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Electric Resistance, Hall Effect, Magneto-Resistance and Seebeck Effect in a Pure Tellurium Film*

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Synopsis

The electric resistance, the Hall effect, the magneto-resistance and the Seebeck effect are investigated with regard to pure tellurium films, deposited by evaporation on glass plates, over the temperatures ranging from −195° to +60°C; the substrates in concern have been baked out in the same high vacuum prior to the metal deposition.

The electric resistance and the weight of the deposits are compared for various thicknesses of the films and a certain regular correlation is found between them.

The Hall coefficient at room temperature increases almost in proportion to the thickness of the film defined from its electric conduction. The Hall coefficient and the thermoelectric power against aluminium are both positive throughout the whole range of temperature which facts show that the current carriers predominantly have a positive sign.

I. Introduction

Tellurium metal is comprised in the class of semiconductor or semi-metal, and it differs from ordinary metals in that the density of free electrons is so small as estimated by Cartwright(1), judging from his conductivity measurements, to be less than one electron per million atoms. Moreover, the electric resistance at normal temperatures shows a negative coefficient, viz., the resistance decreases with the rise of temperature. It would be interesting to investigate the electric and its associated properties of a film of semi-conductor such as tellurium, since the various characteristics of a film are fairly different from those of a bulky state.

In view of the technological appliance, tellurium films can be utilized as a radiation sensitive element, e.g., as a bolometer and a thermopile, owing to its large temperature coefficient of resistance and pre-eminent thermoelectric power.

In the present work the fundamental properties of tellurium films, the electric resistance, the Hall effect, the magneto-resistance and the Seebeck effect, were measured in the temperature range between +60° and −195°C.

II. Experimental apparatus and procedures

(i) Purification of tellurium and the residual impurity.

The raw material was obtained from Kahlbaum and purified by fractionating distillations at 530°C in high vacuum, repeated three times, by the use of an apparatus shown in Fig. 1. On distillation of the metal, the more volatile component such as selenium condensed on the higher portion of the inner glass cylinder or escaped out of it and the least volatile one remained at the bottom of the cylinder and the residual one that of about 80 per cent of an initial charge, corresponding to the purest metal, became deposited thickly on the middle portion of the cylinder. Actually the spectroscopic analysis verified that the trace of selenium could completely removed, and also that copper and tin which were initially contained about $5 \cdot 10^{-6}$ gr and 10^{-7} gr in a single charge, the former could be completely discarded after

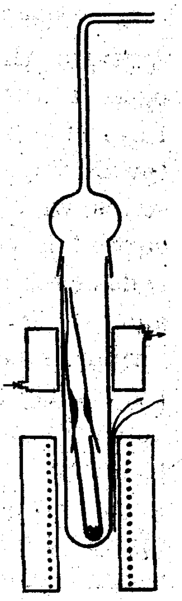
Fig. 1 Apparatus for distillation.

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the second stage of distillation, while the latter, irrespective of its small volatility, still continued its contamination, since the compound Sn-Te distilled, without decomposition, together with tellurium.⁽²⁾

(ii) Preparation of tellurium films.

The apparatus in which the film specimens were prepared is a glass bell jar of about 4.3 l in capacity which is placed on a thick brass discal base as sketched in Fig. 2. At the centre of the jar and some height from the base, a tungsten wire heater wound in a form of conical spiral is held by two binders towards the ends of a pair of bent copper strips which functions simultaneously as a current lead to the heater. And the lower ends of the copper strips themselves are fixed against the brass disk by dint of insulated terminals screwed in through the disk. In the conical heater above mentioned a small porcelain crucible is inserted and a bit of tellurium purified as above is put in it in order to vaporize out. The glass and mica plates on which the metal is to be deposited are held horizontally, about 5 cm apart right above the said crucible, by a specially designed holder. The last cited holder is essentially a flat heater which fulfils the requirement of baking out the glass and mica plates at 300°~400°C prior to the metal deposition, and it is a thin sandwitch type heater composed of three sheets of rectangular (42 ×62 mm) mica plates, of which around the middle one a nichrome wire of No. 32 gauge is wound extending over the total width at every 2.5 mm interval.

