of germanium by Mayburg and Rotondi and others[3] and selenium by Kaneko[4]. In the case of germanium, the generation of acceptors is found by virtue of quenching the crystals after the heat treatments at various elevated temperatures and this acceptor action owes at least partly to the lattice defects which are generated thermally with the activation energy of 1.5~2.2 eV; and in the case of selenium, the crystals quenched from elevated temperatures show marked increases of the electrical conductivity as well as the specific volume but no change of the lattice constant compared with the case before such heat processes, and this means that the defects of Schottky type which provide the acceptor action are generated predomi-

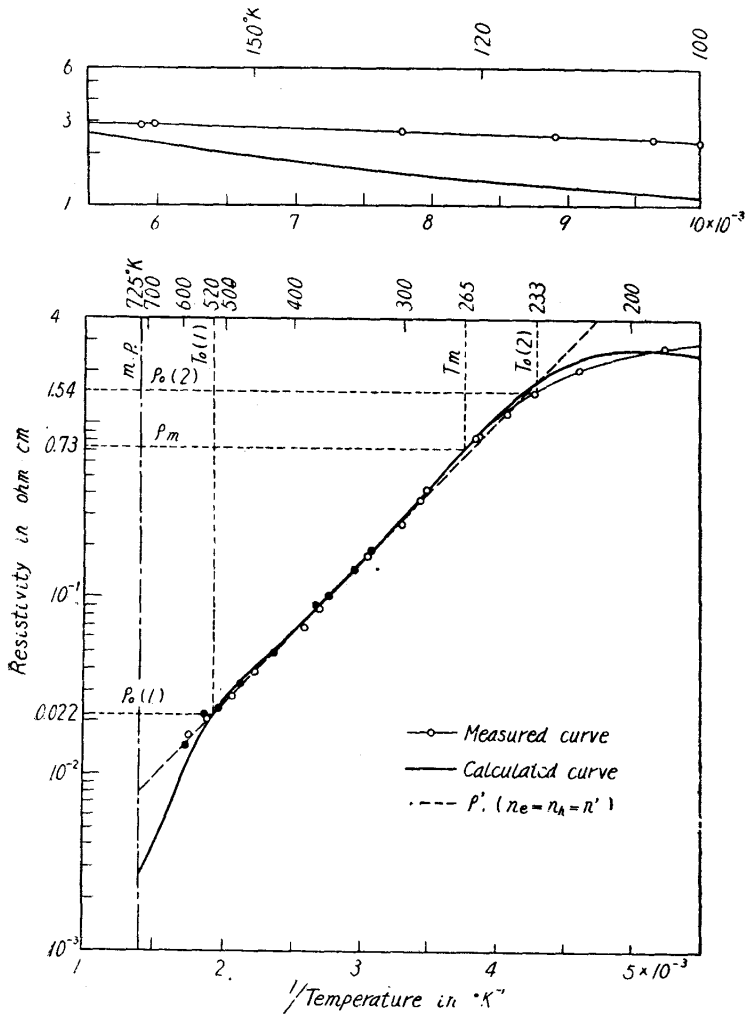

Fig. 1. Electrical resistivity as a function of the inverse absolute temperature. ○ and ● represent respectively the second and the third measurement on the specimen No. 1, i. e. the curves (I, 2) and (I, 3) in the reference (1).

(3) S. Mayburg, L. Rotondi, Phys. Rev., **91** (1953), 1015; R. A. Logan, Phys. Rev., **91** (1953), 757; L. Esaki, Phys. Rev., **89** (1953), 1026; C. Goldberg, Phys. Rev., **88** (1952), 920.

(4) H. Kaneko, Private communication to Prof. Fukuroi.

nantly during the heat treatment and frozen in the interior of the crystal by the quenching process. Thus the similar effect can be naturally conjectured in tellurium also, and it is noticed that this effect was previously discussed in connection with the reversal of the Hall effect in tellurium by Fritzsche[5].

In the present study we leave the above mentioned dual conduction band scheme, and attempt to evaluate the effect of the acceptor action of thermally produced lattice defects to the electrical properties of tellurium, especially the thermoelectric power as well as the Hall effect.

As the experimental data of the electrical properties, i. e. the electrical resistivity, the Hall coefficient and the thermoelectric power, of tellurium, we use the results corresponding to the second measurement of the specimen No. I designated (I, 2) in the reference (1) which was submitted to the previous analysis above mentioned, and these data are inserted again in Fig. 1, 2 and 3 as the empty circles.

