Electrical Properties of Antimony-Doped Tellurium Crystals

著者	FUKUROI Tadao, TANUMA Seiichi, TOBISAWA Shotaro
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	4
page range	283-297
year	1952
URL	http://hdl.handle.net/10097/26509

Electrical Properties of Antimony-Doped Tellurium Crystals*

Tadao FUKUROI, Seiichi TANUMA and Shôtarô TOBISAWA

The Research Institute for Iron, Steel and Other Metals

(Received April 10, 1952)

Synopsis

Electrical resistivity, Hall effect and thermoelectric power of tellurium crystals alloyed with antimony of quantities between 0.002 and 5 atomic per cent have been measured in the temperature range from liquid air temperature to 300°C, and the data are compared with the properties of pure tellurium crystals with a view to clarifying the change of electrical properties accompanying the increase of acceptor impurities. The Values of resistivity and Hall coefficient at about 15°C distribute from 4.2×10^{-1} to 1.7×10^{-3} ohm·cm and from -3.6×10^{3} to $+3.25$ emu respectively as observed for twelve specimens containing antimony up to 5 per cent; and the density and mobility of holes calculated from the above data range from 2.3×10^{15} to 2.3×10^{19} per cm^3 and from more than 4.9×10^{2} to 1.6×10^{2} cm^2/volt·sec respectively. Tenth or hundredth parts of added antimony atoms are deemed to yield the acceptor levels having little or no excitation energy in the temperature range under study. The decrease in hole mobilities with the increase of antimony addition are concluded to be due to the predominance of acceptor ion scattering. Thermoelectric power shows a temperature dependence having a maximum at low temperatures and a minimum at intermediate temperatures in the pure specimens, while it tends to show monotonous characteristics having a roughly linear increase with temperature rise in accordance with the increase of antimony concentration.

I. Introduction

So far, we investigated the electrical properties of the pure tellurium crystals,(1),(2),(3) by carrying out simultaneous measurements of electrical conductivity, Hall effect and magneto-resistance in the temperatures ranging from −190 to 300°C; and thus obtained the values of the width of the forbidden band, the mobilities, the effective masses and the concentrations of electrons and holes as functions of temperatures.(1),(3) Then the other electrical quantities, i. e., the characteristics of thermoelectric power and Ettingshausen-Nernst effect** against the temperatures which have been deduced from the above knowledge, are not incompatible with the experimental data of these quantities measured simultaneously with the three quantities above mentioned.(1),(2) Thus, although the essential electrical properties of tellurium crystal itself as a non-polar intrinsic semiconductor were become clear, another rather important investigation for practical applications remains untouched, that is

---

* The 678th report of the Research Institute for Iron, Steel and Other Metals.

(1) Tadao Fukuroi, Seiichi Tanuma, Shôtarô Tobisawa, Sci. Rep. RITU, A 1 (1949), 373.
Tadao Fukuroi, Sci. Rep. RITU, A 3 (1951), 175.

(2) Tadao Fukuroi, Seiichi Tanuma, Shôtarô Tobisawa, Sci. Rep. RITU, A 2 (1950), 233.

(3) Tadao Fukuroi, Seiichi Tanuma, Shôtarô Tobisawa, Sci. Rep. RITU, A 2 (1950), 239.

** The thermomagnetic effect giving rise to the transversal potential difference on the isothermal line perpendicular to both the longitudinal temperature gradient and the transversal magnetic field.

the study on the effect of impurity addition to the semiconducting properties of the specimens. Even a trace of impurities left in an intrinsic semiconductor is usually sufficient to change markedly its electrical behaviour. In most cases, however, it is difficult to execute a purification of the material that is enough to eliminate completely this impurity effect at ordinary temperatures, such being the case the studies on the properties of the impurity controlled extrinsic semiconductors are to be considered of essential as well as of interest from points of view both of the theory of solid and of the applications to electronics. Our present purport is aimed at the investigation of the said effect of impurity added intentionally to the pure tellurium.

In order to obtain a systematic knowledge of the electrical properties of impurity-doped tellurium, we recollect the following two lines of investigation, that is to say, one that deals with many crystals each of which is added with a specific amount of another element and the other which treats the specimens that are prepared by varying the percentage of an alloying element suitably chosen. The work of C. H. Cartwright and M. Haberfeld-Schwarz(4) may be regarded as one of the most detailed study hitherto made concerning the change of electrical properties of tellurium resulted from the impurity addition. They measured the electrical conductivity and the thermoelectric power on the specimens alloyed with many sorts of metals; i. e. with Sb, Bi, Cu, Ag, Au, Fe, Se, Sn etc. of less than 1 per cent, and found in all specimens the increase of conductivity as contrasted to the pure tellurium crystal and the change of sign in temperature coefficient of conductivity from negative to positive with increasing concentration of the added metals. The thermoelectric power at room temperatures is always positive, that is, the thermoelectric current is generated to the direction from tellurium to the copper wire at the lower temperature junction and its magnitude generally becomes larger as the impurity increases. On the basis of these results, they concluded that the forbidden band width of tellurium is ca 0.6 eV, acceptor excitation energy responsible for antimony addition is 0.11 eV above the valence band and impurity levels in the case of copper addition lay at about the midst of the forbidden band, which levels, therefore, can act as either donors or acceptors. But these conclusions are to be subject to revision in comparison with the results described in this paper, that is to say, the forbidden band width is about 0.34 eV* and the excitation energy of acceptors originated in antimony atoms is less than 0.01 eV. Notwithstanding the reasoning resorted by Cartwright and Haberfeld-Schwarz is based upon the assumption that everyone of the added impurity atoms supplies one current carrier, this assumption has no experimental evidence, hence the Hall effect measurement is indispensable to know the actual carrier concentration. Here we have investigated the change of electrical properties of tellurium crystal due to

---

(4) C. H. Cartwright, M. Haberfeld-Schwarz, Proc. Roy. Soc., London (A), **148** (1935), 648.

* Cartwright and Haberfeld-Schwarz deduced a fairly correct value of 0.35 eV from the resistivity of pure tellurium but they abandoned this for the explanation of resistivities of impure extrinsic tellurium specimens.

antimony addition as an extension of the studies on pure tellurium crystal. Antimony has been selected first of all since it is the adjoining element of tellurium in the periodic table[*] and we may naturally expect that each antimony atom replaced in place of the tellurium atom would contribute one deficit electron viz. a positive hole to the valence band of the crystal.