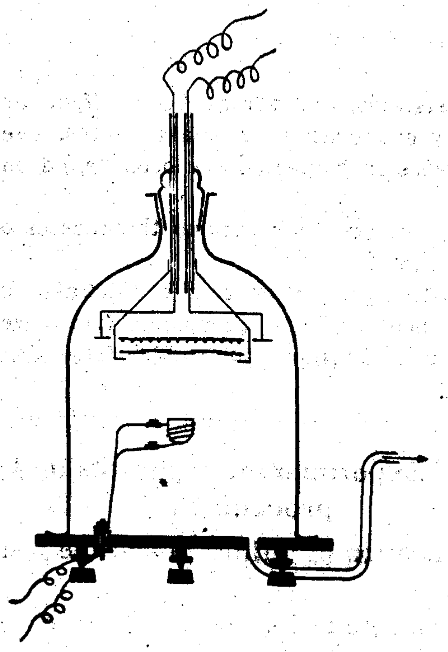

Fig. 2 Apparatus for preparation of a specimen.

The evacuation of the vaporizing vessel is practised by a two stage oil diffusion pump backed by a Cenco-megavac, with a cooperation of coco-nut charcoal trap cooled by liquid air, and thus can attain a vacuum of 10^{-6} mm of mercury. The surfaces of glass on which the metal was deposited were thoroughly cleaned first by boiling in bichromate solution and then by rinsing with pure benzol. And then through a precaution on the thorough evacuation in conjunction with the baking of the substrate prior to deposition, the reproducible results were obtained.

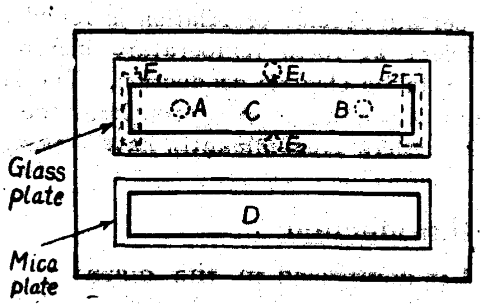

Fig. 3

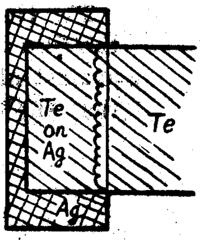

Fig. 4

A screen made of aluminium plate of 1 mm thick as illustrated in Fig. 3 was attached closely in front of the depositing surfaces, and the rôle of two rectangular apertures in it (C and D) is to restrict the regions of deposition. Opening C is for the preparation of specimens under study and two circular eyelets E_1, E_2 on both sides of C are provided for the Hall electrodes; and opening D is for estimating the thickness of a film, at the juxtaposition of C, by weighing the increased weight of a mica lamina with a microbalance. Furthermore, as the direct contact of a tellurium film with the tips of terminal needles, usually scratched the film and eventually resulted imperfect contacts, so that the portions enclosed by dotted lines shown in Fig. 3 correlating to the current (F_1, F_2), potential (A, B) and Hall potential (E_1, E_2) leads, were previously covered thick by depositing aluminium or other metals by evaporation through another screen. In this connexion, during preliminary experiments, when tellurium was condensed on a silver electrode film, the margin of the overlapped region in contiguous to the tellurium film became peeled off as sketched in Fig. 4, and the substrate exposed itself through these naked gaps proving the inadequacy of silver as an electrode material. However, in order to explicate the cause of such a curious phenomenon like this, it would be necessary to examine further with regard to the various combinations of metallic or semi-metallic deposits and such a study will be made, taking advantage of an opportunity. Aluminium or lead in combination with tellurium did not show such a trouble.

(iii) Apparatus and procedures for measuring the electric resistance and the Hall potential difference.

The structures of the specimen holder, of three pairs of electrodes, and of the requisites for varying the temperature condition of the specimen from +60° to −195°C are illustrated in Fig. 5. As seen in the figure, the specimen holder A consists of two ebonite plates ($56\times40\,\mathrm{mm}^2$) which are fixed horizontally separating 6 mm each other, the glass plate on which the metal was deposited is laid on the upper surface of the lower ebonite plate. Two current leads were made by pinning copper wires (1 mm dia.) horizontally against both ends of the film by force of phosphor-bronze sheet springs. Two other pairs of electrode-terminals, B, a pair of which being for the potential leads and the other for the Hall potential leads, were pressed until they come in contact with the aluminium electrodes on the film detailed above by virtue of helical phosphor-bronze hairsprings which were encased in respective guide frame fixed in the upper ebonite plate.

