

*Citation:*

F.M.Jaeger, Researches on the thermic and electric conductivity power of crystallised conductors, in: KNAW, Proceedings, 9 I, 1906, Amsterdam, 1906, pp. 89-98

**Physics.** — “*Researches on the thermic and electric conductivity power of crystallised conductors.*” I. By Dr. F. M. JAEGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of May 26, 1906).

1. Of late years, it has been attempted from various sides to find, by theoretical means, a connection between the phenomena of the thermic and electric conductivity of metallic conductors, and this with the aid of the more and more advancing electron theory.

In 1900 papers were published successively by P. DRUDE<sup>1)</sup>, J. J. THOMSON<sup>2)</sup> and E. RIECKE<sup>3)</sup> and last year by H. A. LORENTZ<sup>4)</sup>.

One of the remarkable results of these researches is this, that *the said theory has brought to light that the quotient of the electric and thermic conductivity power of all metals, independent of their particular chemical nature, is a constant, directly proportional to the absolute temperature.*

When we assume that the electrons in such a metal can move freely with a velocity depending on the temperature, such as happens with the molecules in ideal gases and also that these electrons only strike against the much heavier metallic atoms, so that in other words, their mutual collision is neglected, whilst both kinds of particles are considered as perfectly elastic globes, the quotient of the thermic conductivity power  $\lambda$  and the electric conductivity power  $\sigma$  may be indeed represented by a constant, proportional to the absolute temperature  $T$ .

The theories of DRUDE and LORENTZ only differ as to the absolute value of the quotient; according to DRUDE  $\frac{\lambda}{\sigma} = \frac{4}{3} \left( \frac{\alpha}{e} \right)^2 T$ ; according to LORENTZ  $\frac{\lambda}{\sigma} = \frac{8}{9} \left( \frac{\alpha}{e} \right)^2 T$ . In these expressions  $\lambda$ ,  $\sigma$  and  $T$  have the above cited meaning, whilst  $\alpha$  is a constant and  $e$  represents the electric charge of the electron.

By means of a method originated by KOHLRAUSCH, JAEGER and DIESSELHORST have determined experimentally the values for  $\frac{\lambda}{\sigma}$  with

<sup>1)</sup> P. DRUDE, Ann. Phys. (1900). 1. 566; 3. 369.

<sup>2)</sup> J. J. THOMSON, Rapport du Congrès de physique Paris (1900). 3. 138.

<sup>3)</sup> E. RIECKE, Ann. Phys. Chem. (1898). 66. 353, 545, 1199; Ann. Phys. (1900). 2. 835.

<sup>4)</sup> H. A. LORENTZ, Proc. 1905, Vol. VII, p. 438, 585, 684.

various metals<sup>1)</sup>. The agreement between theory and observation is in most cases quite satisfactory, only here and there, as in the case of bismuth<sup>2)</sup>, the difference is more considerable. From their measurements for silver at 18°, the value  $47 \times 10^6$  may be deduced in C.G.S. units, for the expression  $\frac{\alpha T}{e}$ . (Compare LORENTZ, loco cit. p. 505); according to DRUDE's formula:  $38 \times 10^6$ .

§ 2. I hope, shortly, to furnish an experimental contribution towards these theories by means of a series of determinations of an analogous character, but more in particular with crystallised conductors, and in the different directions of those crystal-phases.

If we take the most common case in which may be traced three mutual perpendicular, thermic and electric main directions in such crystals, the propounded theories render it fairly probable for all such conducting crystals that:

$$\frac{\lambda_x}{\sigma_x} = \frac{\lambda_y}{\sigma_y} = \frac{\lambda_z}{\sigma_z}, \text{ and therefore also: } \lambda_x : \lambda_y : \lambda_z = \sigma_x : \sigma_y : \sigma_z.$$

In conducting crystals, the directions of a greater electric conductivity should, therefore, not only be those of a greater thermic conductivity, but, theoretically, the quotient of the electric main-conductivities should be numerically *equal* to that of the thermic main-conductivities.

Up to the present but little is known of such data. The best investigated case is that of a slightly titaniferous *Haemitate* of

1) W. JAEGER und DIESELHORST, Berl. Sitz. Ber. (1899). 719 etc. Comp. REINGANUM, Ann. Phys. (1900) 2, 398.