In this report, we shall deal with the experiment and the discussion of the results on the electrical resistivity, the Hall effect and the thermoelectric power of tellurium crystals prepared by alloying antimony of various amounts to the purest tellurium so as to minimize the effect of unknown residual impurities.

II. Experimental details

1. Preparation and manipulation of the specimens

As already described, we used very pure tellurium which had been refined by means of vacuum fractional distillations repeated three times so as to contain residual impurities not more than 10^{-4} atomic per cent as determined by the resistivity measurement, and antimony is of *Kahlbaum* purest grade. These metals were pulverized by an agate mortar, weighed and mixed together, and then charged in a *SBB* glass tube of a few mm bore. This tube together with the containing metals was degassed to 10^{-5} mmHg while heating at 180~200°C in an oil bath for a few hours and then sealed off. The sealed metals were then smelted in a nichrome furnace held at 550°C and kept for an hour. The alloy ingot was remelted under a hydrogen atmosphere, which was purified by passing through concentrated sulphuric acid column and a heated copper gauze, and was sucked up in a hard glass capillary inserted vertically in the crucible by means of an injector cylinder connected by rubber tubing to the top of the capillary, and then was solidified slowly from the top by cooling in the furnace. The hard glass was then removed by dissolving away with fluoric acid of 30 per cent, which treatment was effected without eroding the ingot itself. The cylindrical ingot, 2.2~2.8 mm in diameter and 6~9 cm in length, was obtained in most case either as a single crystal, or as a

Table 1.

Number of specimen	Sb concentration in atomic per cent	θ
1[*]	triply distilled Te	6°
2	doubly distilled Te	20°
3	0.0018	p. c.[**]
4	0.0045	45°
5	0.0105	0°
6	0.0157	p. c.
7	0.0439	15°
8	0.0943	5° [***]
9	0.454	p. c., $\theta' \lesssim 10^\circ$
10	1.05	70°
11	5.23	p. c., $\theta' \gtrsim 80^\circ$
12	0.0079 (+18.31 Se)	35°

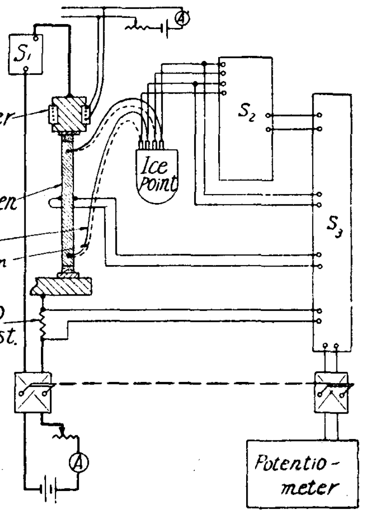
[*] The same specimen as No. 1 in the first report;
[**] Polycrystalline;
[***] Orientation of crystallites.

---

[*] Te : VI b groupe, atomic number 52, atomic weight 127.61
Sb : V b groupe, atomic number 51, atomic weight 121.76
Iodine, another neighbouring element of tellurium, seems to fetch no distinguished extrinsic semiconduction of n-type to tellurium as may simply be expected, instead it gives rise to a slightly increased p-type conduction to the sample, hence it is hardly accepted as an effective impurity element.

polycrystalline rod having nearly parallel orientation of crystallites. Both ends of the rod were cut away with a diamond wheel leaving about 4∼6 cm in length. Specimens of low antimony concentration were prepared by diluting the alloy of higher concentration with pure tellurium. Table 1 summarizes the alloyed antimony concentrations in all the specimens. Table 1 also includes the approximate angle, θ, between the axis of single crystal specimen and the principal crystallographic axis.

2. Apparatus and procedures



S_1, S_2, S_3 : Selector switches

Fig. 1. Schematic diagram of the circuit for measuring the electric resistance, Hall effect and thermoelectromotive force.

This study aims at the measurements of resistivity, thermoelectric power and Hall effect of the specimens just mentioned as functions of temperature. Resistivity is measured by a direct current and potential probe method to eliminate the contact resistance at the electrodes, thermoelectric power against copper is determined by establishing a temperature gradient along the specimen by fixing a heater at an end of the specimen, temperatures being read by the e.m.f.s of copper-constantan thermo-junctions. Hall effect is observed from the transverse voltage set up in a magnetic field. Both ends of a specimen are plated electrolytically with nickel and covered with a solder having a melting point above 350°C, and each end is inserted into a hollow bored in the end of a tapered cylindrical copper plug and a rigid connection between them is secured by fusing the solder. The scheme of measuring circuit is displayed in Fig. 1. With vertical position of the specimens, the upper plugs are attached to the heater bobbins and constantan wire (BS#40, 240 ohm) wound thereon, and the lower plugs are fixed to the common base of copper. The current through the specimens is allowed to flow from the upper heater bobbins to the lower common base plate. This base plate accomodates six specimens, thus enabling the simultaneous measurements of their resistivity and thermoelectric power. Two copper(BS# 35)-constantan(BS# 40) thermojunctions are welded on the surface of each specimen 2 mm apart from the soldered ends by a condenser discharging method. Hall electrodes are welded in a similar way. In the case of single crystals, the two junctions are allocated on the generating line lying in the plane containing the [0001] axis and the centre axis of specimen, and the two Hall electrodes on a diameter perpendicular to this generating line. The resistance of each specimen is read by measuring the potential drop along the specimen between two junction points by way of copper wires by passing a known current, and the thermoelectric power is got by measuring e.m.f., $\Delta\Theta$, in the circuit copper-constantan-copper via the said copper wires under a temperature gradient. Let the temperature reading at two junction points be T_1 and T_2, the power in question is given by $\left(\frac{d\Theta}{dT}\right)_T \fallingdotseq \left(\frac{\Delta\Theta}{T_1-T_2}\right)_{\frac{T_1+T_2}{2}}$, where the temperature difference is kept within 10°. To carry out the Hall effect measurement, the same specimen is laid horizontally in a Dewar's vessel in which a vertical magnetic field of 900~1,000 Oersted is excited from outside by a coreless solenoid. On measuring the resistance and Hall effect, four values of voltages corresponding to the individual reversal of current and magnetic field are averaged in order to eliminate the parasitic thermoelectric or other galvanomagnetic voltages. In particular, the Ettingshausen effect* which superposes on the Hall effect cannot be eliminated in a direct current measurement by the averaging procedure just referred to, then the Hall effect obtained in this way would be a quasi-adiabatic Hall effect instead of a real isothermal one. Though as already mentioned in the former report,⁽³⁾ this quasi-adiabatic values differ by not more than 10 per cent as compared with the real isothermal ones obtained by means of an alternating current method. The vessel used for the resistivity and the thermoelectric power are illustrated in Fig. 2. To change the temperature condition, a liquid air bath supplemented by a heating element is used in the range below room temperature and a nichrome furnace for higher range as the figure shows.