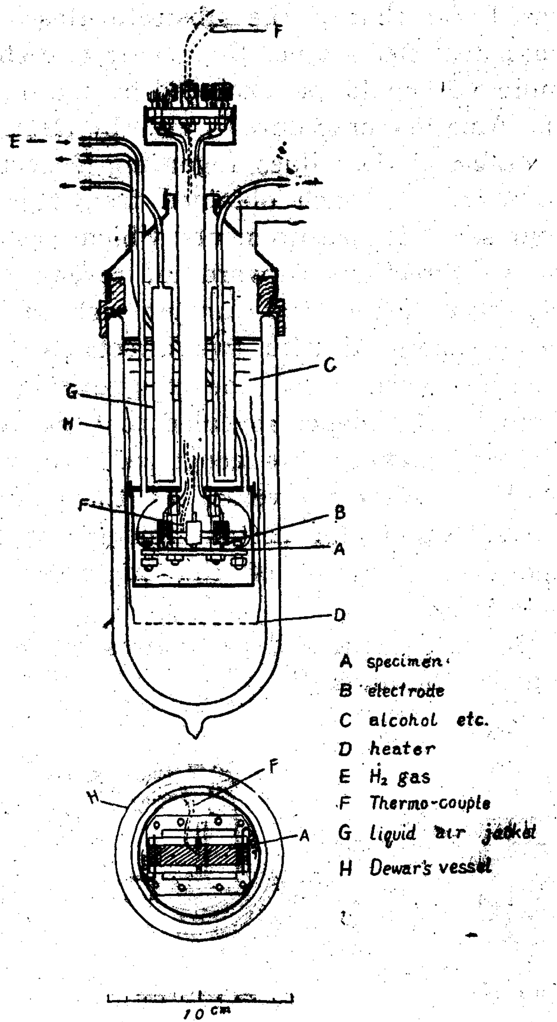

Fig. 5 Experimenting apparatus in vertical and horizontal sections.

Then the holder was placed in a cylindrical brass casket and then inserted into a Dewar's vessel, H. Three pairs of lead wires described above and a pair for a copper constantan thermo-couple, F, were all joined to the uppermost terminals through a thin-walled German silver tube which connecting the aforesaid casket with the brass cap of Dewar's vessel and forming a terminal box at the upper end. And then this Dewar's vessel was introduced in a magnetizing coil of 10 cm inside, 21 cm outside diameter and 10.5 cm high, which gave the central field strength of 1,930 Oe at a current of 8 amp. The field strength was in good proportion to the exciting current and its deviation throughout the length of specimen was less than 1 per cent.

The method for lowering the temperature of specimen was practised either by introducing liquid nitrogen directly into the Dewar's vessel or by pouring it into a double walled jacket, G, attached above the casket and thereby cooling pentan or alcohol, C, contained in the Dewar's vessel; while for raising the temperature a current was transmitted through a constantan wire wound on the heater, D, which was placed beneath the casket. Further, air in the casket was replaced by hydrogen gas introduced through E, with a view to uniforming the temperature distribution by virtue of the outstanding features of hydrogen shown in the thermal conduction as well as in the less condensible tendency.

Next the electrical circuit for the purpose of measuring the electric resistance, the Hall potential and the magneto-resistance is illustrated in Fig. 6. As the electric current led

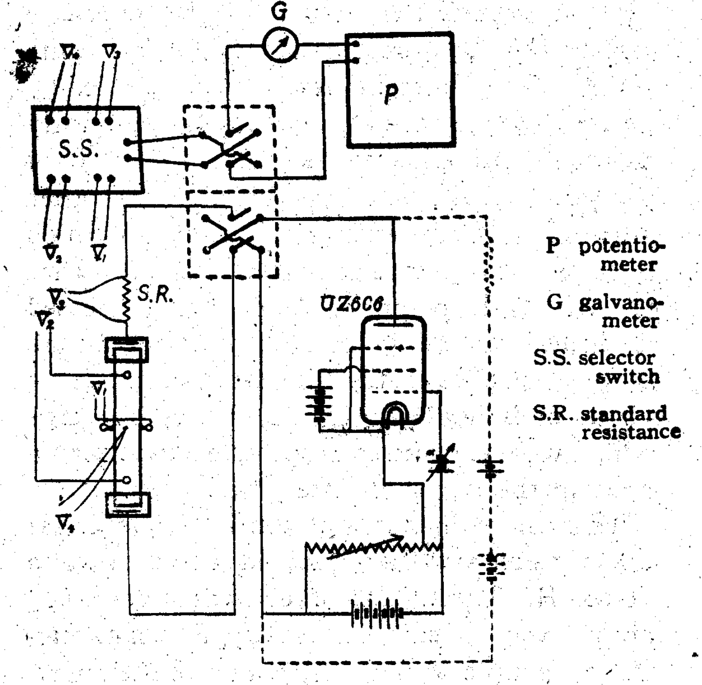

Fig. 6 Measuring circuit diagram.