2) With Al, Cu, Ag, Ni, Zn, the value of  $\frac{\lambda}{\sigma}$  at 18° varies between  $636 \times 10^8$  and  $699 \times 10^8$ ; with Cd, Pb, Sn, Pt, Pd between  $706 \times 10^8$  and  $754 \times 10^8$ ; with Fe between 802 and  $832 \times 10^8$ , therefore already more. With *bismuth*  $\frac{\lambda}{\sigma}$  at 18° =  $962 \times 10^8$ . Whilst in the case of the other metals mentioned the values of  $\frac{\lambda}{\sigma}$  at 100° and at 18° are in the average proportion of 1,3:1, with *bismuth* the proportion is only 1.12. In their experiments, JAEGER and DIESELHORST employed little rods, and bearing in mind the great tendency of bismuth to crystallise, their results with this metal cannot be taken as quite decisive, as the values of the electric and thermic conductivity power in the chief directions of crystallised bismuth differ very considerably.

Swedish origin which has been investigated by H. BÄCKSTRÖM and K. ÅNGSTRÖM<sup>1)</sup> as to its thermic and electric conductivity power. In this ditrigonal mineral, they found for the quotient of the thermic conductivity power in the direction of the chief axis (*c*) and in that perpendicular to it (*a*) at 50°:

$$\frac{\lambda_a}{\lambda_c} = 1.12.$$

For the quotient of the electric resistances *w* at the same temperature they found:

$$\frac{w_c}{w_a} = 1.78, \text{ and, therefore: } \frac{\sigma_a}{\sigma_c} = 1.78.$$

From this it follows that in the case of the said conductor, the theory agrees with the observations as to the relation between the conductivity powers only *qualitatively*, but not *quantitatively*, and — contrary to the usually occurring deviations — the proportion of the quantities  $\lambda$  is *smaller* than that of the quantities  $\sigma$ .

JANNETTAZ's empirical rule, according to which the conductivity for heat in crystals is greatest parallel to the directions of the more complete planes of cleavage, applies here only in so far as haematite which does *not* possess a distinct plane of cleavage, may still be separated best along the base {111} (MILLER), that is to say parallel to the plane of the directions indicated above with *a*.

§ 3. In order to enrich somewhat our knowledge in this respect the plan was conceived to investigate in a series of determinations the thermic and electric conductivity-power of some higher and also of some lower-symmetrical crystalline conductors, and, if possible, of metals also. For the moment, I intend to determine the quotient of the conductivities in the different main directions, and afterwards perhaps to measure those conductivities themselves in an absolute degree.

*I. On the thermic and electric conductivities in crystallised Bismuth and in Haematite.*

Measurements of the thermic and electric conductivity of bismuth are already known.

MATTEUCCI<sup>2)</sup> determined the thermic conductivity, by the well-

<sup>1)</sup> H. BÄCKSTRÖM and K. ÅNGSTRÖM, *Ofvers. K. Vetensk. Akad. Förh.* (1888). No. 8, 533; BÄCKSTRÖM, *ibid.* (1894), No. 10, 545.

<sup>2)</sup> MATTEUCCI, *Ann. Chim. et Phys.* (3). **43**. 467. (1855).

well-known method of INGENHOUSZ, by measurement of the length of the melted off waxy layer which was put on the surface of cylindrical rods of bismuth, cut // and  $\perp$  to the main axis, whilst the one end was plunged into mercury heated at  $150^\circ$ . For the average value of the quotient of the main conductivities — perpendicular and normal to the main axis — he found the value 1.08. JANNETTAZ's rule applies in this case, because the complete cleavability of ditrigonal bismuth takes place along  $\{111\}$  (MILLER), therefore, perpendicularly to the main axis. JANNETTAZ <sup>1)</sup> has applied the SÉNARMONT method to bismuth. He states that in bismuth the ellipses have a great eccentricity but he did not take, however, exact measurements.

A short time ago, LOWNDS <sup>2)</sup> has again applied the SÉNARMONT method to bismuth. He finds for the quotient of the demi-ellipsoidal axes 1.19 and, therefore for the quotient of the conductivities 1.42.

