On the Electromagnetic Properties of Single Crystals of Tellurium. III : Adiabatic and Isothermal Hall Effect, and Ettingshausen Effect

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On the Electromagnetic Properties of Single Crystals of Tellurium. III
Adiabatic and Isothermal Hall Effect, and Ettingshausen Effect*

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Synopsis

A study has been made of the comparison of the adiabatic and the isothermal Hall effects of a tellurium crystal from -180° to $+350^\circ$C. An ordinary d. c. method was used for the adiabatic effect and a potentiometric nil-method utilizing a 1000 cycles a. c. was employed for the isothermal one. The difference of two kinds of Hall coefficients was found to be less than 10 per cent below 230°C, but above 240°C the adiabatic coefficient has a value as low as 85～50 per cent of the isothermal coefficient. This notwithstanding, the remarkable sign reversal is observed at 240°C also in the isothermal Hall coefficient, which fact evinces itself to be one of the essential properties of tellurium.

I. Introduction

In the preceding report⁽¹⁾, we have dealt with the electric conductivity, Hall effect, magneto-resistance effect and Seebeck effect of single crystals of pure tellurium over the temperature range between -190° and $+350^\circ$C; and arrived at the conclusions that the metal instead of undergoing a transformation as presumed by Wold but the whole experimental results hitherto obtained can be consistently interpreted by assuming a model, regarding the energy level of conduction electrons, that it is a P-type extrinsic semiconductor below -100°C and an apparent intrinsic one above 0°C, having a forbidden region of width 0.34 eV between the highest filled band and the next upper normally empty (conduction) band accompanied in addition by the localized "acceptors" impurity level of an order $2\times10^{15}\,\mathrm{cm}^{-3}$ at a close proximity, a few hundredths of eV, above the former band.

When a specimen carrying an electric current is subjected to a transverse magnetic field, an electro-motive force (Hall effect) and a temperature gradient (Ettingshausen effect) are induced to the direction perpendicular to those both of the current and of the magnetic field.

Therefore, in so far as the direct current method is adopted, an e. m. f. cor-

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* The 563rd report of the Research Institute for Iron, Steel and Other Metals.

(1) The present writers, Sci. Rep. RITU., A, 1 (1949), 373; this paper will be referred to hereafter as Paper I.

responding to the Ettingshausen temperature difference is superposed on the Hall e. m. f. proper, as was detailed in Paper I.

Especially in the case of tellurium in contrast with other elements, one is not permitted to set the said effect at defiance because of its large Seebeck potentials pursuant to the Ettingshausen temperature gradient; and furthermore the effect cannot be eliminated simply by taking the mean value of four measurements pertaining to the individual reversal of the current and the magnetic field (Amerio's procedure), since the Ettingshausen effect reverses its polarity together with the Hall effect.

In order to know the net Hall effect, i. e. the isothermal Hall effect, and to calculate the concentration, mobility and mass of the current carrier, it is essential to make the temperature distribution should be uniform throughout the specimen and be kept unaltered due to a magnetic field. One may meet the above requirement either by immersing a specimen in a flowing liquid bath or by resorting to an a. c. method, of which the current changes its polarity in the period shorter than the duration that which is demanded to create the Ettingshausen temperature gradient. Being the former method considered to be inadequate, the present investigation adopted the a. c. method as already used by Wood(2) and Bottom.(3) The Hall measurements by the a. c. method were first performed by Smith(4) and Zahn(5) with regard to bismuth.

Scanlon and Lark-Horovitz(6) have measured the adiabatic Hall effect and the Ettingshausen effects by means of d. c. method, and found that the latter effect passes through a positive maximum value at +160°C, dropping rapidly to zero on either side of the maximum. Being the Seebeck effect positive, the Ettingshausen effect yields an e. m. f. to the negative sense of the Hall effect, and the minimum or the trough of the Hall curve, which shows anomalous double reversal of sign from positive to negative and back to positive again, appears at +160°C. Hence they inferred that the isothermal Hall effect becomes positive throughout the range of temperatures investigated when the Ettingshausen correction be added to the adiabatic Hall data.