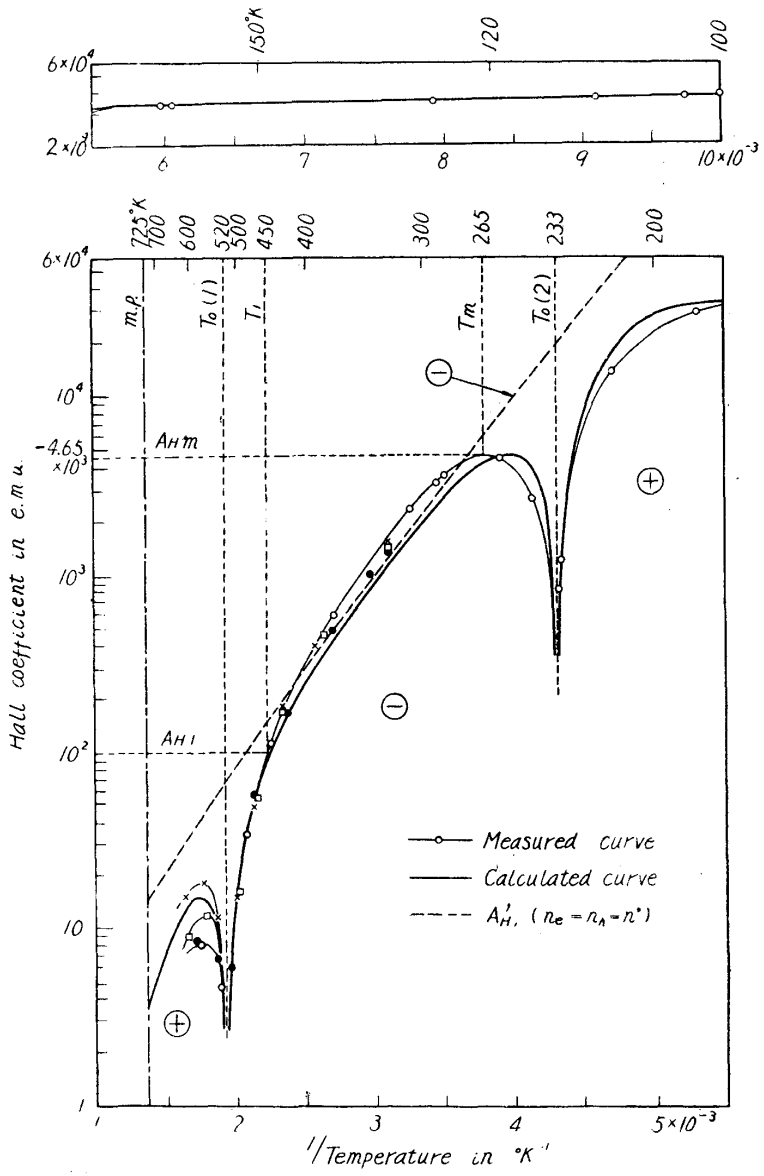

Fig. 2. Hall coefficient as a function of the inverse absolute temperature. ○ and ● represent respectively the second and the third measurement on the specimen No. 1, i. e. the curves (I, 2) and (I, 3) in the reference (1) ; □ and × represent respectively the adiabatic value by the D.C. method and the isothermal one by the 1000 cps A.C. method measured simultaneously in the reference (10).

II. General treatment of a composite semiconductor

We describe first the way to obtain the width of forbidden band and the effective masses and the mobilities of electrons and holes from the deta of the resistivity

(5) H. Fritzsche, Science, **115** (1952), 571.

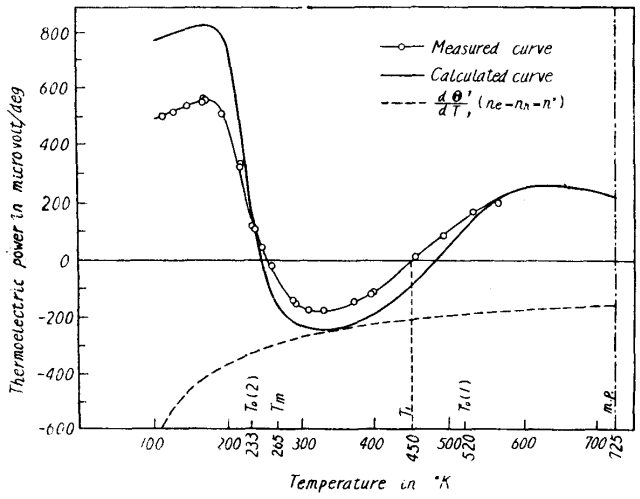

Fig. 3. Thermoelectric power as a function of the isothermal temperature. ○ represents the second measurement on the specimen No. 1, i.e. the curves (I, 2) in the reference (1).

and the Hall effect in case of a composite semiconductor in which the concentrations of electrons and holes vary with each other as the temperature changes.

(1) General expression

The formula of resistivity ρ, the Hall coefficient A_H and the thermoelectric power $\frac{d\Theta}{dT}$ in case of a non-degenerate composite semiconductor are as follows,

$$\rho = \{|e|\mu_h(n_h + n_e b)\}^{-1}$$
$$= 6.24 \times 10^{18}(\mu_h \text{ in } \mathrm{cm^2/volt\cdot sec})^{-1}(n_h + n_e b)^{-1} \text{ ohm}\cdot\text{cm}, \quad (1)$$

$$A_H = \frac{3\pi}{8c|e|}\frac{n_h - n_e b^2}{(n_h + n_e b)^2}$$
$$= 7.35 \times 10^{19}\frac{n_h - n_e b^2}{(n_h + n_e b)^2} \text{ e. m. u.}, \quad (2)$$

$$\left.\begin{aligned}\frac{d\Theta}{dT} &= \frac{k}{|e|}\left\{\frac{1}{n_h + n_e b}\left[(n_h - n_e b)\left(2 + \ln\frac{2(2\pi mk)^{3/2}}{h^3} + \frac{3}{2}\ln T\right) - n_h\left(\ln n_h - \frac{3}{2}\ln\frac{m_h}{m}\right)\right.\right.\\ &\left.\left. + n_e b\left(\ln n_e - \frac{3}{2}\ln\frac{m_e}{m}\right)\right] + \left(\frac{n_e b}{n_h + n_e b}\frac{\beta}{k} - \frac{1}{k}\frac{\partial\chi}{\partial T}\right)\right\},^{\text{reference (2),*}}\\ \frac{k}{|e|} &= 86.2 \text{ microvolt/deg}.\end{aligned}\right\} \quad (3)$$

Furthermore, from the equilibrium condition,

$$\sqrt{n_e n_h} = 2\frac{(2\pi mk)^{3/2}}{h^3}\left(\frac{m_e m_h}{m^2}\right)^{3/4} T^{3/2}\exp\left(-\frac{\Delta E(0) + \beta T}{2kT}\right) \equiv n' \quad (4)$$

In the above equations e and m are the charge and the mass of an electron, k is the Boltzmann constant, n_e, n_h, μ_e, μ_h and m_e, m_h are the concentrations, the mobilities and the effective masses of electrons in the conduction band and holes in the valence band respectively, b is the ratio of μ_e to μ_h, $\Delta E(T) = \Delta E(0) + \beta T$ is the width of the forbidden band, β is the temperature coefficient of ΔE and $\frac{\partial\chi}{\partial T}$ is the rate of energy shift of the upper edge of the valence band due to the change of temperature.