through the specimen was naturally varied in consequence of the change of resistance due to the effect of magnetic field, the following circuit was used intending to keep the current constant. Namely, by connecting the specimen (ca. 10^4 ohms) and a standard resistance of 10^3 ohms in series with the anode circuit of a pentode UZ 6C6, applying 100 volts on the screen grid and 450 volts on the anode, thus corresponding to the operating condition that the anode current is nearly in saturation with respect to the anode voltage, then the circuit becomes equivalent to the circuit as shown by the broken line in Fig. 6; i. e. it becomes identical eventually with a circuit ballasted by more than one megohm and in consequence the variation of the primary current can be so much reduced as to be imperceptible notwithstanding the considerable change of the specimen's resistance. This amount of current was usually fixed at between 0.2 and 0.5 mA by biasing a suitable tension on the control grid of the pentode and it could be increased to as much as 2 mA in order to raise the sensitivity of the measurement, although the temperature rise of the specimen due to Joule's heat is undesirable. Then the potential differences, V_1 between the Hall electrodes, V_2 between the potential leads, V_3 between both ends of the standard resistance and V_4 the EMF of the thermocouple, were succesively measured by a Yokogawa's Precision Type Potentiometer involving the use of a selector switch.

It is naturally expected that the observed values of V_1 and V_2 comprise the thermogalvanomagnetic effects which were set up in the transversal (Ettingshausen effect) and the longitudinal direction respectively. However, the EMF arising from these accompanying effects was quite small owing to the minute heat capacity of the specimen compared with that of the substrate glass. Any parasitic effects other than these two effects, moreover, could be excluded by the light of the Amerio's procedure⑶, viz., by taking the averages of the values, regarding respectively to V_1 and V_2, each obtained from the next four sets of measurements which pertained to two directions forward and reverse of the specimen current and further each of them being combined with two directions of the exciting current of the magnetizing coil. Actual performance revealed that no appreciable differences were recognized in the values of V_1 or V_2 on reversal of the specimen current except for certain amounts of differences on reversal of the magnetic field polarity.

(iv) Apparatus and procedures for measuring the thermo-EMF.

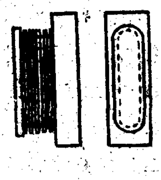

Fig. 7a Construction of the heater used for measuring thermo-EMF.

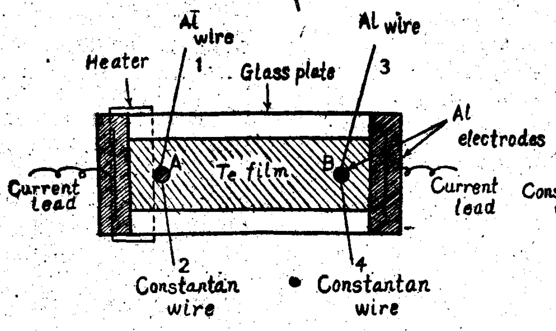

Fig. 7b Arrangement for measurement of thermo-EMF.

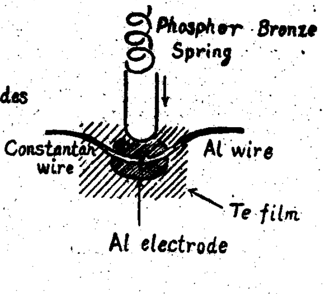

Fig. 7c Sketch of electrode contacts at A and B.

For the measurement of thermo-EMF of tellurium film against aluminium, a certain small temperature gradient was given along the length of the specimen described above by attaching a heater, firmly by a spring, in contact with the glass substrate towards the opposite side of an end of the specimen. The heater in question, shaped like that shown in Fig. 7a, is made of a copper bobbin, all surface of which except the contact one with glass being glazed and baked with bakelite varnish, and constantan wire of BS No. 40 wound on it in five layers non-inductively, whose resistance amounting to 436 ohms. This heater developed a temperature difference of 3°~4° between both ends of a specimen when a current of 20~30 mA was allowed to flow.