Bottom(3) has measured the Hall e. m. f. by a. c. with frequencies between 10^3 and 10^4 cycles per sec., employing an apparatus constructed so as to enable the effect to be observed directly on the screen of an oscilloscope. He stated that the isothermal Hall effect is positive between the temperatures 20° and 400°C.

If the above descriptions be true, all data in Paper I which were deduced from the adiabatic Hall effect might involve substantial errors; so that this is the very reason why we have undertaken the present investigation.

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(2) L. A. Wood, Phys. Rev., 41 (1932), 231.

(3) V. E. Bottom, Phys. Rev., 74 (1948), 1218 (A).

(4) A. W. Smith, Phys. Rev., 35 (1912), 81.

(5) H. Zahn, Ann. d. Phys., 47 (1915), 49.

(6) W. Scanlon, K. Lark-Horovitz, Phys. Rev., 73 (1948), 1256 (A).

While, quite recently, when the major portion of this experiment had been performed, a note of Bottom(7) was again published, saying that the purest sample of tellurium made by multiple distillations has a Hall constants of +5000 in the impurity range, becoming negative between the temperatures of −40° and +230°C, and then back to positive again above that range. Provided the purity of the sample is not good enough, double reversal of the sign disappears. In case of pure sample one reversal always occurs at +230°C, while the temperature at which the other reversal occurs moves towards the higher temperature with increase of the impurity content. These results are almost in agreement with our data obtained in this and the preceding investigation.(1)

II. Apparatus and procedures

The apparatus used to control the temperature condition of the sample and to apply a uniform magnetic field to it is the same as that illustrated in Fig. 1 of Paper I.

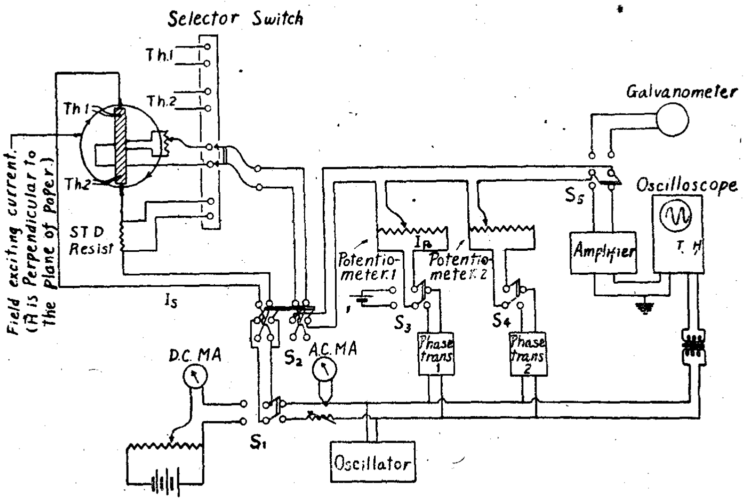

Fig. 1. The circuit for measuring the Hall effects by means of both d. c. and a. c. methods.

The former workers resorted to the method which observe the Hall voltage directly from the deflection of the oscilloscope image. But this method seemed to be inadequate for the highly accurate investigation, we adopted here a nil-method, i. e. the oscilloscope was merely used as a zero indicator, through which we could be dispensed with the determinations of the oscilloscope sensitivity and the amplification constant. The measuring circuit is outlined diagrammatically in Fig. 1. The main course of this experiment being intended to find out the disparity between the adiabatic and the isothermal Hall effects, the circuits have been assembled so as to facilitate the successive measurements of two Hall e. m. f. induced by the direct and alternating primary currents.

The primary currents were allowed to flow through the specimen via the platinum electrodes, which were welded at both ends of the specimen by means of a sharp-pointed hydrogen flame, either from the storage battery or from the oscillator to be described below. As the Hall electrodes those of Koláček type(8)

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(7) V. E. Bottom, Phys. Rev., 75 (1949), 1310 (A).