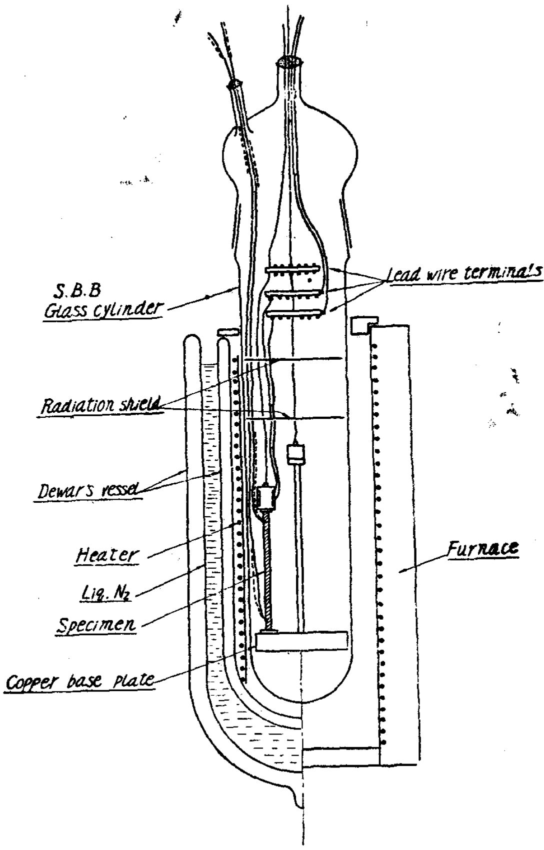


Fig. 2. Specimen holder and temperature regulating vessel for measuring thermo-e. m. f. and electric resistance.

III. Experimental results

In Table 2 are listed the values of the resistivity, ρ, and the Hall coefficient, A_H, measured simultaneously at room and liquid air temperatures. And these data correspond to arrow-marked points in Fig. 3 and circles in Fig. 4. In Fig. 4 the observed two points in each specimen No. 4 to 11 have been connected with a straight line as these two points have nearly the same value. Figs. 3 and 5 show the characteristic

---

[*] The galvanomagnetic effect giving rise to the transversal temperature difference on the equipotential line perpendicular to both the longitudinal electric current and the transversal magnetic field. Since the direction of thermo-e.m.f. due to this temperature difference alters with the reversal of current or magnetic field, hence the averaging procedure cannot eliminate this effect.

curves of the resistivity, ρ, and the thermoelectric power, $d\Theta/dT$, versus temperatures, simultaneously measured in the range from -190 to $+300$°C. The sign of a thermoelectric power is defined positive if the thermoelectric current flows from the hot to the cold junction in the specimen when the circuit is closed. As are visualized in the figures, the resistivity and the Hall coefficient markedly change in accordance with the antimony addition. Namely, the pure specimen No. 1 (the data corresponding to the curves (I, 2) in the first report⁽¹⁾) exhibits a nearly pure intrinsic conduction at room temperatures, and if antimony content in the alloys is increased, the transition temperature, at which the intrinsic conduction supercedes the extrinsic one, displaces to higher temperatures as well as the resistivity much diminishes and the hall coefficient also decreases remarkably such that it becomes as small as 10^{-4} of that of pure specimen if the antimony concentration attains a few per cent. These facts indicate as described below that the carrier density in the extrinsic range is increased by several orders of magnitude

Table 2. Resistivities and Hall coefficients at room and liquid air temperatures.

Number of specimen	At room temperature			At liquid air temperature		
	ρ Ωcm	A_H emu	T°K	ρ Ωcm	A_H emu	T°K
1*	4.16×10^{-1}	-3.62×10^{3}	286	2.41	3.91×10^{4}	102
2	4.44×10^{-1}	-1.50×10^{3}	281	3.94×10^{-1}	1.66×10^{4}	81
3	3.07×10^{-1}	6.91×10^{2}	287	1.38×10^{-1}	7.21×10^{3}	79
4	8.57×10^{-2}	4.98×10^{2}	276	3.31×10^{-2}	7.61×10^{2}	87
5	9.79×10^{-2}	8.65×10^{2}	285	3.40×10^{-2}	1.04×10^{3}	85
6	7.19×10^{-2}	5.18×10^{2}	287	2.71×10^{-2}	6.32×10^{2}	79
7	5.92×10^{-3}	59.5	288	—	—	—
8	4.98×10^{-3}	42.9	284	2.12×10^{-3}	44.6	87
9	1.82×10^{-3}	12.8	285	7.52×10^{-4}	12.7	79
10	1.38×10^{-3}	6.73	276	5.96×10^{-4}	6.45	79
11	1.69×10^{-3}	3.25	288	8.19×10^{-4}	2.70	78
12	1.10×10^{-2}	77.6	287	5.17×10^{-3}	77.1	79

* The data of specimen No. 1 were extracted from the first report.