As for two junction points to measure the thermo-EMF use were made that the pair of aluminium electrodes A and B which were employed as the potential leads in resistance measurement (Fig. 7b); i. e. the said EMF caused in the circuit Al–Te film–Al due to the temperature difference between A and B was measured by touching aluminium wires 0.3 mm in diameter against each aluminium electrode by force of springs. Each tip of these aluminium wires was rolled flat to about 0.1 mm thick and joined by aluminium solder with each tip of constantan wires of BS No. 35 which was flattened to the same thickness; and in terms of these two aluminium-constantan thermo-couples, the temperatures of two junction points A and B were measured separately.

The relation between EMF of aluminium-constantan thermo-couple and temperatures was calibrated in the range between 30° and −195°C in comparing with the indication of a platinum resistance thermometer which was examined previously at several fixed points.

III. Experimental results

(i) Electrical resistance *vs.* thickness of the films.

In comparing the results, the definition of the film thickness is essential; whilst the accurate determination of it is a matter of considerable difficulty. Therefore, for convenience' sake, we shall take the next quantity in order to adopt the weight of deposited metal as an indicator of the thickness:

$$d_\rho = \frac{M}{A.\rho},$$

in which A means the area of the film, M its weight and ρ the usual density of the metal. Provided a film had the same structure or equivalent density as that of the bulky metal, d_ρ would represent the true thickness of the film, but usually this is not the real case. By way of another indicator of the thickness, we shall calculate the next expression:

$$d_\sigma = \frac{\sigma.a}{R.b}$$

where σ is the specific resistance of the metal in bulky state, R the resistance observed for the specimen, a the length and b the width. If the specific resistance of a film is equal to σ (0.2 Ω cm at 20°C for tellurium*), d_σ would give the true thickness of the film, but this is also not necessarily in accord with the facts.

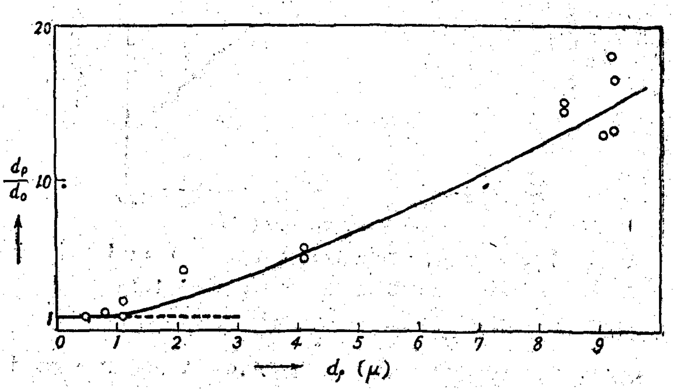

Fig. 8 d_ρ/d_σ ratio plotted against d_ρ.

Actual evaluation of d_ρ and d_σ with respect to the tellurium films at variance with the thickness gave a result as shown in Fig. 8 in the relation between d_ρ/d_σ and d_ρ. It shows that d_ρ/d_σ is nearly unity when d_ρ is less than 1μ, i. e., d_ρ and d_σ is almost equivalent to each other. But as the thickness d_ρ increases the value of d_ρ/d_σ increases in proportion to d_ρ, which fact implys that d_σ increases not so much as d_ρ, in other words, the decrease in resistance does not run in parallel with the increase in thickness.

And the films which belong to the region of $d_\rho/d_\sigma=1$ ($d_\rho \leqq 1\mu$) show a dull metallic luster, but as the thickness increases they

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* Specific resistance of tellurium is generally reported (in Gmelin et al.) as 0.2 Ω cm at 20°, but the value obtained by us later on as regards the purest metal in bulk is ca. 0.35 Ω cm.

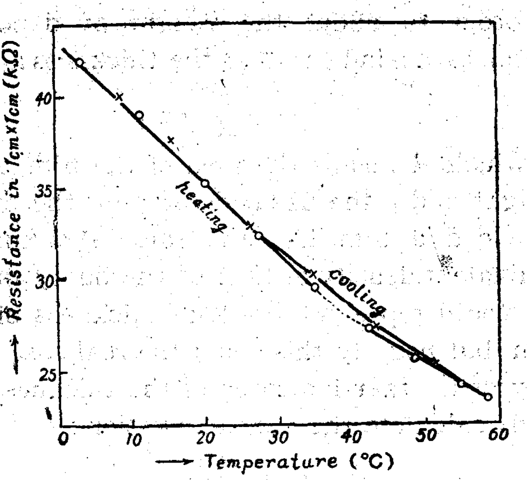

Fig. 9 Electric resistance *versus* temperatures. (d_σ =0.06μ)