(2) Mobility ratio and forbidden band width

From Eq. (2) and (4), the condition that the Hall coefficient becomes zero is,

$$\left.\begin{aligned} n_e &= n'/b,\\ n_h &= n'b.\end{aligned}\right\} \quad (5)$$

* Eq. (16) and (17) in the reference (2) including a few misscoppies of the original manuscript should be read as Eq. (3) here.

And the condition that the Hall coefficient takes the extreme value is obtained in the following way. Let n_a be the activated acceptor concentration, $n_h - n_e = n_a$ holds and Eq. (2) is expressed as next,

$$A_H = \frac{3\pi}{8c|e|} \frac{n_a + n_e(1-b^2)}{\{n_a + n_e(1+b)\}^2} . \qquad (6)$$

At such temperatures that all of the acceptors N_{ex} due to impurity atoms and frozen-in lattice defects are ionized but the number of lattice defects in thermal equilibrium is yet negligible, $n_a(=N_{ex})$ remains constant, and further, if b is assumed to be temperature-independent, the condition that A_H takes an extreme value is given by $\frac{\partial A_H}{\partial n_e} = 0$, that is,

$$\left.\begin{aligned} n_e &= \frac{1}{b-1} N_{ex}, \\ n_h &= \frac{b}{b-1} N_{ex}. \end{aligned}\right\} \qquad (7)$$

By substituting Eq. (4),

$$\left.\begin{aligned} n_e &= n'/\sqrt{b}, \\ n_h &= n'\sqrt{b}. \end{aligned}\right\} \qquad (8)$$

While $\frac{\partial^2 A_H}{\partial n_e^2}$ takes the value $\frac{2(1+b)^2\{N_{ex}(2b+1) + n_e(b^2-1)\}}{\{N_{ex} + n_e(1+b)\}^4}$ which is always positive in the ordinary case of $b \gtrsim 1$, thus A_H(extreme) takes the *minimum* value as the next expression,

$$A_{Hm} = -\frac{3\pi}{32c|e|} \frac{(b-1)^2}{bN_{ex}} . \qquad (9)$$

From Eq. (5) and Eq. (8), the resistivity ρ_0 and ρ_m respectively at the temperature T_0 at which the Hall coefficient becomes zero and at T_m at which the Hall coefficient takes the minimum value are given by

$$\rho_0 = \{|e|(b+1) \cdot \mu_h(T_0) \cdot n'(T_0)\}^{-1}, \qquad (10)$$

and

$$\rho_m = \{2|e|\sqrt{b} \cdot \mu_h(T_m) \cdot n'(T_m)\}^{-1}. \qquad (11)$$

In case that the carrier mobilities are prescribed by the lattice scattering alone, the next expressions hold[6],*

$$\left.\begin{aligned} \mu_e &= \sqrt{8\pi}\, e\hbar^4 c_{ii}/3E_{1c}^2 m_e^{5/2} k^{3/2} T^{3/2}, \\ \mu_h &= \sqrt{8\pi}\, e\hbar^4 c_{ii}/3E_{1v}^2 m_h^{5/2} k^{3/2} T^{3/2}. \end{aligned}\right\} \qquad (12)$$

where c_{ii} is the elastic constant, E_{1c} and E_{1v} are the energy shift of the edges of the conduction and valence bands respectively owing to the unit dilation of the lattice constant. As c_{ii}, E_{1c} and E_{1v} scarcely depend upon temperature, μ varies with $T^{-3/2}$ and b does not vary with temperature as assumed in deducing Eq. (7), namely,

$$b = \left(\frac{m_e}{m_h}\right)^{-5/2} \left(\frac{E_{1c}}{E_{1v}}\right)^{-2} \simeq \left(\frac{m_e}{m_h}\right)^{-5/2}. \qquad (13)$$

(6) e. g., W. Shockley, *Electrons and Holes in Semiconductors* (D. Van-Nostland Co., New York, 1950), 333.

* These μ_e and μ_h are denoted as μ_{eL} and μ_{hL} respectively in Eq. (24).

Then $\Delta E(0)$ is given from Eq. (4), (10), (11) and (12) as follows,

$$\Delta E(0) = 2k\left(\frac{1}{T_m} - \frac{1}{T_0}\right)^{-1}\left(\ln\frac{\rho_m}{\rho_0} + \ln\frac{2\sqrt{b}}{b+1}\right). \tag{14}$$

The Hall coefficient at purely extrinsic and exhaustive range, namely in the case that no electron exists and all acceptors are ionized,

$$A_{Hex} = \frac{3\pi}{8c|e|}\frac{1}{N_{ex}}. \tag{15}$$

Combinning Eq. (9) and (15), b is expressed by the two Hall values,

$$-\frac{(b-1)^2}{4b} = \frac{A_{Hm}}{A_{Hex}}. \tag{16}$$

Substituting the experimental values listed in Table 1 for Eq. (14) and (16), we obtain the actual values of b and $\Delta E(0)$,

$$b = 2.1, \tag{17}$$

$$\Delta E(0) = 0.32\,\text{eV} \text{ from } \rho_0(1) \text{ and } \rho_m, \tag{18}$$

and

$$\Delta E(0) = 0.27\,\text{eV} \text{ from } \rho_0(2) \text{ and } \rho_m. \tag{18'}$$

We abandan the latter value of $\Delta E(0) = 0.27\,\text{eV}$ which is determind by the use of $\rho_0(2)$ at $T_0(2)$, because the hole mobility μ_h of this specimen in the temperature range lower than ca 250°K is found to imply some other extrinsic scattering mechanism besides the lattice phonon scattering as shown later in Fig. 6, therefore Eq. (12) is not valid exactly at $T_0(2)$ and then Eq. (14) cannot be applicable.