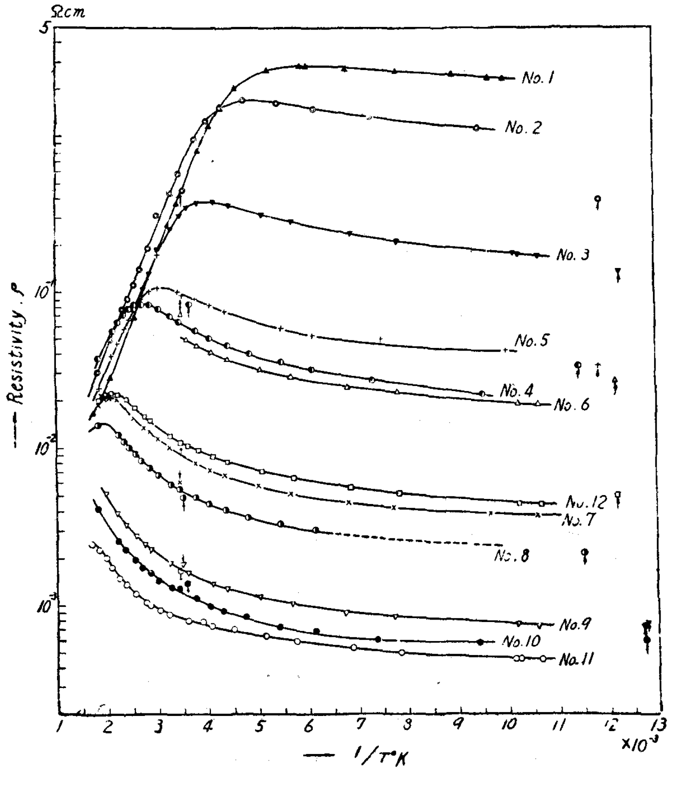


Fig. 3. Resistivity of antimony-doped tellurium crystals as a function of the inverse absolute temperature measured simultaneously with thermoelectric power. The arrow-marked points correspond to the simultaneous measurments with Hall coefficient.

with the addition of antimony. On the other hand the thermoelectric power takes no such a large range of values as appears in Hall coefficient as a function of the antimony concentration. However, the temperature characteristic of the thermoelectric power indicates a complicated behaviour with the antimony addition as shown in Fig. 5.

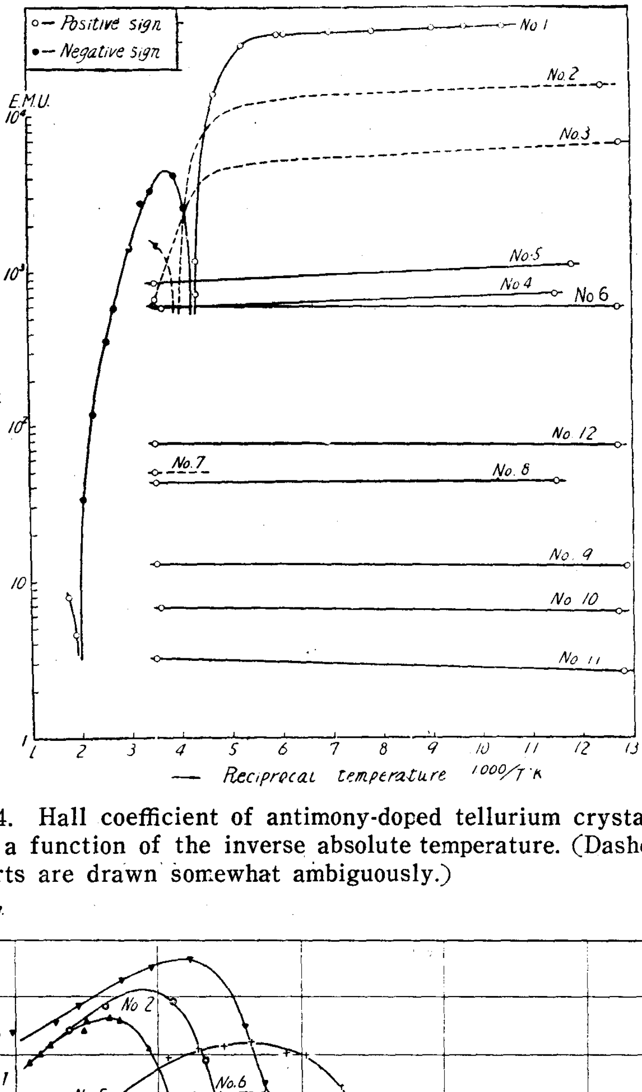


Fig. 4. Hall coefficient of antimony-doped tellurium crystals as a function of the inverse absolute temperature. (Dashed parts are drawn somewhat ambiguously.)

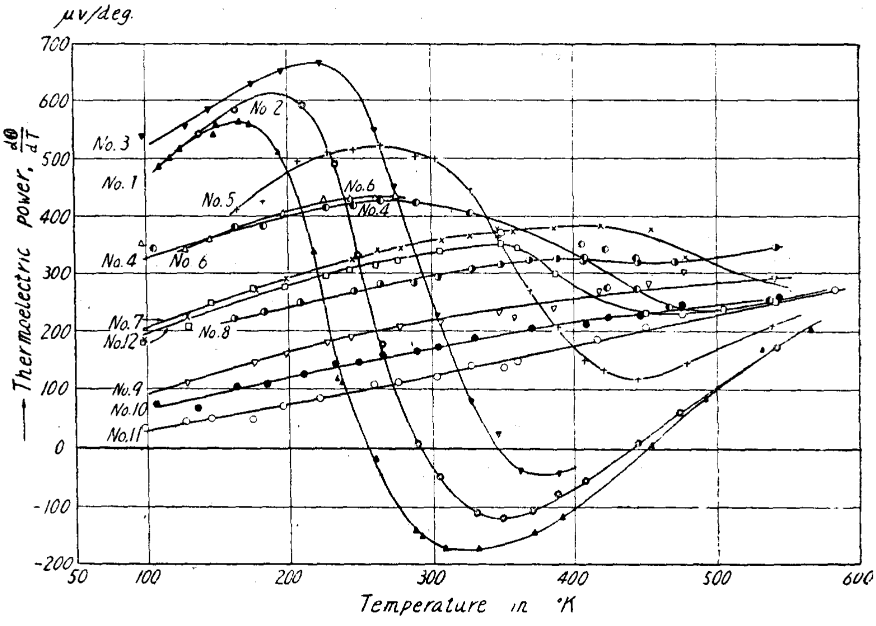


Fig. 5. Thermoelectric power of antimony-doped tellurium crystals against copper as a function of the absolute temperature.