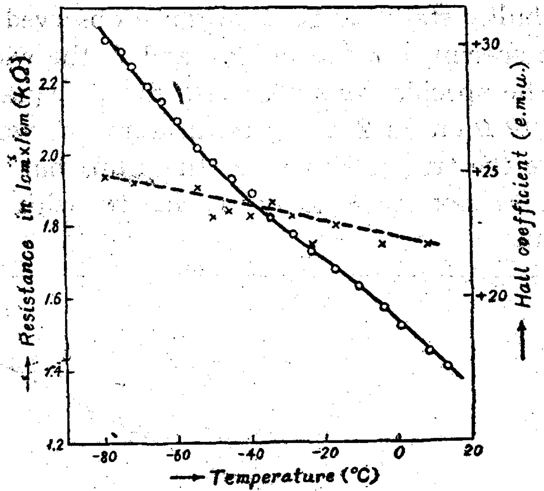

Fig. 10 Electric resistance (∘) and Hall coefficient (×) *versus* temperatures. (d_σ =1.43μ)

show an appearance as if they were covered with fine sooty black powders.

(ii) Electrical resistances and Hall coefficients *vs.* temperatures.

Relations between resistances and temperatures are illustrated in Figs. 9~12, the thicknesses of the films being 0.06, 1.43, 0.28 and 0.087μ respectively; and in Figs. 10~12 the temperature variations of the Hall coefficient are also given. These measurements were usually started from the lowest temperature and performed by fixing the temperature for a certain period of time whenever necessary in the course of the heating stage.

At the temperature range between −100° and −80°C, certain amounts of irregularities are recognized both in resistance and in Hall coefficient.

(iii) Hall coefficients *vs.* thicknesses of the films.

Hall coefficients (A_H) at room temperature measured with respect to the films whose thicknesses being 0.08, 0.20, 0.32, 0.34, 0.91 and 1.30μ are given in Fig. 13. It appears that the Hall coefficient becomes smaller as the film thickness is thinner; and further the former quantity is almost in proportion to the latter one as may be given by the next expression: $A_H=52\times d_\sigma$ when d_σ is measured in micron. But some deviations from this relations were observed for very thin films.

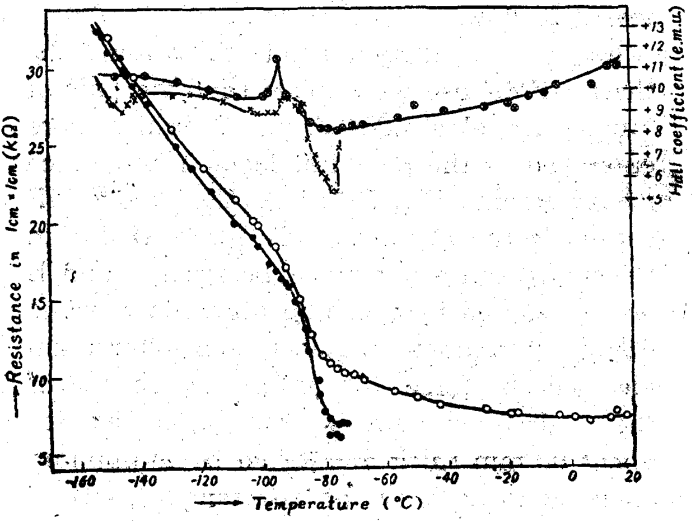

Fig. 11 Electric resistance (∘ •) and Hall coefficient (⊗×) *versus* temperatures. (d_σ =0.28μ)