Table 1

$T_0(1) = 520°K$	$T_1 = 450°K$	$T_m = 265°K$	$T_0(2) = 233°K$
$\rho_0(1) = 0.022$ ohm·cm		$\rho_m = 0.73$ ohm · cm	$\rho_0(2) = 1.54$ ohm · cm
$A_H = 0$	$A_{H1} = -100$ e.m.u.	$A_{Hm} = -4.65\times10^3$ e.m.u.	$A_H = 0$

$A_{Hex} = +3.20\times10^4$ e.m.u. (extrapolated from the low temperature measurements)
$N_{ex} = 2.30\times10^{15}$

(3) Effective masses and mobilities

The activated acceptor concentration n_{a0} at zero Hall coefficient is expressed as follows, by applying Eq. (4) and (5) to the relation $n_h - n_e = n_a$

$$n_{a0} = \frac{b^2-1}{b}n' = \frac{b^2-1}{b}\cdot\frac{2(2\pi mk)^{3/2}}{h^3}\left(\frac{m_e m_h}{m^2}\right)^{3/4} T_0^{3/2}\exp\left(\frac{-\beta}{2k}\right)\exp\left(\frac{-\Delta E(0)}{2kT_0}\right). \tag{19}$$

At $T_0 = T_0(2) = 233°K$, $n_{a0} \fallingdotseq N_{ex} = 2.3\times10^{15}$ per c.c. as found in Fig. 4 which is calculated from the low temperature measurements of Hall effect, b and $\Delta E(0)$ is given by Eq. (17) and (18), we can calculate $\frac{m_e m_h}{m^2}$ from Eq. (19) if β is given. Now we use the value of β obtained by Moss[7] from the experiments of the infra-red absorption, that is,

$$\beta = +1.9\times10^{-4}\ \text{eV/deg}. \tag{20}$$

Thus we obtain the next value,

(7) T. S. Moss, Phys. Rev., **79** (1950), 1011, *Photoconductivity in the Elements* (Butterworth Scientific Publications, London, 1952), 226, $\beta = 2.1\sim1.7\times10^{-4}$ eV/deg. According to his private communication to Prof. Fukuroi, $\Delta E = 0.355\sim0.390$ eV at the liquid air temperature and $\beta = 1.9\times10^{-4}$ eV/deg.

$$\frac{m_e}{m} \cdot \frac{m_h}{m} = 0.61 . \quad (21)$$

Then the value of effective masses m_e and m_h are calculated from Eq. (13), (17) and (21),

$$\left.\begin{aligned} \frac{m_e}{m} &= 0.68 \\ \frac{m_h}{m} &= 0.91 \end{aligned}\right\} \quad (22)$$

Thus we arrive at the evaluation of Eq. (4) which is the expression for the carrier concentration n' in the case of purely intrinsic semiconductor, by the use of Eq. (18), (20) and (21).

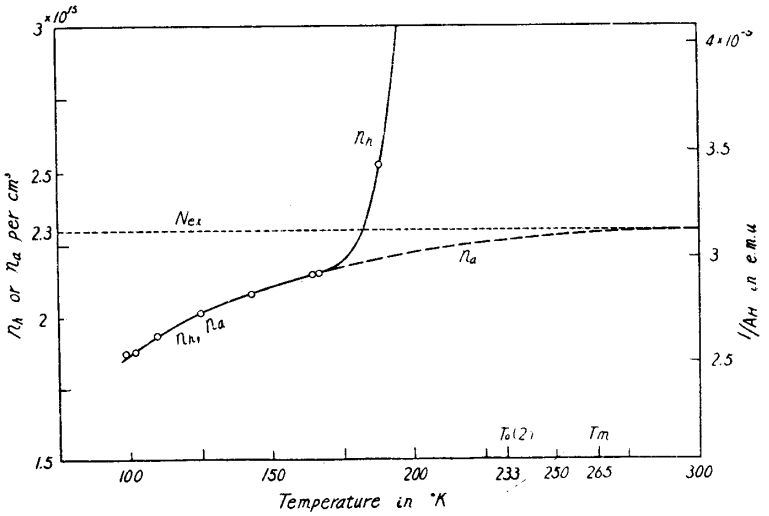

Fig. 4. Concentrations of holes and activated acceptors as determined from the Hall data at low temperatures. The values designated as ○ are calculated from $n_h = 7.35 \times 10^{19}$. $(|A_H| \text{ in emu})^{-1}$ cm^{-3}, and the curve n_a are extrapolated from the completely extrinsic part of the curve n_h.

$$n' = 1.12 \times 10^{15} T^{3/2} \exp\left(- \frac{1.85 \times 10^3}{T} \right) . \quad (23)$$

The mobility μ_L in the lattice scattering range, which is expressed approximately as $\mu_L = \text{constant} \cdot T^{-3/2}$ from Eq. (12), is obtained from Eq. (10) or (11) by employing Eq. (17) and (23) and the data in Table 1. When calculations are performed at $T_0(1) = 520°K$,* it follows,

$$\left.\begin{aligned} \mu_{hL} &= 2.8_8 \times 10^6 T^{-3/2} \text{ cm}^2/\text{volt} \cdot \text{sec}, \\ \mu_{eL} &= b\mu_{hL} = 6.0_6 \times 10^6 T^{-3/2} \text{cm}^2/\text{volt} \cdot \text{sec}, \end{aligned}\right\} \quad (24)$$

and at room temperature ($T = 300°K$), $\mu_{hL} = 553$ cm^2/volt·sec and $\mu_{eL} = 1160 cm^2$/volt·sec.