IV. Discussion of the experimental results

1. Conductivity of pure crystals

The resistivity, ρ, and the Hall effect, A_H, are given as follows when a semiconductor contains both electrons and holes obeying the classical statistics,

$$\rho^{-1} = |e|\,(n_h\mu_h + n_e\mu_e)\,, \tag{1}$$

$$A_H = \frac{3\pi}{8c|e|}\,\frac{n_h\mu_h^2 - n_e\mu_e^2}{(n_h\mu_h + n_e\mu_e)^2}\,, \tag{2}$$

where n and μ are the density and the mobility of the carriers and suffixes h and e pertain to the holes and the electrons.

In the intrinsic range electrons are excited to the conduction band directly from the valence band and an equivalent number of holes are produced behind, hence putting $n_h = n_e$ in the above equation, we have

$$\rho^{-1} = |e|\,n(\mu_h + \mu_e)\,, \tag{3}$$

$$A_H = \frac{1}{8c\,|e|\,n}\,\frac{\mu_h - \mu_e}{\mu_h + \mu_e}\,. \tag{4}$$

In this case, applying the law of mass action to the excitation crossing over the forbidden band, the width of which is $\varDelta E(T)$ or $\varDelta E(0) + \beta T$, the carrier density, n, is expressed as follows,

$$n = \nu\left(\frac{m_h m_e}{m^2}\right)^{3/4} \exp\left(-\frac{\beta}{2k}\right) \exp\left(\frac{\varDelta E(0)}{2kT}\right), \tag{5}$$

where

$$\nu = 2\left(\frac{2\pi mk}{h^2}\right)^{3/2} T^{3/2}\,, \tag{6}$$

and m_h and m_e are the effective masses of holes and electrons respectively. The mobilities are determined from the scattering of carriers by the phonons of lattice vibration only in the purer specimen and takes the following expression.

$$\mu = \left(\frac{m_{\text{eff.}}}{\alpha}\right)^{-5/2} T^{-3/2}\,. \tag{7}$$

Thus we get,

$$\rho = A \exp\left(-\frac{\varDelta E(0)}{2kT}\right). \tag{8}$$

in which the factor A remains constant in general but changes very slowly with temperature in the present case since the charge carriers in tellurium have temperature dependent mean effective masses. Therefore, $\log\rho$ gives a straight or at least nearly straight line against T^{-1}, which fact corresponds to the straight portions of the curves of specimens No. 1, 2, 3 in Fig. 3 having the inclination of $\varDelta E(0) = 0.34$ eV determined in the previous paper.(1)

2. Approximate estimation of extrinsic carrier density

In the specimens alloyed with antimony more than about 0.01 per cent, the magnitudes of both resistivity and Hall coefficient seems to be appreciably affected by the impurity concentrations, that is to say, the extrinsic conduction preponderates.

Extrinsic semiconductors contain either electrons or holes alone as charge carriers, then the expressions of ρ and A_H in Eqs. (1) and (2) become as follows,

$$\rho^{-1} = |e| n\mu \,, \tag{9}$$

$$A_H = \pm \frac{3\pi}{8c|e|n} \,, \tag{10}$$

or

$$n \doteqdot 7.34 \times 10^9 \times (A_H \text{ in emu})^{-1} \,,$$

where A_H has the positive sign in the case of hole conduction and the negative one in the case of electron conduction. Te–Sb alloys take the positive sign as Table 2 shows, so the carriers are found to be holes in the valence band. Moreover, the fact that the values of A_H show no appreciable changes between room temperature and liquid air temperature reveals the approximate constancy of hole density, namely, the nearly complete ionization of acceptor impurity centres even at liquid air temperature.

Table 3. Concentrations and mobilities of holes at room and liquid air temperatures.

Number of specimen	At room temperature*			At liquid air temperature*		
	n_h cm^{-3}	C atom.%	$\mu_h$cm^{2}volt^{-1}sec^{-1}	n_h cm^{-3}	C atom.%	$\mu_h$cm^{2}volt^{-1}sec^{-1}
1	(2.3×10^{15})**	(7.7×10^{-6})	—	1.9×10^{15}	6.4×10^{-6}	1.38×10^{3}
2	—	—	—	4.4×10^{15}	1.5×10^{-5}	3.59×10^{3}
3	—	—	—	1.0×10^{16}	3.4×10^{-5}	4.46×10^{3}
4	1.5×10^{17}	5.0×10^{-4}	4.95×10^{2}	9.6×10^{16}	3.2×10^{-4}	1.96×10^{3}
5	8.5×10^{16}	2.9×10^{-4}	7.51×10^{2}	7.1×10^{16}	2.4×10^{-4}	2.60×10^{3}
6	1.4×10^{17}	4.8×10^{-4}	6.13×10^{2}	1.2×10^{17}	3.9×10^{-4}	1.99×10^{3}
7	1.2×10^{18}	4.2×10^{-3}	8.54×10^{2}	—	—	—
8	1.7×10^{18}	5.9×10^{-3}	7.33×10^{2}	1.6×10^{18}	5.6×10^{-3}	1.79×10^{3}
9	5.7×10^{18}	1.9×10^{-2}	6.00×10^{2}	5.8×10^{18}	1.9×10^{-2}	1.43×10^{3}
10	1.1×10^{19}	3.6×10^{-2}	4.16×10^{2}	1.1×10^{19}	3.8×10^{-2}	9.21×10^{2}
11	2.3×10^{19}	7.6×10^{-2}	1.64×10^{2}	2.7×10^{19}	9.1×10^{-2}	2.80×10^{2}
12	9.5×10^{17}	3.2×10^{-3}	6.01×10^{2}	9.5×10^{17}	3.2×10^{-3}	1.27×10^{3}

* The exact temperature readings are listed in Table 2.

** This value was estimated from the n_h vs. T curve of Fig. 11 of the first report.

The values of hole density at room and at low temperatures calculated from Eq. (10) are listed in Table 3, together with the values of atomic percentage of hole densities deduced from the formula $C = 100n/2.97\times10^{22} = 3.37\times10^{-21}n$, the denominator 2.97×10^{22} being the density of lattice atoms in a tellurium crystal.

