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# DIRECT MEASUREMENT OF THE THOMSON HEAT BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

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## ABSTRACT

The Thomson heat is a very small thermoelectric heat effect that appears in a conductor that is subjected simultaneously to an electric potential difference and a temperature difference. From the Thomson coefficient, which is a property of the material, important information can be obtained concerning the electrical properties of conductors and semi-conductors. In the past, several researchers have tried to measure the effect with varying degrees of success. In this paper a method is proposed which should in principle allow the Thomson heat to be measured accurately and directly.

## INTRODUCTION

When a system of conducting or semi-conducting wires is subjected to an electric potential difference or a temperature difference or both, several thermoelectric effects can appear. The Seebeck effect is well-known: this is the name given to a difference in potential between the terminals of a combination of wires of two different metals when the contact points of the metals are kept at different temperatures (a thermocouple).

The simplest system in which a thermoelectric effect appears is a wire of a single metal subjected to a temperature gradient. The resulting heat flow will be accompanied by an electron flow, which will give rise to an electric potential difference $\Delta V$ between the terminals of the wire. This electric potential difference per unit temperature difference $\Delta V/\Delta T$ is called the thermoelectric power of the material. In order to measure the thermoelectric power of a metal A one has to connect the end points of the wire A to a potentiometer by means of two wires of another metal B (Fig. 1). Because the points of contact with the potentiometer have to be at the same temperature it is clear that one measures not only $\Delta V/\Delta T$ of metal A but

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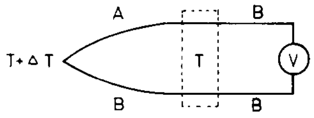


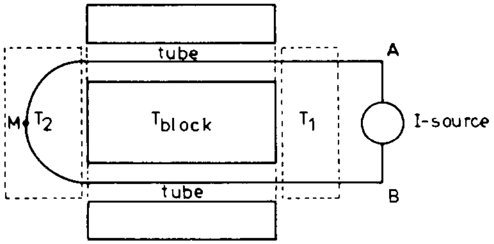


Fig. 1. Scheme of a thermocouple.

Fig. 2. Principle of the method for measuring the Thomson heat with a differential calorimeter. $T_1$ and $T_2$ are thermostats, AMB is the nickel wire passing through the tubes.

also the contribution $\Delta V/\Delta T$ of metal B. The combined system of wires A and B is a thermocouple. In tables [1] the thermoelectric power is generally given for the thermocouple as a whole and not for the single metals, although the obvious advantage of the latter method would be that the thermoelectric power of a chosen combination of materials could be estimated in advance. The problem with determining the (absolute) thermoelectric power of a single material is evident in the set up illustrated in Fig. 1: material B should not contribute to $\Delta V$. As can be shown by the theory of irreversible thermodynamics this is the case when material B is in a superconducting state. An experimental set-up with one of the new high temperature ($T_c \approx 90$ K) superconductors would be the most elegant method to obtain the absolute thermoelectric power in this temperature range. For higher temperatures however, the only way to determine this physical quantity is by measuring in some way the Thomson heat, a small heat effect appearing in a single material subjected simultaneously to a temperature difference and an electric potential difference. A constant temperature difference $\Delta T$ between the end points of a wire will cause a temperature gradient and thereby a heat flow at each point of the wire. If one prevents the wire from exchanging heat with its surroundings, for instance by keeping the surroundings at each point at the same temperature as the wire, a stationary state will develop with a constant heat flow. An electric potential difference superposed on the temperature gradient in the wire will exert a force on the electrons in the metal which transport the thermal energy. As a consequence the temperature gradient will be disturbed and thereby the stationary state. The wire will then exchange heat with the surroundings in order to restore the gradient. This heat effect, which is very small, was predicted in 1854 by Thomson and is therefore called the Thomson heat. Several researchers have tried to measure the effect with varying degrees of success [2–5]. This heat depends on the same properties of the material as those which are responsible for the thermoelectric power and accordingly there is a direct relation between the two effects. The magnitude of the