We remark that β, the temperature coefficient of the variation of forbidden region, can be estimated from the above data by the Fukuroi's procedure(8). By this treatise, β is regarded as the superposition of two parts, one of which originates from the lattice dilation, say, β_{I}, and the other originates from the lattice vibration, say, β_{II}. As the result of the calculations employing the above determined values of $\frac{m_e}{m}$, $\frac{m_h}{m}$, μ_{eL} and μ_{hL}, we obtain the following values**,

$$\beta_{\text{I}} = + 2.6 \times 10^{-4} \text{ eV/deg},$$
$$\beta_{\text{II}} \simeq - 0.7 \times 10^{-4} \text{ eV/deg}.$$

Therefore $\beta = \beta_{\text{I}} + \beta_{\text{II}} \simeq + 1.9 \times 10^{-4}$ eV/deg.

This coincides with Eq. (20) and our adoption of the datum by Moss is found to be self consistent.

* If employing the value at $T_m = 265°K$, we obtain $\mu_{hL} = (2.1)^{-1} \mu_{eL} = 2.8_5 \times 10^6 T^{-\frac{3}{2}} cm^2$/volt·sec, which almost agrees with Eq. (24).

** β_{I} is obtained as the product of the thermal expansion coefficient and $|E_{1c}| + |E_{1v}|$ which is calculated from Eq.(12), and β_{II} is only the average of two values one of which is calculated by the theory of Fan, $\beta_{\text{II}} = -1.0 \times 10^{-4}$ eV/deg, and the other by the theory of Mutô and Ôyama, $\beta_{\text{II}} = -0.4 \times 10^{-4}$ eV/deg. (H. Y. Fan, Phys. Rev., **82** (1951), 96; T. Mutô, S. Ôyama, Progr. theor. Phys., **5** (1950), 833; **6** (1951), 81)

(8) T. Fukuroi, Sci. Rep. RITU (A), **3** (1951), 175.

III. Concentrations of lattice defects and charge carriers

We consider that the upper reversal of Hall sign at $T_0(1)$ results from the increased acceptors due to the lattice defects which are generated in thermal equilibrium, of which density N_d is expressed as follows[9] if the defects of Schottky type predominate as in the case of selenium above mentioned,

$$N_d = N_L \alpha \exp\left(-\frac{\varepsilon(0)}{2kT}\right) \tag{25}$$

where N_L is the density of lattice sites, α is a numerical constant as the product of two factors one of which is originated from the change of the vibrational modes of lattice atoms neighbouring to the vacancy and the other owes to the temperature coefficient of the activation energy for generating a vacancy and $\varepsilon(0)$ is the temperature independent part of the activation energy.

The next relation holds from Eq. (5) when the Hall coefficient becomes zero, if we put ΔE_1 the activation energy of acceptor levels on avarage, and ϕ the height of Fermi level both measured from the top of the valence band,

$$\frac{b^2-1}{b} n' = n_a = \frac{N_d + N_{ex}}{1 + \exp\left(\frac{\Delta E_1 - \phi}{kT_0}\right)}. \tag{26}$$

As b, $n'(T)$ and N_{ex} are known respectively from Eq. (17), (23) and Table 1, we can calculate the value of N_d at $T_0(1)$ from Eq. (26) by the use of next approximation*,

$$n_a = n_h - n_e \fallingdotseq N_d + N_{ex}. \tag{27}$$

We obtain

$$N_d(520^\circ\mathrm{K}) = 6.1 \times 10^{17}. \tag{28}$$

There exists no way to deduce $\varepsilon(0)$ uniquely from the present data, thus we take somewhat ambiguous choice to determine $N_d(T_1)$ at one convenient temperature T_1 to fit the calculated value of Hall coefficient with observed one, namely, we calculate first n_e and n_h at T_1 by the use of Eq. (2), (4) and (23) and then obtain N_d from Eq. (27). In practice, we adopt $T_1 = 450^\circ\mathrm{K}$ at which temperature the adiabatic Hall coefficient is found to coincide with the isothermal one[10] and that the thermoelectric power becomes zero[10]. By the use of $A_{H1} = -100$ emu as shown in Table 1, we find at $450^\circ\mathrm{K}$: $n_h = 2.33\times10^{17}$, $n_e = 1.33\times10^{17}$, and

$$N_d(450^\circ\mathrm{K}) = 9.9\times10^{16}. \tag{29}$$

It follows from Eq. (25),

$$\varepsilon(0) = -k\left(\frac{1}{T_0} - \frac{1}{T_1}\right)^{-1}\left\{\ln N_d(T_0) - \ln N_d(T_1)\right\}. \tag{30}$$

Thus substituting for Eq. (28) and (29), we obtain

$$\varepsilon(0) = 0.52 \text{ eV}, \tag{31}$$

* This approximation is checked to give an error in $N_d(T_0)$ not more than 3 per cent if $\Delta E_1 < 0.01$ eV or 10 per cent if $\Delta E_1 \sim 0.1$ eV, because ϕ amounts to 0.2 eV at $T_0(1)$ with 6×10^{17} acceptors/cc.

(9) e.g., N. F. Mott, R. W. Gurney, *Electronic Processes in Ionic Crystals*, (Clarendon Press, Oxford, 1940).

(10) T Fukuroi, S. Tobisawa, S. Tanuma, Sci. Rep. RITU (A), **2** (1950), 239.

and $$N_d = 6.8 \times 10^{22} \exp\left(-\frac{6.0\times10^3}{T}\right). \tag{32}$$

α in Eq. (25) is determined by Eq. (32) and $N_L = 3.0\times10^{22}$ in tellurium,

$$\alpha = 2.3 \tag{33}$$

Finally, n_e and n_h are expressed as functions of the temperature from Eq. (4) and (27),

$$\left.\begin{aligned} n_e &= \frac{1}{2}(-N + \sqrt{N^2 + 4n'^2}) \\ n_h &= \frac{1}{2}(N + \sqrt{N^2 + 4n'^2}) \end{aligned}\right\} \tag{34}$$

where $N = N_d + N_{ex}$.