The last research is from PERROT <sup>3)</sup>. By the SÉNARMONT method he finds as the axial quotient of the ellipses about 1.17 and consequently for the quotient of the conductivities  $\perp$  and // axis 1.368, which agrees fairly well with the figure found by LOWNDS. Secondly, PERROT determined the said quotient by a method proposed by C. SORET, which had been previously recommended by THOULET <sup>4)</sup>, namely, by measuring the time which elapses between the moments when two substances with known melting points  $\vartheta_1$  and  $\vartheta_2$  placed at a given distance at different sides of a block of the substance under examination begin to melt. As indices were used; *α-Naphthylamine* ( $\vartheta = 50^\circ$  C.), *o-Nitroaniline* ( $\vartheta = 66^\circ$  C.), and *Naphthalene* ( $\vartheta = 79^\circ$  C.).

As the mean of all the observations, PERROT finds as the quotient of the main conductivities 1,3683, which agrees perfectly with his result obtained by SÉNARMONT's method.

He, however, rightly observes that this concordance between the two results is quite *an accidental one*, and that the method of THOULET and SORET must *not* be considered to hold in all cases. The proof thereof has been given by CAILLER in a theoretical paper; <sup>5)</sup> the agreement is caused here by the accidental *small* value of a quotient  $\frac{hl}{k}$ , in which  $l$  represents the thickness of the little plate of bismuth

<sup>1)</sup> JANNETTAZ, Ann. de chim. phys. 29. 39. (1873).

<sup>2)</sup> L. LOWNDS, Phil. Magaz. V. 152. (1903).

<sup>3)</sup> L. PERROT, Archiv. d. Science phys. et nat. Genève (1904. (4). 18. 445.

<sup>4)</sup> THOULET, Ann. de Chim. Phys. (5). 26. 261. (1882)

<sup>5)</sup> C. CAILLER, Archiv. de Scienc. phys. et nat. Genève (1904). (4). 18. 457.

and  $h$  and  $k$  the coefficients of external and internal conductivity.

§ 4. I have endeavoured to determine the quotient of the chief conductivities by the method proposed by W. VOIGT.

As is wellknown, this method is based on the measurement of the angle, formed by the two isotherms at the line of demarcation between two little plates which have been joined to an artificial twin, when the heat current proceeds along the line of demarcation. If  $\lambda_1$  and  $\lambda_2$  are the two chief conductivities of a plate of bismuth cut parallel to the crystallographic main axis, and if the angle which the two main directions form with the line of demarcation equals  $45^\circ$ , then according to a former formula<sup>1)</sup>:

$$\frac{\lambda_1}{\lambda_2} = \operatorname{tg}\left(45^\circ + \frac{\varepsilon}{2}\right)$$

§ 5. The bismuth used was kindly furnished to me by Dr. F. L. PERROT, to whom I again wish to express my hearty thanks.

The prism investigated by me is the one which Dr. PERROT in his publications<sup>2)</sup> indicates with  $M$ , and for which, according to SÉNARMONT'S method, he found for  $\frac{\lambda_a}{\lambda_c}$  the value 1,390. The prism given to Dr. VAN EVERDINGEN yielded in the same manner for  $\frac{\lambda_a}{\lambda_c}$  the value 1,408.

Two plates were cut parallel to the crystallographic axis, in two directions forming an angle of  $90^\circ$  and these were joined to twin plates with  $\varphi = 45^\circ$ .

It soon appeared that in this case the VOIGT method<sup>3)</sup> was attended by special difficulties which, as Prof. VOIGT informed me, is generally the case with *metals*. First of all, it is difficult to find a coherent coating of elaidic acid + wax; generally the fused mixture on the polished surface forms droplets instead of congealing to an even layer. Secondly, the isotherms are generally curved and their form presents all kinds of irregularities, which are most likely caused by the great specific conductivity of the metals, in connection with the peculiarity just mentioned. On the advice of Prof. VOIGT I first covered the metallic surface with a very thin coating of varnish; this dissolves in the fused acid, and causes in many cases a better cohesion, but even this plan did not yield very good results.

<sup>1)</sup> These Proceedings. (1906). March p. 797.