Thomson heat is a function of the electric current $I$, the temperature gradient $\mathrm{d}T/\mathrm{d}x$, the time $t$ and of the properties of the material; it is given by [6–8]

$$Q_{\mathrm{T}} = \mu I(\mathrm{d}T/\mathrm{d}x)t \tag{1}$$

In this equation $\mu$ is the Thomson coefficient, representing the quantity of heat which is exchanged with the surroundings when an electric charge of 1 C is transported over a temperature difference of 1 K. The Thomson coefficient is positive when a (positive) electric current flows in the direction of increasing temperature and heat is absorbed [8].

The relation between the Thomson coefficient and the thermoelectric power can be derived from linear irreversible thermodynamics and is given by [9]

$$\mu = -T\left(\frac{\mathrm{d}^2V}{\mathrm{d}T^2}\right) \tag{2}$$

From eqn. (2) it follows that

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\text{at temp. } T} = \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{T=0} + \int_0^T \frac{\mu}{T}\,\mathrm{d}T \tag{3}$$

Now the thermoelectric power $\mathrm{d}V/\mathrm{d}T$ is the derivative with respect to temperature of an electric potential. For a metal of constant composition the electric potential is linearly dependent on the electrochemical potential. Therefore $\mathrm{d}V/\mathrm{d}T$ is an entropy and according to the Third Law it vanishes at $T = 0$. So eqn. (3) reduces to

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\text{at temp. } T} = \int_0^T \frac{\mu}{T}\,\mathrm{d}T \tag{4}$$

From this equation it follows that, when the Thomson coefficient $\mu$ for a metal is measured as a function of $T$, the absolute thermoelectric power of the metal can be determined.

A more pronounced heat effect connected with the conduction of an electric current through a wire is the Joule heat. Whereas the Thomson heat only appears in the presence of a temperature gradient and reverses its sign when the direction of the current is reversed, the Joule heat is independent of a temperature gradient and is always positive. It is a typical irreversible process. Because of this the Thomson heat will always be accompanied by the Joule heat, which is proportional to the square of the current

$$Q_{\mathrm{J}} = \frac{I^2}{\sigma} = RI^2t \tag{5}$$

In this equation $\sigma$ is the conductivity and $R$ is the resistance of the metal.

Because the Thomson coefficient $\mu$ in eqn. (1) is very small, one has to apply a strong electric current $I$ to obtain a measurable Thomson heat. However, this will increase the Joule heat quadratically, which will then hinder the measurement of the Thomson heat. The principle of the DSC technique is that it allows the effect of the Joule heat to be eliminated by using the sign reversion of the Thomson heat, as will be explained in the next section. Nevertheless it is important to reduce the Joule heat as much as possible; this can be done by making the conductivity high. The only way to achieve this is to choose a wire with the largest possible diameter. This in turn leads to problems with limitations of the current and makes special precautions necessary.

## EXPERIMENTAL

In order to measure the small Thomson heat in the presence of the (generally) larger Joule heat directly one needs a calorimeter that is sensitive enough to measure heat effects along (part of) a wire. An instrument which seems to meet these demands is a differential calorimeter of the Calvet type as built by Setaram. It consists of two tubes of sintered silicon each being 145 mm long and having a diameter of 8 mm. Both tubes are enclosed in a thermostatically-programmed block that can also serve as a constant-temperature heat sink. Around the middle part of each tube sensors are built in over a length of 15 mm in order to measure the heat flow through the wall of the tube towards the block. The signal given by the calorimeter as a whole is the difference between the heat flows from the two tubes.