The curves of n', N_d, n_e, n_h and N_{ex} are represented in Fig. 5 and the curve designated as n_a in the figure is the activated acceptors in the extrinsic region which is coppied from Fig. 4.

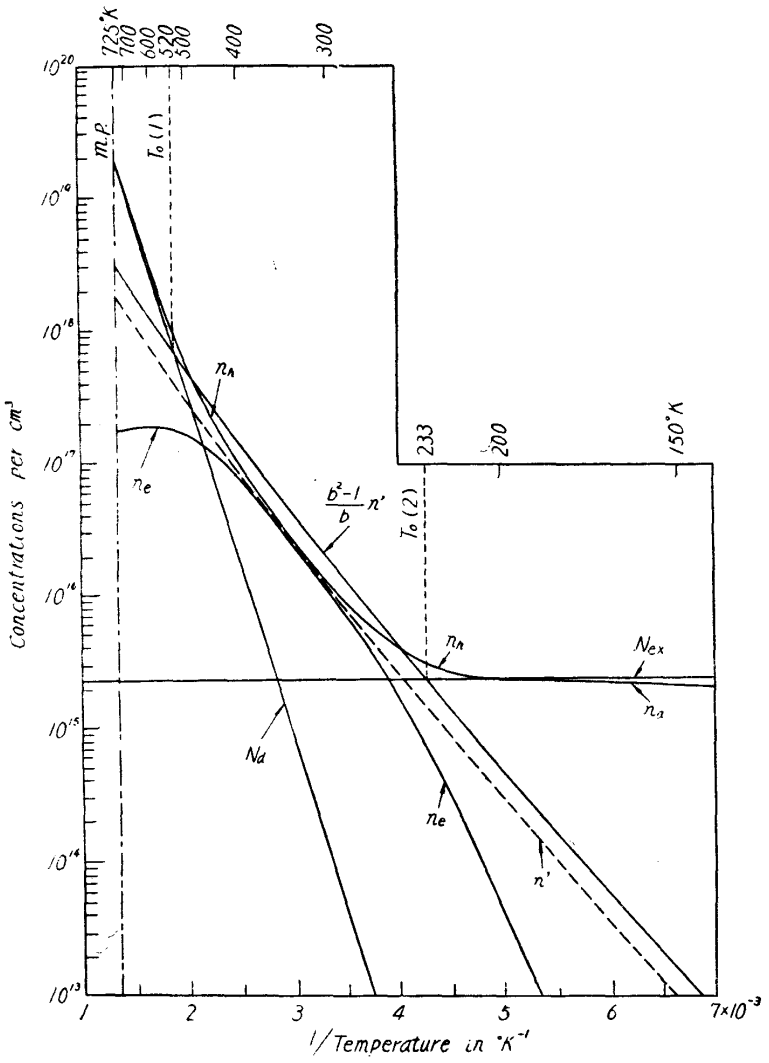

Fig. 5. Concentrations of electrons n_e, holes n_h, lattice defects N_d and extrinsic acceptors N_e as functions of the inverse absolute temperature.

IV. Calculation of resistivity, Hall effect and thermoelectric power

(1) Carrier mobilities

We have determined the carrier mobilities prescribed by the lattice scattering, μ_{eL} and μ_{hL} in Eq. (24). While the scattering mechanism due to the activated and neutral acceptors should also be taken into account, but here we shall estimate the effect of activated acceptors alone because of the approximation that all the acceptors is activated in the concerning temperature range. The mobility prescribed by the ionized impurity scattering is[11],

$$\mu_{\substack{eI\\h}} = \frac{2^{7/2}\kappa^2(kT)^{3/2}}{\pi^{3/2}Ne^3(m_{\substack{e\\h}})^{1/2}} \Big/ \ln\left[1 + \left(\frac{3\kappa kT}{eN^{1/3}}\right)^2\right], \tag{35}$$

(11) E. Conwell, V. F. Weisskopf, Phys. Rev., **77** (1950), 36.

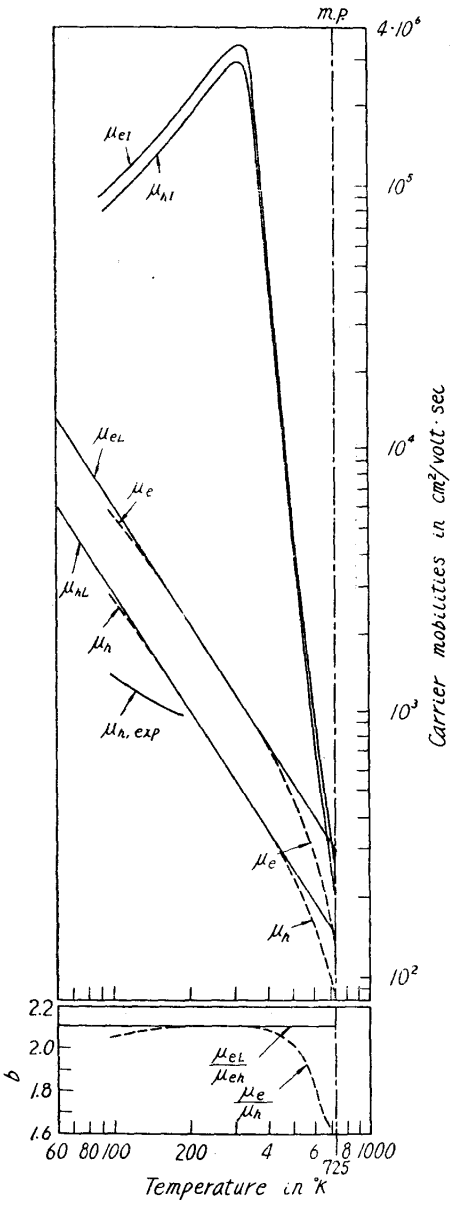

Fig. 6. Electron and hole mobilities due to lattice scattering, μ_{eL} and μ_{hL}, acceptor ion scattering, μ_{eI} and μ_{hI}, and of resultant, μ_e and μ_h; and mobility ratio b calcutated as functions of the inverse absolute temperature. The curve denoted as $\mu_{h,\,\mathrm{exp}}$ is obtained at lower temperatures by the use of experimental curves of resistivity and Hall coefficient as $\mu_{h,\,\mathrm{exp}}$ cm²/volt·sec $= 8.49\times10^{-2}\cdot(|A_H|$ in emu$)\cdot(\rho$ in ohm·cm$)^{-1}$.