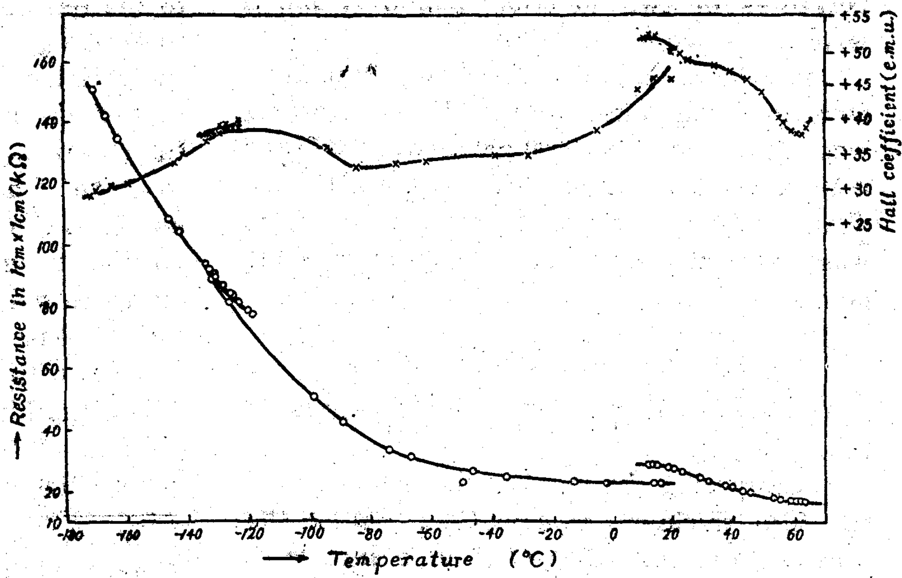

Fig. 12 Electric resistance (∘) and Hall coefficient (×) *versus* temperatures. (d_σ =0.087μ)

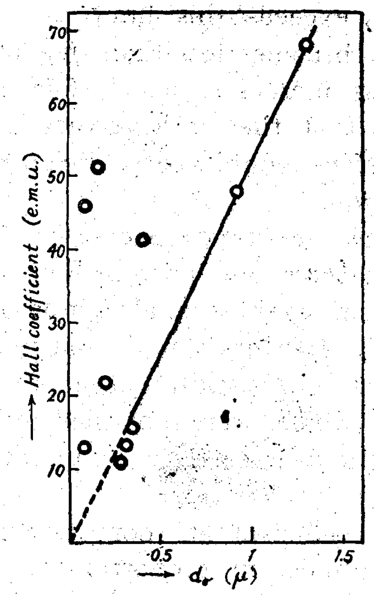

Fig. 13 Hall coefficient *versus* film thickness.

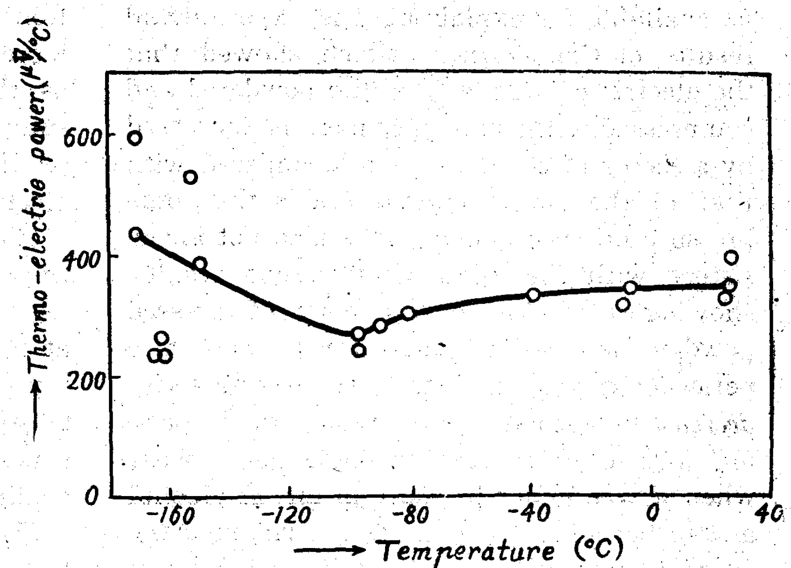

Fig. 14 Thermoelectric power as a function of temperature.

(iv) Magneto-resistances *vs.* temperatures.

Denote the increase of resistance R due to the magnetic field H by ΔR, then the following relationship could be confirmed.

$$\frac{\Delta R}{R} = BH^2.$$

The constant B determined for a film of 0.32μ thick at a field strength of 1,802 Oe is as follows:

Table 1

Temp. :	15°C	-136.5°C
R :	$14.0\times10^3\ \Omega$	$79.1\times10^3\ \Omega$
B :	4.19×10^{-11}	8.26×10^{-10}
A_H :	$+13.5$	$+15.6$

(v) Thermo-EMF *vs.* temperatures.

Thermo-electric power of the film of $d_\sigma = 0.28\mu$ against aluminium in the temperature range between +32° and −170°C is illustrated in Fig. 14. However, the data at the range below −100°C are inevitably less accurate due to a high resistance of the film at that range.

It was observed that the thermo-electric power is positive throughout the whole range of temperature but a nearly linear relationship exists between the said power and the reciprocal of absolute temperature in the interval of +32°~−100°C.