(8) F. Koláček, Ann. d. Phys., 39 (1912), 1491.

were adopted, i. e., one electrode being fixed at the mid point on one generating line of the specimen, and the other one branched into two were fixed at two points which situated on the diametrically opposite generating line of the former, making the distance of about 1 mm around the mid point. All of these electrodes were made of platinum wires of BS $\#45$ and welded at the stated points by dint of the condenser discharging method described before. As visualized in Fig. 1, the branched Hall electrodes were connected each other through a potentiometric resistor, and the sliding contact of this potentiometer was carefully adjusted so as to render its potential exactly equilibrated with that of the opposite Hall electrode while the magnetic field was not being applied. The a. c. source is the *Yokogawa's* Y-A type vacuum tube oscillator, which affords the maximum output current of 35 mA when a resistance of 650 Ω is loaded, of which higher harmonics involved is less than two per cent over the frequencies ranging from 100 to 10,000 cycles per second.

The amplifier installed ahead of the oscilloscope is a four stages resistance-capacitance coupled cascade amplifier having maximum voltage gain of 105 decibels. The total amplification factor including the oscilloscope amplifier amounts to 120 decibels and 1 mm deflection of the oscilloscope image corresponds to three microvolts of the input voltage to be measured.

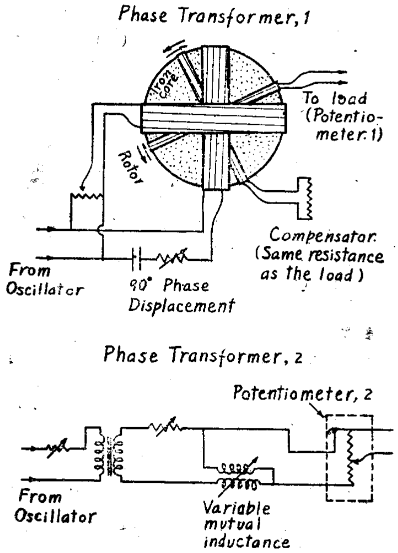

Fig. 2. The detailed circuits of the phase shifting transformers 1 and 2 in Fig. 1.

The somewhat detailed construction of the phase shifting transformer "1" and "2" are blocked out in Fig. 2. The former is the *Drysdale's* phase shifting transformer which can displace and adjust the phase of the output current by any desired angle to the input one without altering the amplitude, and the latter is an ordinary whole range phase shifting circuit composed of a variable resistance and a variable mutual inductance.

When the magnetic field was not exercised on the specimen, the potentiometers designated by "1" and "2" were set at zero readings, and the sliding contact position of the potentiometric resistor connecting the branched Hall electrodes were adjusted in such a way that the galvanometer showed no deflection when a direct current was passed through the specimen. Then, it may not be expected also that any deflection of oscilloscope image would be induced when the alternating current is led through the specimen under this state of adjustment, but this is contrary to the case because superfluous voltages of the oscillator frequency and 50 cycles of line voltage inevitably intrude into the grid circuit of the amplifier owing to an induction between leading wires of the circuits in face of all efforts toward the circuit shielding and render an exact measurement of true voltages inaccessible. By reducing the capacity of the fourth stage coupling condenser in the amplifier and shunting the input terminals of the oscilloscope with a proper condenser-choke filter, the 50 cycles' component of the parasitic voltages just mentioned has nearly been removed. While, in order to remove the principal high frequency component, the phase shifting transformer "2" and the potentiometer "2" had to be employed. Namely, the output voltage of the potentiometer "2" was regulated so as to be equal in amplitude but displaced 180° in phase relative to the parasitic component in question. Through these procedures the fluorescent image on the oscilloscope screen was found to appear like Fig. 3 **C** after the perfect compensation, that which had appeared like **A** originally and something like **B** in an imperfect stage of compensation. Even in the image **C** the second harmonic term remains without compensated, on the contrary doubled in magnitude; however, in actual practice this residue hardly introduces an error no more than one per cent to the result.

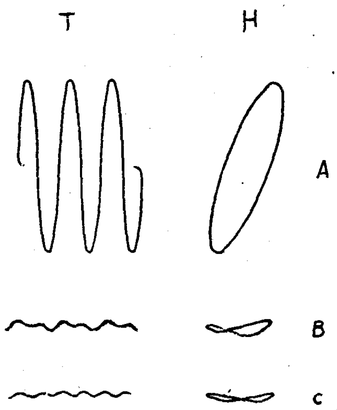

Fig. 3. Oscilloscope images of the a. c. Hall voltages. **A, B** and **C** are the images corresponding respectively to the uncompensated, incompletely and completely compensated states. The sinusoidal wave patterns as the images **T** were observed in general and in the case of small Hall voltages the Lissajous figures as the images **H** were employed.