3. Detail of the temperature dependence of the Hall coefficient

Next, we go into particulars of the slight but unusual temperature dependence of the Hall coefficient. The law of mass action yields the next formula for hole concentration, when it is applied to the electron distribution in semiconductors, whose energy levels taking part in conduction are the valence band and the acceptor levels, the energy separation between them being ΔE_h.(5)

$$n = \frac{\nu}{2}\left(\frac{m_h}{m}\right)^{3/2} e^{\frac{-\Delta E_h}{kT}} \left[\left\{ 1 + \frac{4N}{\nu}\left(\frac{m_h}{m}\right)^{3/2} e^{\frac{\Delta E_h}{kT}} \right\}^{1/2} - 1 \right] , \tag{11}$$

---

(5) R. H. Fowler, *Statistical Mechanics*, 2nd Ed., London (1936), Section 11, 6.

where N is the acceptor level density per unit volume and ν has the same meaning in Eq. (6). In the case of strong ionization in hand, $T \gg \Delta E_h/k$, then an approximation applies

$$n = N\left\{1 - \frac{N}{\nu}\left(\frac{m_h}{m}\right)^{3/2} e^{\frac{\Delta E_h}{kT}}\right\}, \tag{12}$$

where $\nu = 4.89 \times 10^{15} T^{3/2}$,

$= 3.50 \times 10^{18}$, at $T = 80°\mathrm{K}$,

and $= 2.54 \times 10^{19}$, at $T = 300°\mathrm{K}$.

It is expected that N and ΔE_h ought to be determined by fitting Eq. (12) to the experimental relation of n vs. T. Actually, however, even the most inclined n vs. T characteristic of the purest specimen No. 1 in the extrinsic range is still too flat to assign any finite value for ΔE_h as already pointed out in the first report,(1) except that it was found to be less than 0.01 eV. In the antimony-doped tellurium specimens, since the variation of n against T becomes still more small, ΔE_h in each alloy cannot be obtained from Eq. (12) in the range in question. In order to know ΔE_h more definitely, more detailed investigations on the temperature behaviour of the Hall coefficient at extreme low temperatures are required. Even though $\Delta E_h = 0$ is assumed, Eq. (12) shows the increase of n with rising temperature due to the term ν in it. While the observed decrease in Fig. 4 of A_H or n^{-1} with increasing temperature are far smaller than that expected. In fact, the specimen No. 9 shows no variation of A_H with temperature and No. 11 and 12, on the contrary, even tend to increase in A_H with increasing temperature. This unexpected fact leads us not only to hesitate the application of Eq. (12) to the present data, but to suspect the generality of the character that the carrier density must increase with rise in temperature on the basis of the usual semiconductor model. In an effort to trace the origin of this somewhat involved problem, the relation between A_H and n, viz., Eq. (10) must be reconsidered. The numerical coefficient $3\pi/8$ in the equation results from the assumption that the mean free path of a carrier is independent of its own velocity. While this assumption is only valid for the carriers obeying classical statistics in which mean free path is subjected to the scattering by lattice phonons alone. In actual case, the mean free path of holes or electrons in extrinsic semiconductors is also influenced by the scattering due to impurity ions or atoms. H. Jones(6) who considered the effect of impurity ion scattering has given that

$$A_H = p \cdot \frac{1}{c|e|n}, \tag{13}$$

the coefficient p is calculated as the function of ρ_I/ρ and found to take the value as indicated in Fig. 6, in which ρ_I is the assumed resistivity resulted only from the impurity ion scattering. As shown in this figure, p decreases from $3\pi/8 = 1.18$ to the minimum value 1.07 corresponding to the increase of ρ_I/ρ from 0 to 0.20. Since the temperature dependences of ρ and ρ_I are not equal, the value of ρ_I/ρ in

---

(6) H. Jones, Phys. Rev., **81** (1951), 149.

one specimen cannot remain constant throughout the temperature range under measurement. Therefore, when n is calculated from Eq. (13) by taking into account the variation of p as a function of temperature using ρ_I/ρ as a parameter, the increase of A_H with rising temperature does not neccessarily entail the decrease of n with increasing temperature, so far as the ratio of maximum to minimum value of A_H over the temperature range in concern does not exceed the corresponding ratio of p, viz., $1.18/1.07=1.103$. That is to say, the apparent decrease of n with increasing temperature as deduced from Eq. (10) may be a spurious issue caused by ignoring the effect of impurity scattering. With regard to the specimens No. 10 and 11, the ratio of Hall coefficients at low temperatures and at room temperature is smaller than 1.103, so that the above reasoning would apply to this case. We are, however, not entirely satisfied in such a deduction because we have lately found that the Hall coefficient observed for the intermetallic compounds of tellurium, for instance Sb_2Te_3, increases more than the above-mentioned limit, 1.103, from liquid air to room temperature. In this case at least a part of the increase of A_H would be due to the *decrease* of n with rising temperature. These results will be described in a separate paper. For a more satisfactory explanation, a complicated energy level scheme around the top of valence band and the acceptor levels might be required, but we cannot go into further here. In the following discussions, we adopt provisionally the values of n calculated from Eq. (10) for the sake of simplicity.

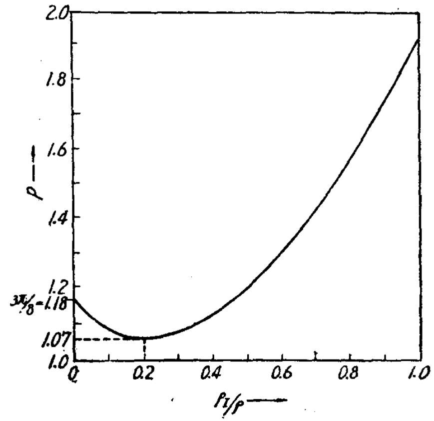


Fig. 6. The coefficient, p, relating Hall coefficient to carrier density in the relation $A_H=p\dfrac{1}{c|e|n}$, calculated by *H. Jones* as a function of the ratio ρ_I/ρ indicating the weight of impurity ion scattering against the total scattering of carriers.