where N is the concentration of the scattering centre, that is $N = N_{ex} + N_d$ and κ is the dielectric constant. In the case of tellurium, κ is found as 23 from the value of reflactive index $n = 4.8$ measured by Moss[12], μ_I becomes as follows,

$$\left.\begin{aligned}\mu_{eI} &= 2.1\times10^{18}T^{3/2}/\\ &\quad N\cdot\ln[1+1.7\times10^{9}T^{2}N^{-2/3}]\,\mathrm{cm^2/volt\cdot sec},\\ \mu_{hI} &= 1.8\times10^{18}T^{3/2}/\\ &\quad N\cdot\ln[1+1.7\times10^{9}T^{2}N^{-2/3}]\,\mathrm{cm^2/volt\cdot sec}.\end{aligned}\right\}\quad(36)$$

and the mobility ratio b_I due to the impurity scattering alone is,

$$b_I = \left(\frac{m_e}{m_h}\right)^{-1/2} = 1.2 \qquad (37)$$

The resultant mobilities can be calculated from the approximate relations as below,

$$\left.\begin{aligned}\mu_e &= (\mu_{eL}^{-1}+\mu_{eI}^{-1})^{-1},\\ \mu_h &= (\mu_{hL}^{-1}+\mu_{hI}^{-1})^{-1}.\end{aligned}\right\}\quad(38)$$

Fig. 6 shows the computed results of μ_L, μ_I and μ of electrons and holes and $b(=\mu_e/\mu_h)$. The curve designated as $\mu_{h,\,\mathrm{exp}}$ is obtained directly from the data of resistivity and Hall coefficient in the extrinsic range. A discrepancy is found between $\mu_{h,\,\mathrm{calc}}$ and $\mu_{h,\,\mathrm{exp}}$, and these pattern is similar to the case of a very pure silicon specimen reported by Pearson and Bardeen[13], but the cause of this discrepancy is not clarified.

Furthermore, in order to compare the previously obtained experimental values of hole mobilities corresponding to the variously impurity (antimony) doped specimens[14]*, μ_h at 80°K and 283°K are calculated by the use of Eq. (24), (36) and (38) as functions of the concentration of acceptors. The result is inserted with the experimentally determined values in Fig. 7. As the figure shows, a remarkable discrepancy is found between the

* The ordinate scale of Fig. 9(a) and 9(b) in the reference (14) should be read as the scale of Fig. 7 in the present paper.

(12) T. S. Moss, Proc. Phys. Soc. (B), **65** (1952), 62.
(13) G. L. Pearson, J. Bardeen, Phys. Rev., **75** (1949), 865.
(14) T. Fukuroi, S. Tanuma and S. Tobisawa, Sci. Rep. RITU (A), **4** (1952), 283.

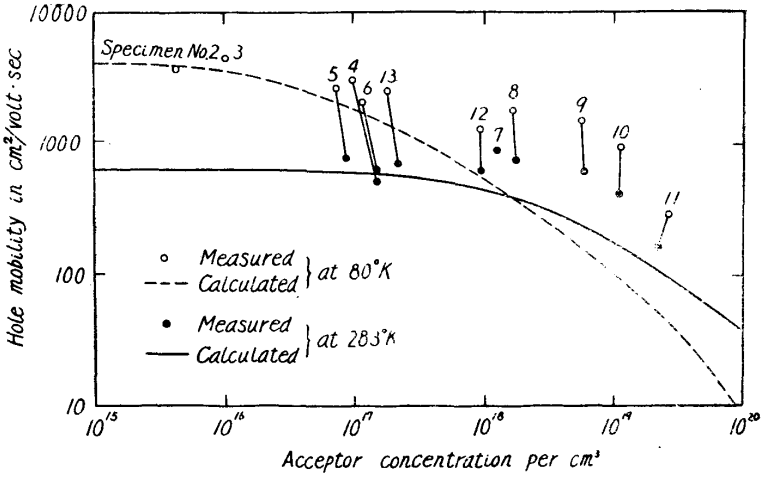

Fig. 7. Variation of hole mobility with acceptor concentration. ○ and ● represent respectively the experimentally determined value in the extrinsic range by the same formulae for $\mu_{h,exp}$ in Fig. 6, and the hole concentration of each specimen determined by the same formulae for n_h in Fig. 4 is taken as the value of the abscissa scale. (Reference (14))

experimental and calculated values, namely, though the observed μ_h of the purer samples agrees with the calculated μ_h consisting substantially of the lattice scattering mecanism, while the specimens which are densely doped with antimony maintain higher values of μ_h than the calculated ones. This fact suggests that the interaction potential to cause a collision of a carrier with an ionized acceptor is rather weaker than the potential of Coulomb type according to the point charge approximation of the trapped electron, and perhaps some screening effect may enter in the collision potential for a large orbit of the trapped electron. Now, at any rate, concerning the present specimen too, it is conjectured that the contribution of the acceptor scattering to μ_e and μ_h is overestimated by applying the formula of Conwell and Weisskopf, say, Eq. (36), therefore we rather adopt the calculated μ_{eL} and μ_{hL} as the resultant mobilities and the constant mobility ratio b of Eq. (17) in the undergoing calculations.