Next, when the magnetic field is excited, the net isothermal Hall voltage appears on the screen and this quantity is to be compensated, as far as the sensitivity of the apparatus is attainable, by means of the potentiometer "1" and the phase shifting transformer "1" in like manner as described above. Then the readings of the transformer "1" and the potentiometer "1" correspond to the inverse phase and the amplitude of the isothermal Hall voltage of interest here.

The occurrence of the reversal of sign in the isothermal Hall effect has been recognized by the rapid but continuous change of the phase difference by the amount 180° between the currents in the specimen and in the potentiometer "1" under the perfectly compensated state, this is known from the readings of the phase transformer "1", when the temperature has been changed quite gradually around the temperature in concern.

The adiabatic Hall voltage, viz. the Hall voltage for a direct current, was measured by reversing the switches "S_1", "S_3" and "S_5" in Fig. 1 and disconnecting "S_4", thus the measurement was carried out much the same manner as described in Paper I; the mean value of four measurements pertaining to the individual reversal of the current and the magnetic field was taken as usual in order to eliminate the parasitic effects other than the Ettingshausen effect.

The isothermal and adiabatic Hall coefficients are calculated from the observed Hall voltages in the following ways. The reading α of voltage drop in the standard resistance, R_0 ohms, connected in series with the specimen and that β corresponding to the Hall voltage, V_H, are measured by the potentiometer "1"; on condition that the currents both in the specimen, I_s, and the current in the potentiometer "1", I_p, are kept unchanged throughout the measurements of potentials α and β, the next relationships hold.

$$R_o I_s = \alpha I_p \tag{1}$$

$$V_H = \beta I_p = R_o I_s \frac{\beta}{\alpha} \tag{2}$$

Then,

$$A_H = \frac{\pi D V_H}{4 H I_s} 10^9 \text{ emu} = \frac{\pi D R_o \beta}{4 \alpha} \cdot 10^9 \text{ emu} \tag{3}$$

in which D denotes the diameter of spcimen in cm and H the magnetic field strength in oersted. It should be noted that the absolute values of I_s and I_p are not required as seen from Eq. (3), of which the accurate measurements cannot always be done with facility in the case of alternating current.

Thus the isothermal and the adiabatic Hall coefficients, $A_{H,i}$ and $A_{H,a}$ can be procured by the successive measurements pertaining to the alternating and the stationary currents.

As for the specimen temperature, the average has been taken of the readings observed by two pairs of copper-constantan thermocouples, "Th. 1" and "Th. 2" in Fig. 1.

III. Experimental results

The specimen dealt with in this experiment is the "specimen I" in Paper I, that is a single crystal made of Kahlbaum tellurium purified by repeated fractional vacuum distillations, containing 10^{-3} per cent tin as an impurity. It has a circular section of 0.16 cm in diameter and 2.2 cm long, whose length makes an angle of 6.0^0 with the principal [0001] axis.

For the alternating current method, 1000 cycles sinusoidal wave was employed. It is known from the works of Smith,⁽⁴⁾ Zahn,⁽⁵⁾ Wood,⁽²⁾ and Bottom⁽³⁾ that the isothermal Hall effect can be adequately observed with this frequency. As Fig. 4 shows, a linear relationship exists between the a.c. Hall voltage $V_{H,i}$ and the magnetic field strength, alike with the case of d.c. Hall voltage