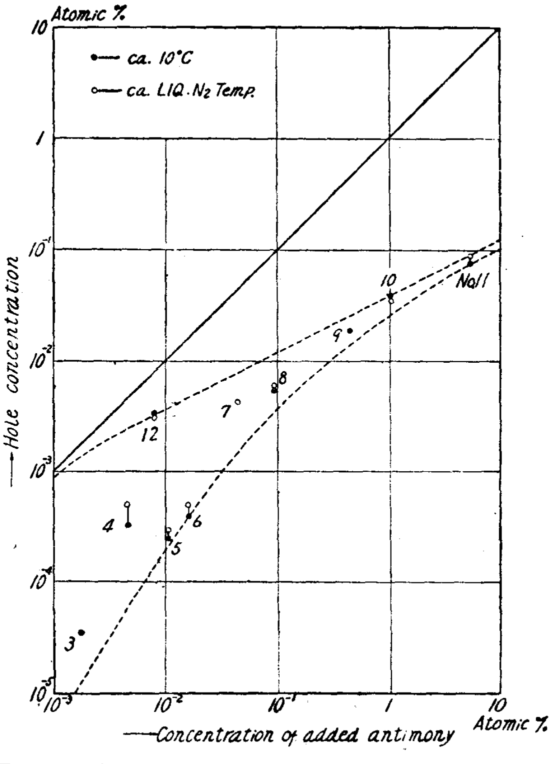


Fig. 7. The relation between the concentration of added antimony and hole concentration which approximately represents the concentration of effective acceptor centres.

4. Relation between the concentration of added antimony and the acceptor level.

From the above consideration, ΔE_h is approximately zero in all the specimens observed, so that the acceptor atoms are almost ionized and yield nearly the same number of holes throughout the temperatures in question, then we can regard the hole density n at room temperature to give approximately the total acceptor level density. Fig. 7 shows the relationship between the density of added antimony and the hole density, which plot is of use to estimate the percentage of acceptor formation from the added antimony. If every antimony atom added plays a role of an acceptor centre, all points should align on the full line making 45° to the coordinate axis. But actually all points are roughly contained in a band below this straight line, that is, only one tenth to some hundredth out of added atoms can act as acceptors, and this ratio, acceptor conc./total Sb conc. $= \gamma$, tends to decrease with increasing antimony addition. An acceptor centre in a tellurium crystal alloyed with antimony which has one less valence electron than tellurium is naturally supposed to be formed by an antimony atom occupying a lattice point of tellurium substitutionally. However, if we are allowed to assume the correctness of the equilibrium diagram(7) of Te-Sb system of Fig. 8, to the extreme end of tellurium, an addition of antimony should give rise to a two phase mixture of tellurium and β phase (Sb_2Te_3), and no single antimony atom can exist as a substitutional solid solution after equilibrium is established. We may infer that, when the specimen solidifies from the melt, a major portion of antimony atoms segregate as an intermetallic compound of β-phase, while the γ part amounting to about one to ten per cent of the total antimony atoms become *frozen in* the tellurium lattice sites due to the supercooling before they can join to one of the β-phase nuclei. But this inference as yet remains to be established by dint of the experimental study on γ's corresponding to quenched and well annealed specimens from one and the same melt.

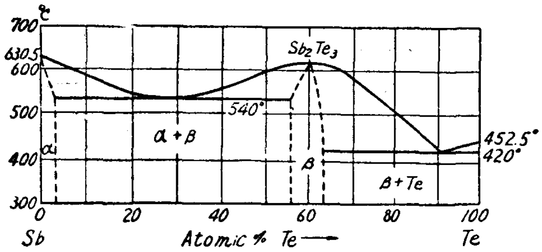


Fig. 8. The equilibrium phase diagram of tellurium-antimony system determined by *Y. Kimata.*

5. Hole mobility

Next we have investigated the hole mobility as a function of the impurity concentration. Neglecting the correction factor in the sense of Fig. 6, the mobility μ in the extrinsic range is led from Eqs. (9) and (10), that is,

$$\mu = \frac{8c}{3\pi}\frac{A_H}{\rho} = 8.50\times10^2\,\frac{A_H\,(\mathrm{emu})}{\rho(\mathrm{ohm\cdot cm})}\ \mathrm{cm^2/volt.sec.} \tag{14}$$

μ_h values in Table 3 are calculated from the above formula using the values of ρ and A_H in Table 2. Figs. 9*a* and 9*b* represent the hole mobility plotted against carrier concentration and added antimony concentration respectively. As shown in Fig. 9*a*, μ_h has as high value as several thousands cm^2/volt. sec. at liquid air temperature in pure sample, decreasing monotonously with the increase of carrier concentration, and also from Fig. 9*b*, μ_h decreases with increase of antimony concentration. These figures clearly indicate that impurity scattering is responsible

---

(7) M. Hansen, *Aufbau der Zweistofflegierungen*, Berlin (1936), 1052. Y. Kimata, Mem. Coll. Sci. Kyôto Univ., 1 (1915), 115.

for the decrease of mobility. Even if either one of the regularities in Figs. 9*a* and 9*b* has any real physical significance, the other also would show an apparent regularity because of some definite correlation displayed in Fig. 7. Hence it is not yet decided whether the acceptor ions or the compound β phase play more important rôle as scattering centres. But, in contrast to the monotonous change in Fig. 9*a*, the series of points corresponding to room temperature in Fig. 9*b* seems to show a maximum around 0.1 per cent antimony and such a character can hardly be explained by a usual theory, hence we have conception that the scattering due to acceptor ions is responsible for the reduction of hole mobility, and that the regularity in Fig. 9*b* would be an apparent consequence.