If a homogeneous wire of a conducting material is led through the tubes in the way shown in Fig. 2 and an electric current is passed through it, the Joule heat that is developed in the two tubes will be equal. Since a differential calorimeter registers the difference between the two heat effects, there will in principle be no signal. This can easily be verified. In practice, because of inhomogeneities in the wire and geometrical factors, the signal will generally not be exactly zero; a correction for this deviation will be treated in the section on the choice of materials. If a temperature gradient is now imposed on the wires by cooling down the wire on one side of the calorimeter tubes and heating it on the other side a Thomson heat will arise in both wires; its sign will depend on the direction of the electric current with respect to heat flow. Therefore the Thomson heat will have a different sign in each tube. The heat production per unit time, the power $P$, in the wires can therefore be given by

$$P = Q_J/t + Q_T/t = RI^2 - \mu I \, \Delta T \tag{6}$$

In this equation $\Delta T$ is the temperature difference over the length of wire $\Delta x$ that is situated in the calorimetric fluxmeter zone of the tube.

As the DSC signal is the difference $\Delta P$ between the heat production in the two wires we find

$$\Delta P = \Delta R I^2 - (\Delta T \Sigma \mu) I \tag{7}$$

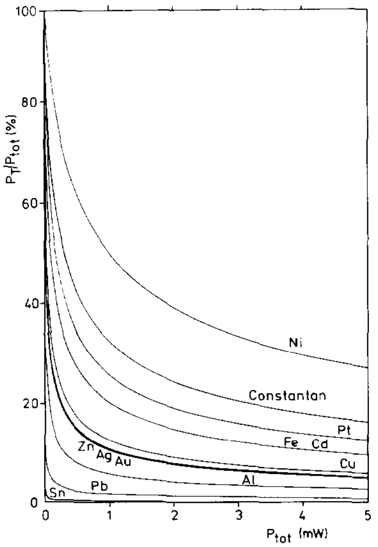
In the ideal case of a homogeneous and strain-free wire the Joule heat is cancelled out and only (twice) the Thomson heat is measured. In practice however a small Joule heat effect will be detected because of imperfections; this means that $\Delta R$ has a small value. The best way to determine the coefficients $\Delta R$ and $\Delta T \Sigma \mu$ of eqn. 7 is to make a second order polynomial fit of the total heat effect $\Delta P$ as a function of the current at constant $\Delta T$. The results of this procedure are given in the next two sections.

## CHOICE OF MATERIALS

The Thomson coefficient is a property of the material and it has different values for different metals; so has the Thomson heat. To test the method we preferred to measure under favourable circumstances, which means that $Q_T/(Q_T + Q_J)$ should be as large as possible. This leads to the following result

$$\frac{Q_T}{Q_T + Q_J} = \frac{\Delta T \mu I}{RI^2 \pm \Delta T \mu I} = \frac{\Delta T \mu I}{(L/A\sigma)I^2 \pm \Delta T \mu I} = \frac{1}{(I/\Delta T)(L/A)(1/\sigma\mu) \pm 1} \tag{8}$$

where $A$ is the surface of the cross-section of the wire, $L$ the length of the



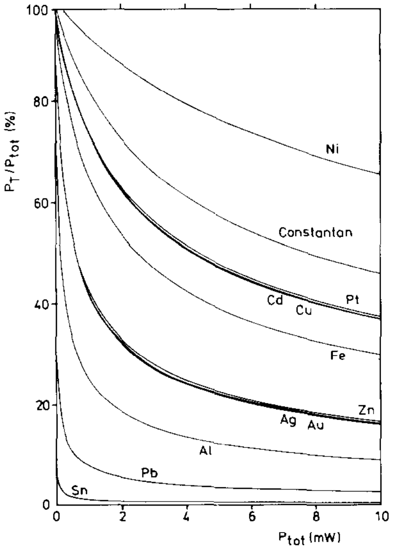


Fig. 3. The calculated ratio $P_T/P_{total} = Q_T/(Q_T + Q_J)$ as a function of the total heat production $P_{total}$ for wires with a diameter of 1 mm.