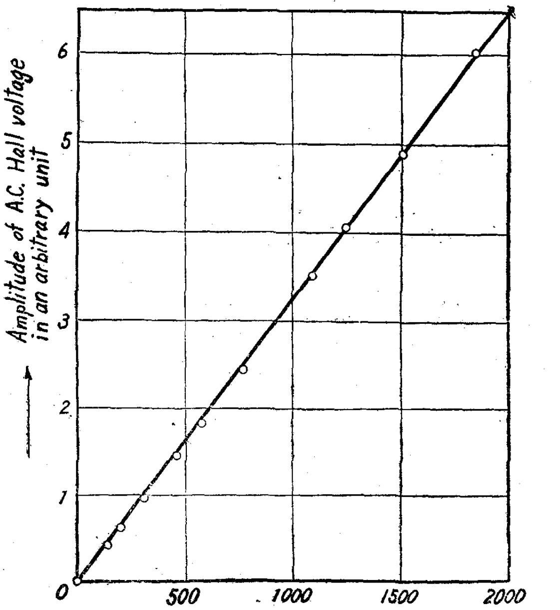

Fig. 4. Linear relationship between the isothermal Hall voltage and the magnetic field strength, an alternating current of 1000 cycles being led through the specimen. $t = -170°\text{C}$, $A_{H,i} = +3.25 \times 10^4$ emu.

$V_{H,a}$ which was shown in Fig. 5 of Paper I. In Fig. 5 the adiabatic and isothermal Hall coefficients, $A_{H,a}$ and $A_{H,i}$, are plotted as functions of temperature, which have been observed successively and alternately with increasing temperature from −180° to 350°C; the ordinate scale is taken in three ways pursuant to the absolute magnitudes of the effect in three temperature ranges, since they markedly diminish with rising temperature. Each value of $A_{H,a}$ and $A_{H,i}$ was carefully measured after the temperature being well fixed constant. The two curves in Fig. 5 are not in accord with each other; nevertheless, the difference of two curves, $A_{H,a}$-$A_{H,i}$, is less than 10 per cent of $A_{H,i}$ below about 230°C, which fact confirms that the use of $A_{H,a}$ in place of $A_{H,i}$ in the discussion of Paper I does not introduce an appreciable error below 230°C, and also it has been borne out that the noticeable sign reversal of $A_{H,a}$ around 240°C in Paper I is an essential property of the net Hall effect, viz. $A_{H,i}$. Although, the substitution of $A_{H,a}$ for $A_{H,i}$ above 240°C gives the underestimation as low as 85~50 per cent of the net Hall effect. Thus enabling to say that the main purpose of the present study has been achieved.

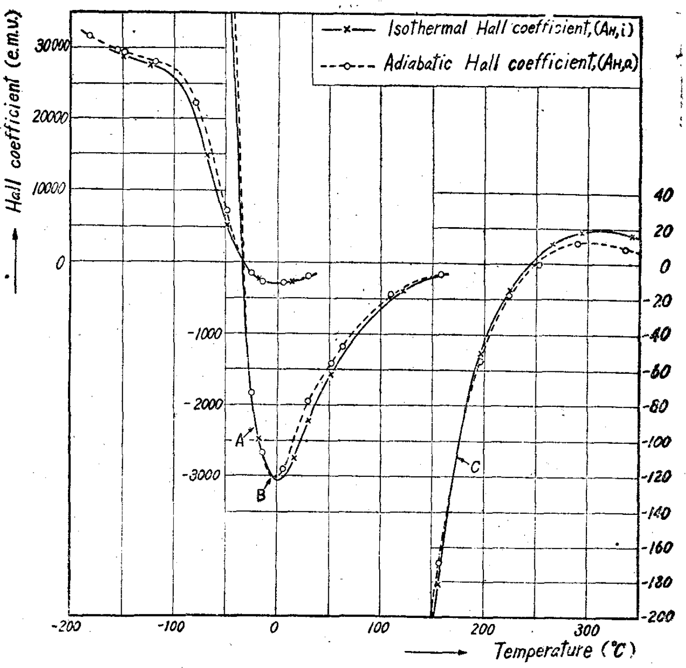

Fig. 5. Comparison of the adiabatic and the isothermal Hall coefficients which are measured simultaneously. Ordinate is represented in three different scales with ratios of (1 : 10 : 250) in three temperature ranges.