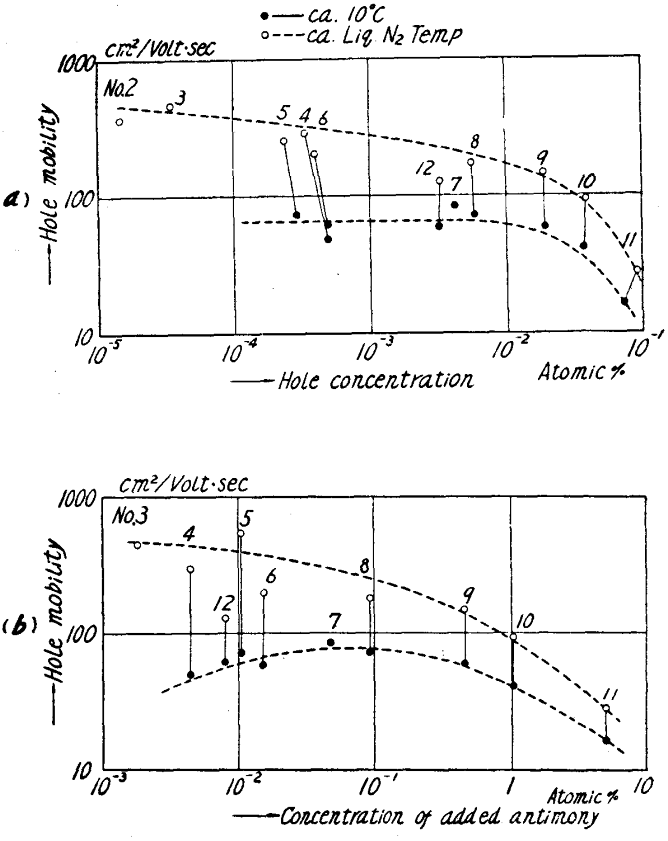


Fig. 9. (a) Hole mobility plotted against the hole concentration which, in the present extrinsic semiconducting case, means the acceptor ion concentration.

(b) Hole mobility plotted against the concentration of added antimony.

6. Thermoelectric power

It has been found that the curves of the thermoelectric power plotted against temperatures change systematically with the addition of antimony, as shown in Fig. 5. The curves of pure specimens change the sign from positive to negative and again positive with increasing temperatures, corresponding to the analogous behaviour of Hall coefficient in Fig. 4. In case the amount of antimony is slightly increased the curves no longer show negative sign but minima at intermediate temperatures, and further addition of antimony causes the decrease of the magnitude at low temperatures rendering the curves to increase monotonously and linearly with rising temperature. In order to render legible the change of thermoelectric power due to the variation of acceptor concentration at any specified temperature, the values of $d\Theta/dT$ have been plotted against $\log n$ in Fig. 10 with the use of both the smoothed out characteristics of $d\Theta/dT$ vs. T in Fig. 5 and the room temperature values of carrier density of an individual specimen listed in Table 3.

Lastly we shall deal with the specimen No. 12 which contains 18.3 atomic per cent selenium and 0.0079 per cent antimony. The thermoelectric power of this specimen is different from the values extended from other specimens which do not contain selenium as shown in Fig. 10. That is to say, the decrease of $d\Theta/dT$ in the high temperature range takes place as in Fig. 5 at a lower temperature than expected. This quantitative singularity may be ascribed to the selenium alloying. Tellurium constitutes a solid solution in any proportion with selenium which belongs to the same group of element and has the similar crystal structure with tellurium. Therefore selenium atoms solved substitutionally in tellurium would not give rise to any primary impurity centre in the tellurium lattice. In consequence, no definite influence of such a large amount of selenium as much as 18 per cent is yet apparent in Figs. 3, 4 and 7. The cause of the above mentioned singularity appeared only in the thermoelectric power may conceivably be ascribed to the mobility change which is effected from the scattering due to the vibration of tellurium-selenium lattice, vibrational mode of which would possibly differ from that of the pure tellurium lattice.

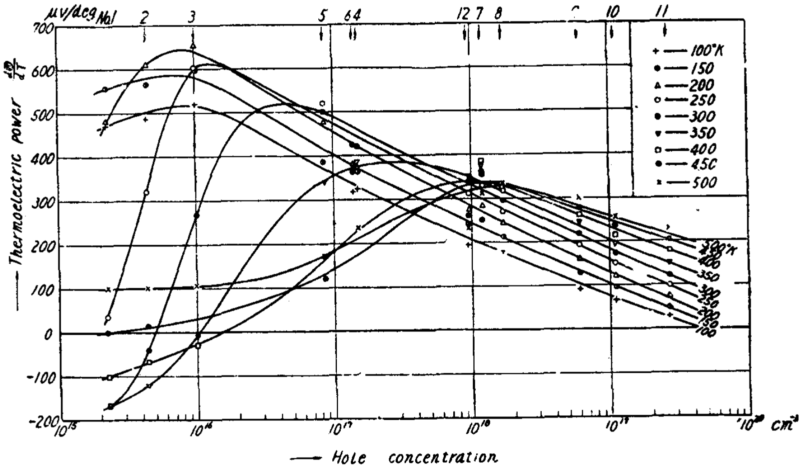


Fig. 10. Thermoelectric power plotted against the hole concentration at room temperature, which is approximately equal to the acceptor concentration.

The characteristics of thermoelectric power *versus* temperature or impurity concentration shall be discussed further in the forthcoming paper.

V. Summary

(1) As to the twelve specimens of pure tellurium and antimony-doped tellurium crystals containing 0.002 to 5 atomic per cent antimony, the resistivity and thermoelectric power are measured simultaneously over the range from -190 to 300°C, and the Hall coefficients also determined at room temperature and at the lowest temperature in the said range.

(2) The resistivity and the Hall coefficient of the purer samples represent the characteristics of the intrinsic conductivity in a high temperature range; whereas the antimony content increases by 5.2 per cent, resistivity decreases from 4.2×10^{-1} to 1.7×10^{-3} ohm-cm at room temperature and from 2.4 to 8.2×10^{-4} ohm-cm at liquid air temperature, and Hall coefficient changes from -3.6×10^{3} to $+3.3$ emu at room temperature and from $+3.9\times10^{4}$ to $+2.7$ emu at liquid air temperature. The Hall coefficient of the alloys containing more than 1 per cent antimony increases monotonously with rising temperatures.

(3) The mobility of current carriers decreases with antimony content owing to the increase of impurity ion scattering, i.e. as antimony added by 5.2 per cent the

mobility decreases from more than 5.0×10^2 to 1.6×10^2 cm^2/volt.sec at room temperature and from 4.5×10^3 to 2.8×10^2 cm^2/volt. sec at liquid air temperature.

(4) The thermoelectric power shows a complicated but systematic temperature variation, that is to say, it changes its sign from positive to negative and again to positive with the temperature rise in pure tellurium, while the said negative region becomes positive minimum at intermediate temperatures by a small addition of antimony, and then it becomes to show monotonously increasing behaviour with temperature for the alloys of higher antimony content.

A part of expenses for this work was defrayed from the Scientific Research Fund of the Ministry of Education.