Fig. 4. The same plot as Fig. 3 for wires with a diameter of 5 mm.

part of the wire in the sensitive zone of the tube, and $\sigma$ the specific conductivity of the metal.

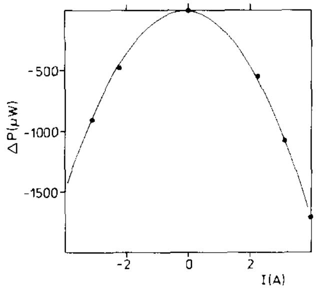
For the final ratio shown in eqn. (8) to be as large as possible, the first term in the denominator should be as small as possible. It consists of three factors, each depending on different properties of the experimental set up: $I/\Delta T$ contains variables in the experiment, $L/A$ contains constants that are fixed by the geometry of the set up, and $\sigma\mu$ contains only material-dependent constants.

Obviously the choice of the factor $\sigma\mu$ is important; it can be estimated from data in the literature [10,11]. In Figs. 3 and 4 the value of the ratio $P_T/P_{total} = Q_T/(Q_T + Q_J)$ is given as a function of the total power $P_{total} = P_T + P_J$ for a number of metals and for chosen values of $\Delta T$ and $A$. The graphs are given for small values of $P_{total}$; the actual measuring range is to the right of the pictures. The value of $L$ follows from the geometry of the calorimeter and is taken to be 15 mm, following the DSC manual. From these graphs it can be seen that nickel has the highest ratio and for this reason was chosen for the experiment.

## RESULTS

### *Testing the method*

The first measurements were done to test for imperfections in the set up, particularly for inhomogeneities in the wire and asymmetry in the detectors. An experiment was carried out in which the difference in the heat produced in the two legs of a nickel wire (Fig. 2) was measured as a function of the current at zero temperature gradient. After interchanging the wires with respect to the tubes the experiment was repeated. The plot of the two functions is given in Figs. 5 and 6 respectively. The coefficients of a second order polynomial fit are given in Table 1.



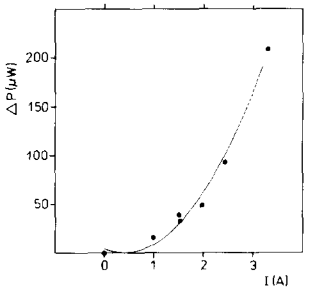


Fig. 5. The power difference $\Delta P$ as a function of the electric current $I$ at $\Delta T = 0$.

Fig. 6. The same plot as Fig. 5 but with the wires interchanged.

TABLE 1

Coefficients of the power difference in the case of zero temperature gradient $\Delta P(I) = C_0 + C_1 I + C_2 I^2$. $\Delta P$ in $\mu$W; $I$ in amps

| | $C_0$ ($\mu$W) | $C_1$ ($\mu$V) | $C_2$ ($\mu\Omega$) |
|---|---|---|---|
| Normal | $-6 \pm 21$ | $-26 \pm 40$ | $-99.9 \pm 2.0$ |
| Reversed | $4 \pm 9$ | $-19 \pm 11$ | $24 \pm 3$ |

In the case of an ideal wire (perfectly homogeneous, no strain) and perfect detectors no heat effect should be found $[\Delta P(I) = 0]$. In practice the deviation from zero will be due partly to the properties of the wire and partly to imperfections in the detectors. In view of the fact that with an ideal set of tubes, interchanging the (imperfect) wires will result in a calorimeter signal with the opposite sign, whereas with a perfect wire, interchanging will make no difference in the signal, it can be deduced that 62 $\mu\Omega$ of $\Delta R$ in eqn. 7 is caused by the wires and 38 $\mu\Omega$ of $\Delta R$ by the detectors. From Table 1 it follows that the effect is almost exclusively determined by the term with $C_2$, as it should be; the contribution of the other two terms is negligibly small. The effect is about 1% of the total heat production, as can be seen from Table 2; no correction will be made for this effect at this stage of the experiment. In another experiment the heat production in the two legs of the wire was measured separately by applying a current between the middle M of the wire (Fig. 2) and end A and then between M and B. The results are given in Table 2.