$A_{H,a}$-$A_{H,i}$ computed from Fig. 5 is plotted in Fig. 6. As seen in the figure, $A_{H,a}$ and $A_{H,i}$ reverse their relative magnitudes three times, i. e., these reversals take place at the points A, B and C in Fig. 5, and 6. If any difference exists between the adiabatic and the isothermal Hall effects which are observed simultaneously on the same specimen, it should be attributable to the Ettingshausen effect inherent in the adiabatic Hall effect. Because the Ettingshausen-Nernst effect (the transverse potential difference) and the Righi-Leduc effect (the transverse temperature difference), which are ascribable to a small inevitable longitudinal temperature gradient and the magnetic field, can be eliminated by taking the mean value of two adiabatic voltages pertaining to both directions of the primary current; and any effect which is proportional to the square of magnetic field strength, e. g. the magneto-resistance effect* which may be generated in case the line connecting

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* This effect will not be developed in the case of perfectly balanced Hall electrodes of Kolâcek type.

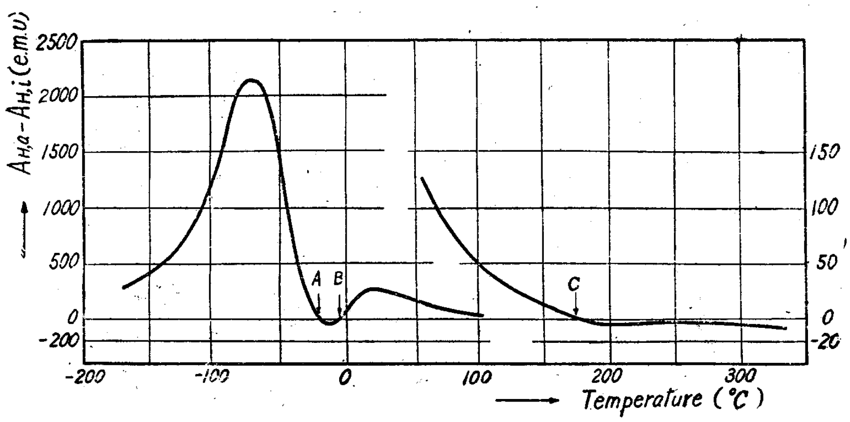

Fig. 6. The difference between the adiabatic and the isothermal Hall coefficients, $A_{H,a}$–$A_{H,i}$, which is estimated from Fig. 5. Ordinate scale is magnified tenfold above ca. 75°C. The temperature readings of points A and C in Fig. 5 and in this figure at which the difference of both coefficients vanishes coincide exactly with those of points A and C in Fig. 8 at which the thermoelectric power becomes zero.

two Hall electrodes be not exactly at right angle to the stream line of the current, can also be eliminated by averaging the values measured in connection with two polarities of the magnetic field. Under these considerations the next relationship is found among the adiabatic Hall voltage $V_{H,a}$, the isothermal Hall voltage V_{Hi} and the Ettingshausen temperature difference T_E,

$$V_{Ha}=V_{Hi}-T_E\cdot\left[\frac{d\Theta}{dT}\right]_{\perp.H.Pt} \tag{4}$$

in which $[d\Theta/dT]_{\perp.H.Pt}$ represents the thermoelectric power* of tellurium against platinum electrodes in the transverse direction to the specimen axis under magnetic field, and the minus sign of the second term in the right hand side results from the definitions of the related effects as shown in Fig. 7.

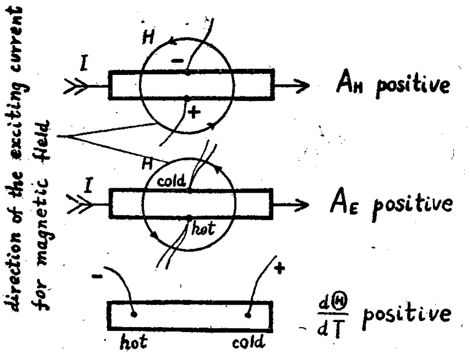

Fig. 7. The sign conventions of Hall effect, Ettingshausen effect and thermoelectric power