IV. Discussion of the results

Pure tellurium film can be enrolled in an abnormal impurity semi-conductor, since the Hall coefficient is positive and the temperature coefficient of resistance is negative throughout the temperature range under investigation. Attempt to obtain the energy difference between the top of fully occupied band and the upper impurity level (electron acceptors) or the empty conduction band to which the electrons to be excited did not give a consistent result, and it will be reconsidered basing upon the experimental results with regard to the bulky tellurium which is reported in the next paper.

It is recognized that the electric conductivity of an ordinary metal in the film state is smaller than that of the bulky state. There has been generally explained that this effect is due either to the shortening of the mean free paths of the conduction electrons by collisions with the boundaries of the film or to the smallness of the electron concentration participating in the conduction.

However, as for the film of tellurium the free electron concentration might be considered to be rather larger than that of the metal in bulk if deduced from the data on the Hall coefficient by assuming that the electron concentration is inversely proportional to the Hall coefficient. If this assumption be allowed to be justified, the above cited result that the Hall coefficient increases almost in proportion to the film's thickness may also be explained by taking account the free electrons, which are either accommodated in the so-called Tamm's level⑷ localized on the surface or freed from the positively charged atoms adsorbed on the surface, in addition to the ordinary electron concentration pertaining to the conduction in bulky metal.

This hypothesis, uncertain as it is, will also be available for explaining the experimental results of Cartwright(5) which showed that the electric conductivity of the powdered and compressed tellurium specimen is increased by a factor of ten or more as compared with that of the single crystal under the some pressure of 1,000kg/cm^2. It is also not inconsistent with the other Cartwright's results, showing that the conductivity of pressed powder *increased* on exposure to air for a period of a year and that the conductivity *decreased* considerably by momentarily passing an electric current through the powder when it was under pressure in air, in alcohol and in benzene, which procedure changed the specimen from a dull gray to a silver brilliance and welded into a rigid compact piece.

The present result on thermo-EMF in addition shows that the positive hole conduction is predominant in tellurium film in agreement with the result on Hall coefficient; here we should like to add that our result at issue is very similar to that of Hochberg and Sominski(6) on the thermo-EMF of selenium in the range between +60° and −120°C.

Summary

(1) Electric resistance, Hall coefficient, magneto-resistance and thermo-EMF are measured with regard to pure tellurium films, deposited by evaporation on glass plate, over the temperature range between +60° and −195°C; the substrates in concern have been baked out in the same high vacuum prior to the metal deposition.

(2) The electric resistance is measured, by means of a potentiometer, from the potential difference between a pair of aluminium electrodes deposited on both ends of the said tellurium film.

(3) The thickness of a film can be estimated either from the weight of the deposited metal or from the electric resistance, viz., the former thickness is given by $d_\rho = M/A\cdot\rho$ where M is the weight of the deposit, A its area and ρ the usual density of tellurium, and the latter one is defined by $d_\sigma = \sigma/R \times a/b$ where σ the specific resistivity of tellurium in bulk, R the resistance of the film having the length a and the width b.

When d_ρ/d_σ is plotted against d_ρ, the quotient is nearly unity for d_ρ less than 1 micron while it increases almost in proportion to d_ρ as d_ρ exceeds this limit, i. e. the increment of d_σ becomes less than that of d_ρ as the thickness increases, which fact presumably means that the black velvety layer on the film surface would not participate in electric conduction.

(4) The electric resistance decreases with the rise of temperature as shown in Figs. 10~12, wherein the curves show an abrupt descent at about −100°C. Irreversible phenomena to some extent were occasionally observed between the data which were obtained in the course of rising and descending temperature conditions.

(5) The Hall coefficient at room temperature increases almost in proportion to the thickness of the film as shown in Fig. 13, viz., when the thickness d_σ is measured in micron the Hall coefficient is given by $A_H = 52 \times d_\sigma$. The temperature change of Hall coefficient is fairly small throughout the range between +60° and −195°C, except an irregular change at about −100°C.

(6) The magneto-resistance effect at the field strength of 1,802 Oe is measured and obtained the results shown in Table 1.

(7) The thermo-electric power of a film of about 0.3 micron thick against aluminium is positive throughout the temperature range under study and varies as shown below:

Temp. °C	+27	−39	−80	−97
$\alpha \frac{\mu V}{°C}$	+397	+327	+301	+267

(8) Some explanatory discussion was attempted on the mechanism of electrical conduction in a tellurium film, basing on the above described results and those had been obtained by Cartwright.

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