According to these measurements the resistance difference $\Delta R = 430 \pm 170$ $\mu\Omega$, which is four times the value found in the first experiment. The probable reason for this is that small fluctuations in the current occur during the experiment. In difference measurements the effects of these fluctuations cancel each other out whereas in the separate measurements they do not. The main reason for doing separate measurements was to estimate the length of the sensitive area in the calorimeter tubes. From the coefficient $C_2$, which represents the detected resistance of the part of the wire that is in the sensitive area, one can estimate the length of the sensitive area if the

TABLE 2

Coefficient of the power developed in each leg of the wire separately. $P(I) = C_0 + C_1 I + C_2 I^2$. $P$ in mW; $I$ in amps

| | $C_0$ (mW) | $C_1$ (mV) | $C_2$ (m$\Omega$) |
|---|---|---|---|
| A | $0.0 \pm 0.4$ | $-0.3 \pm 0.5$ | $4.00 \pm 0.16$ |
| B | $-0.27 \pm 0.14$ | $0.94 \pm 0.24$ | $-4.43 \pm 0.07$ |

TABLE 3

Coefficients of the Thomson heat measurements. $\Delta P(I) = C_0 + C_1 I + C_2 I^2$. $\Delta P$ in $\mu$W; $I$ in amps

| $T$ (K) | $C_0$ ($\mu$W) | $C_1$ ($\mu$V) | $C_2$ ($\mu\Omega$) |
|---|---|---|---|
| 330 | $15 \pm 17$ | $244 \pm 5$ | $-97.4 \pm 2.5$ |
| 347 | $20 \pm 30$ | $361 \pm 4$ | $-97.1 \pm 2.8$ |

resistance per unit length of the wire is known. Since the nickel wire had a resistance of $165.2 \pm 0.7$ m$\Omega$ m$^{-1}$ the effective length of the detector was calculated to be about 25 mm. This is 10 mm more than the value given in the manual of the DSC.

The length of the detector zone is an important quantity because it determines the value of the temperature difference $\Delta T$ in eqn. (6), if a specific temperature gradient is imposed.

### *Measurement of the Thomson heat*

To measure the Thomson effect a temperature gradient was created by raising the temperature of one of the thermostats shown in Fig. 2. The gradient was simply taken to be the temperature difference between the two thermostats divided by the length of the wire between them.

The temperature difference $\Delta T$ in eqn. (7) is the gradient multiplied by the effective length of the detector. We determined the Thomson coefficient at two temperatures: 330 and 347 K.

Again the measurements were fitted to a second order polynomial: the results are given in Table 3 and Fig. 7.

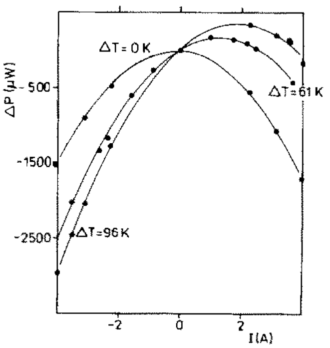


Fig. 7. The power difference $\Delta P$ for a nickel wire as a function of the current $I$ at three different values of $\Delta T$. At zero temperature gradient ($\Delta T = 0$) no Thomson heat appears and the curve is symmetrical around $I = 0$. At $\Delta T \neq 0$ the asymmetric Thomson heat causes a shift of the curve.