On the other hand, from the definitions of the coefficients, we get

$$\left.\begin{aligned} V_{Ha} &= A_{Ha}\, H\, i_s D \\ V_{Hi} &= A_{Hi}\, H\, i_s D \\ T_E &= A_E\, H\, i_s D \end{aligned}\right\} \tag{5}$$

where i_s stands for the current density in the specimen. Then, Eq. (4) becomes

$$A_E=-(A_{Ha}-A_{Hi})\Big/\left[\frac{d\Theta}{dT}\right]_{\perp.H.Pt} \tag{6}$$

although no exact value of $[d\Theta/dT]_{\perp.H.Pt}$ being known, this quantity may be substituted without appreciable error with $[d\Theta/dT]_{\parallel.0.Cu}$ which has been measured on the same specimen as in Fig. 8 by the following reasons. First, in the relation:

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* $\frac{d\Theta}{dT}$ in $\mu V/deg$ is equal to $10^2\,\frac{d\Theta}{dT}$ in emu.

$_{\mathrm{Te}}(d\Theta/dT)_{\mathrm{Pt}}={}_{\mathrm{Te}}(d\Theta/dT)_{\mathrm{Cu}}-{}_{\mathrm{Pt}}(d\Theta/dT)_{\mathrm{Cu}}$ the magnitude of $_{\mathrm{Pt}}(d\Theta/dT)_{\mathrm{Cu}}$, as seen in Table 1, is negligibly small in comparison with that of $_{\mathrm{Te}}(d\Theta/dT)_{\mathrm{Cu}}$ in Fig. 8, hence $_{\mathrm{Te}}(d\Theta/dT)_{\mathrm{Pt}}\fallingdotseq{}_{\mathrm{Te}}(d\Theta/dT)_{\mathrm{Cu}}$.

Table 1. Thermoelectric power $_{\mathrm{Pt}}\left(\frac{d\Theta}{dT}\right)_{\mathrm{Cu}}$. (9)

t° C	−180	−100	0	100	200	300
$_{\mathrm{Pt}}\left(\frac{d\Theta}{dT}\right)_{\mathrm{Cu}}$ $\mu V/deg$	+5.3	−1.0	−5.8	−9.3	−11.9	−14.2

Next, the change of thermoelectric power by applying a magnetic field being not yet measured with tellurium, but this change has been found to be roughly analogous to and has the same order of magnitude as the magneto-resistance effect in the case of bismuth.(10) If the same is the case with tellurium, the change would be less than $10^{-7}H^2$ per cent of $[d\Theta/dT]_0$, i. e. one per cent at the highest. Finally, it is required that the temperature at which the difference $A_{\mathrm{H}a}-A_{\mathrm{H}i}$ becomes zero must coincide with the point at which $[d\Theta/dT]_{\perp}$ becomes zero, lest the magnitude of A_E should become infinite at that point. This fact is also satisfied with regard to $[d\Theta/dT]_{\parallel}$ as evident from the points A and C both in Fig. 6 and in Fig. 8. These results might be taken to prove the approximate equality of $[d\Theta/dT]_{\perp}$ and $[d\Theta/dT]_{\parallel}$.

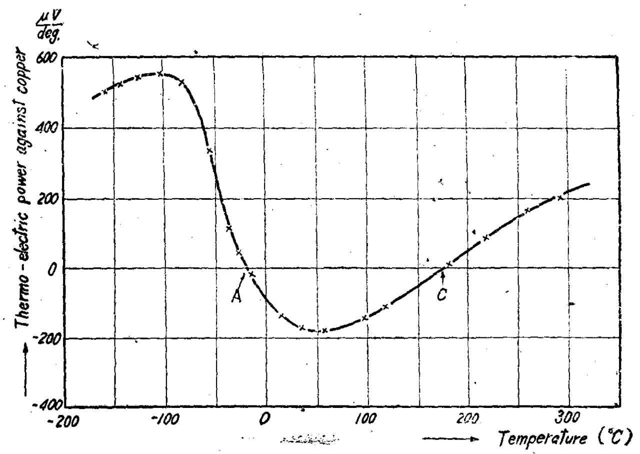

Fig 8. The thermoelectric power of the specimen I against copper without magnetic field, which is transcribed from the curve I2 of Fig. 9 in the paper I.