(2) Resistivity, Hall effect and thermoelectric power

Now we compute the resistivity, the Hall coefficient and the thermoelectric power of this specimen in the temperature range in concern by Eq. (1), (2) and (3), substituting Eq. (34) for n_e and n_h, Eq. (24) for μ_e and μ_h, Eq. (17) for b, Eq. (22) for m_e and m_h and Eq. (20) for β, and as for $\frac{\partial\chi}{\partial T}$ in Eq. (3), we may assume $\frac{\partial\chi}{\partial T}=\frac{\beta}{2}$ because the large part of β consists of the shift of band edges due to the dilation of lattice, namely $|E_{1c}|+|E_{1v}|$, in which $|E_{1c}|\fallingdotseq|E_{1v}|$ holds in the present discussion as is deduced from Eq. (12) and (13).

The calculated curves are shown in Fig. (1), (2) and (3) to compare with the experimental results. In these figures, the dashed curves designated as ρ', A_H' and $\frac{d\Theta'}{dT}$ correspond to the ideally complete crystal with no impurity nor lattice defect in which $n_e=n_h=n'$ holds, and these are calculated by the next formulae.

$$\rho'=\{|e|(1+b)\mu_{hL}n'\}^{-1}, \tag{39}$$

$$A_H'=\frac{3\pi}{8c|e|}\cdot\frac{1-b}{1+b}\cdot\frac{1}{n'}, \tag{40}$$

$$\frac{d\Theta'}{dT}=\frac{k}{|e|}\left\{\frac{1-b}{1+b}\left(2+\frac{\Delta E(0)}{2kT}\right)+\frac{3}{10}\ln b+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right\}. \tag{41}$$

In Fig. (1) this ρ' curve must intersect with the ρ curve at $T_0(1)$ and $T_0(2)$ at which Eq. (5) holds, because the condition $\rho=\rho'$ gives the same relation $n_h=n_e b^2$ as Eq. (5) if μ_h and b remain unchanged between two cases corresponding to ρ and ρ'. This is the case between the ρ' curve and the calculated ρ curve as figure shows, but the measured curve intersects with the ρ' curve a little higher temperature than $T_0(2)$ and this mainly results from the fact that the low temperature ($<$ ca 250°K) hole mobility $\mu_{h,\,\mathrm{exp}}$ does not coinside with μ_{hL} as is shown in Fig. 6.

In Fig. 2, a few different observations are inserted in the high temerature region of impurity insensitive, among which ○, ● and □ designate the adiabatic values and × designates the isothermal one. They almost coinside each other except the isothermal curve above ca $T_0(1)$, and exactly speaking, the calculated curves should be compared with the isothermal measurement in this temperature range because Eq. (2) means the isothermal effect.

On the thermoelectric power, the following concise expressions are derived at the temperature T_0 and T_m where Eq. (5) and (8) hold respectively.

$$\left[\frac{d\Theta}{dT}\right]_{T=T_0}=\frac{k}{|e|}\left\{\frac{b-1}{b+1}\left(2+\frac{\Delta E(0)}{2kT}\right)-\frac{7}{10}\ln b+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right\}, \tag{42}$$

$$\left[\frac{d\Theta}{dT}\right]_{T=T_m}=\frac{k}{|e|}\left(-\frac{1}{5}\ln b+\frac{\beta}{2k}-\frac{1}{k}\frac{\partial\chi}{\partial T}\right), \tag{43}$$

where $b=\left(\frac{m_e}{m_h}\right)^{-5/2}$ has been assumed.

These expressions are convenient for the prompt comparison of the theoretical and experimental magnitudes of the thermoelectric power when the carrier concentrations etc. are yet unknown. The calculated values of above formulae are listed in Table 2 compared with the practical values.

Table 2

Specified Temperature	Observed Value of $\frac{d\Theta}{dT}$	Calculated Value of $\frac{d\Theta}{dT}$
$T_0(1)$ = 520°K	+145 μV/deg	+126 μV/deg
T_m = 265 (observed) / 254 (calculated)	− 55	− 13
$T_0(2)$ = 233	+150	+260

Generally speaking, all of the calculated curves for ρ, A_H and $\frac{d\Theta}{dT}$ fully explain the experimental values throughout the measured temperature range but for the inessential quantitative discordances and the chief causes of them can be mentioned as follows.

(1) Disregarding of the crystal anisotropy especially large in a single crystal of tellurium as in the present specimen.

(2) The use of μ_{eL} and μ_h owing to the lattice scattering alone for the resultant mobilities in order to avoid the overestimation of the impurity scattering. The influence of this approximation may enter at higher temperatures. Concerning this point, it is interesting to investigate the state of electron trapped by a

lattice defect.

(3) The approximation of Eq. (27) which makes the difference $n_h - n_e$ larger than the exact treatment if possible.

(4) The disagreement of low temperature hole mobility shown in Fig. 6 which has been disregarded in the calculation of ρ and $\frac{d\Theta}{dT}$. As for the thermoelectric power, the term 2 in Eq. (3) should be replaced by $\frac{1}{kT}\int_0^\infty l(\eta)\,\eta\,\frac{\partial f_0}{\partial \eta}\,d\eta \Big/ \int_0^\infty l(\eta)\eta^2\,\frac{\partial f_0}{\partial \eta}\,d\eta$ where l is the mean free path, f_0 is the distribution function and η is the energy of a carrier. When a scattering mechanism other than the lattice vibration takes place, this integral takes a temperature dependent value instead of 2.

In conclusion, it is desirable to make an examination for the presence of direct evidences of the lattice defects concerning the type and the energy of them by the experiments on the calorimetry, the dilatometry and so forth.

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