TABLE 4

Parameters of the Thomson heat measurements

| $T$ (K) | Gradient ($\mathrm{K\,m^{-1}}$) | $\mu$ ($\mu\mathrm{V\,K^{-1}}$) | $\Delta R$ ($\mu\Omega$) |
|---|---|---|---|
| 330 | $410 \pm 50$ | $-11 \pm 1.5$ | $-97.4 \pm 2.5$ |
| 347 | $640 \pm 50$ | $-12 \pm 1.5$ | $-97.1 \pm 2.8$ |

TABLE 5

Literature values for the Thomson coefficient of nickel and the results of this work

| Authors | Ref. | $T$ (K) | $\mu$ ($\mu\mathrm{V\,K^{-1}}$) |
|---|---|---|---|
| Maxwell et al. | 3 | 283 | $-58.0 \pm 1.2$ |
| | | 293 | $-40.0 \pm 2.0$ |
| Maxwell et al. | 3 | 314.2 | $-34 \pm 4$ |
| | | 314.2 | $-31 \pm 11$ |
| Maxwell et al. | 3 | 313 | $-27.6 \pm 1.6$ |
| | | 315.2 | $-26.2 \pm 1.6$ |
| Tregouet and Goureaux | 5 | 330 | $-20.5$ |
| | | 347 | $-21.5$ |
| Borelius et al. | 12 | 304 | $-17.14$ |
| This work | | 330 | $-11 \pm 1.5$ |
| | | 347 | $-12 \pm 1.5$ |

The magnitude of the Thomson coefficient can be calculated from the values in Table 3; the values obtained are given in Table 4, together with other relevant parameters.

## DISCUSSION

In the experiment it has been shown that in principle the method described is suitable for measuring the very small Thomson heat directly. Although the appearance of the larger Joule heat cannot be prevented, the effect of it can be eliminated by using the fact that in the calorimetric difference technique two equal quantities cancel each other out. An additional advantage of this method is that possible imperfections in the material come to light in a direct way, as has been demonstrated.

The main problem is how to determine the effective length of the sensitive zone of the calorimetric tubes; from this length the magnitude of the temperature gradient is derived. This gradient is a factor in the expression for the Thomson heat (eqn. 1).

A separate experiment is in preparation in which the tubes of the Setaram calorimeter will be explored with a small heat probe in order to find the sensitivity as a function of the position. To improve the results a better representation is needed for the temperature as a function of position. It is expected that these two improvements will produce a more reliable value for the temperature gradient.

We are also planning the construction of a special calorimeter for measuring the Thomson heat. In our plans attention will be given to the geometry of the sensitive zone as well as to the overall sensitivity.

## REFERENCES

1 CRC Handbook of Chemistry and Physics (Ed. R.C. Weast), CRC Press, Boca Raton, Florida, 1984, 65th edn., E-93.
2 G. Borelius, W.H. Keesom, C.H. Johansson and J.O. Linde, Proc. K. Ned. Akad. Wet., 36 (1932) 10.
3 G.M. Maxwell, J.N. Lloyd and D.V. Keller, Jr., Rev. Sci., 38 (1967) 1084.
4 A.M. Guenault, N.S. Lawson and S.D. Veazey, Am. J. Phys., 46 (1978) 399.
5 Y. Tregouet and G. Goureaux, C. R. Acad. Sci. Ser. C, 269 (1969) 379.
6 C.A. Dominicali, Rev. Mod. Phys., 26 (1954) 237.
7 H.B. Callen, Phys. Rev., 73 (1948) 1349.
8 D.K.C. MacDonald, Thermoelectricity: an Introduction to the Principles, Wiley, New York, 1962.
9 H.B. Callen, Thermodynamics, Wiley, New York, 1961, p. 299.
10 Numerical Data and Functional Relationships in Science and Technology (Eds. H. Landolt and R. Bornstein), Springer-Verlag, Berlin, Heidelberg, 1968, 6th edn., Vol. 6/II, 984.
11 Ref. 1, F-118.
12 G. Borelius, W.H. Keesom, C.H. Johansson and J.O. Linde, Proc. K. Ned. Akad. Wet., 33 (1930) 17.