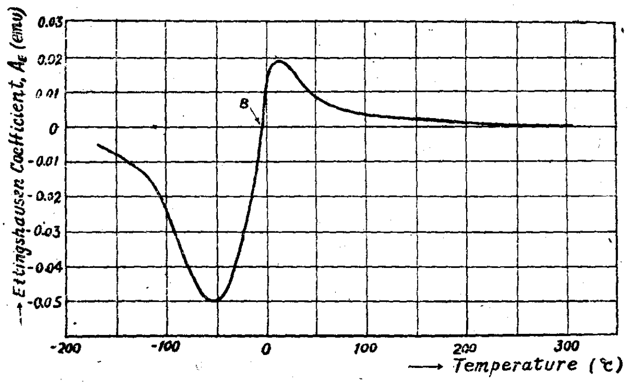

Fig. 9. The quantity, $-(A_{\mathrm{H},a}-A_{\mathrm{H},i})\Big/\frac{d\Theta}{dT}$, which is considered to be the Ettingshausen coefficient. This reverses its sign at the temperature of point B in Fig. 6.

In Fig. 9, A_E is plotted as a function of temperature, which is positive in the high temperature range and reverses its sign at point B, the same as that labelled B in Figs. 5, and 6, becoming highly negative at low temperatures.

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(9) F. Roeser, A. I. Dahl, J. Res. Nat. Bur. Stand., 20 (1938), 351.
(10) M. La Rosa, Nuov. Cim. (6), 18 (1919), 26.

The thermodynamical relation as next, which is generally called the Bridgman-Lorentz relation,(11) has been known to hold between the Ettingshausen coefficient A_E and the Ettingshausen-Nernst coefficient $A_{EN,i}$:

$$A_{EN,i} \equiv \frac{B_{EN,i}}{\kappa} = \frac{A_E}{T} \qquad (7)$$

where κ is the thermal conductivity, and $B_{EN,a} = 2\,B_{EN,i}$ of the same specimen has been depicted in Fig. 5 of the preceding paper (Paper II). The above requirement, however, seems to be in contradiction to the experimental results, since the observed value of A_E at 25°C exceeds by a factor of about nine in comparison with that computed from B_{ENa}, and still more the signs of A_E and B_{EN} are contrary to each other below −6°C.

Concerning the cause of this discrepancy, several factors may be responsible for, say, the anisotropic nature of a tellurium crystal, the Peltier effect at the platinum electrodes and so forth. Though, a further inference on this problem will tend to become too far-fetched discussion at the present stage of investigation. And a straightforward d. c. measurement of the Ettingshausen effect might lend itself to settle the matter.

Résumé

(1) In Paper I, the adiabatic Hall effect of a pure tellurium single crystal was found to reverse twice its sign; one reversal occurs at low temperature side from positive to negative corresponding to the transition from the P-type semiconductor to the intrinsic semiconductor and the other occurs at about 240°C from negative to positive again with rising temperature. So it has been required to decide whether or not the latter sign reversal is the essential behaviour of the net Hall effect, in order to elucidate the electronic structure of tellurium.

(2) The adiabatic Hall effect and the net, isothermal, Hall effect were measured alternately and successively with increasing temperature from −180° to 350°C. The former effect was observed by an ordinary d. c. method as Paper I and the latter effect was worked out by passing an a. c. of 1,000 cycles through the specimen and adopting a null potentiometric method utilizing an oscilloscope as the zero indicator.

(3) The experimental results show that the difference of two kinds of Hall coefficients is less than 10 per cent below 230°C, which fact proves that exploitation of $A_{H,a}$ in place of $A_{H,i}$ in Paper I does not introduce an appreciable error, but above 240°C such a substitution gives the underestimation as low as 85~50 per cent of the net effect. Although, the remarkable phenomenon of sign reversal at 240°C has been confirmed to be an essential property of tellurium.

(4) The quantity which may be substantially accepted as the Ettingshausen effect has been worked out from the data of $A_{Ha} - A_{Hi}$ and $d\Theta/dT$, but this quantity does not seem to satisfy the Bridgman-Lorentz relation between the Ettingshausen-Nernst coefficient obtained in Paper II.

We wish to acknowledge that a part of the expenses for this study has been subsidized by the Scientific Research Funds from the Ministry of Education.

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(11) A. Sommerfeld, N. H. Frank, Rev. Mod. Phys., 3 (1931), 1.