<sup>2)</sup> p. 4, note 10.

<sup>3)</sup> VOIGT, Göttinger Nachr. (1896). Heft 3, p. 1—16; *ibid.* (1897). Heft 2. 1—5

However, at last, I succeeded in getting a satisfactory coating of the surface by substituting for white wax the ordinary, yellow bees-wax. This contains an adhesive substance probably derived from the honey, and, when mixed in the proper proportion with elaidic acid it yields the desired surface coating.

I have also coated <sup>1)</sup> the bottoms of the plate and the sides, except those which stand ⊥ on the line of demarcation with a thick layer of varnish mixed with mercury iodide and copper iodide. During the operation the heating was continued to incipient darkening (about 70°).

The plates should have a rectangular or square form, as otherwise the isotherms generally become curved.

It is further essential to heat *rapidly* and to raise the copper bolt to a fairly high temperature; the isotherms then possess a more straight form and give more constant values for  $\epsilon$ .

I executed the measurements on the double object table of a LEHMANN'S crystallisation microscope on an object glass wrapped in thick washleather, to prevent the too rapid cooling and solidification of the coating.

After numerous failures, I succeeded at last in obtaining a long series of constant values. As the mean of 30 observations, I found  $\epsilon = 22^{\circ}12'$  and therefore:

$$\frac{\lambda_a}{\lambda_c} = 1,489.$$

§ 6. The value now found is somewhat greater than that found by PERROT. I thought it would be interesting to find out in how far a similar deviation was present in other cases, and whether when compared with the results obtained by the methods of SÉNARMONT, JANETTAZ and ROENTGEN, it has always the same direction.

In fact, the investigation of many minerals has shown me that all values obtained previously, are *smaller* than those obtained by the process described here.

I was inclined at first to believe that these differences were still greater than those which are communicated here. Although a more extended research, including some plates kindly lent to me by Prof. VOIGT, showed that these differences are not so serious as I suspected, at first the deviation exists *always in the same direction*.

For instance, I measured the angle  $\epsilon$  of a plate of an *Apatite*-crystal from Stillup in Tyrol and found this to be  $17^{\circ}$ . From the

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<sup>1)</sup> RICHARZ'S method of experimenting (Naturw. Rundschau, **17**, 478 (1902)) did not give sufficiently sharply defined isotherms and was therefore not applied.

position of the isotherms it also follows that  $\lambda_c > \lambda_a$  so that  $\frac{\lambda_c}{\lambda_a} = 1,35$ .

In a quartz-plate obtained from Prof. VOIGT I found  $\varepsilon = 30\frac{1}{2}^\circ$ , therefore  $\frac{\lambda_c}{\lambda_a} = 1,75$ . In a plate of *Antimonite* from Skikoku in Japan cut parallel to the plane {010},  $\frac{\lambda_c}{\lambda_a}$  was found to be even much larger than 1,74, which value is deduced from the experiments of SÉNARMONT and JANNETTAZ as they find for the quotient of the demi ellipsoidal axes 1.32.

For *Apatite* they find similarly 1,08, for quartz 1,73, whilst TUCHSCHMIDT determined the heat-conductivity of the latter mineral according to WEBER'S method in absolute degree. His experiments give the value 1,646 for the quotient  $\frac{\lambda_c}{\lambda_a}$ .

The deviations are always such that if  $\lambda_1 > \lambda_2$ , the values of the quotient  $\frac{\lambda_1}{\lambda_2}$  turn out to be *larger* when VOIGT'S method is employed instead that of DE SÉNARMONT. The method employed here is, however, so sound in principle, and is so much less liable to experimental errors, that it certainly deserves the preference over the other processes.

Finally, a sample of *Haematite* from Elba was examined as to its conducting power. A plate cut parallel to the *c*-axis was found not to be homogeneous and to contain gas-bubbles. I repeatedly measured the angles  $\varepsilon$  of a beautifully polished preparation of Prof. VOIGT, and found fairly constantly  $10\frac{1}{2}^\circ$ , whilst the position of the isotherms showed that  $\lambda_a$  was again larger than  $\lambda_c$ .

For the *Haematite* we thus obtain the value:  $\frac{\lambda_a}{\lambda_c} = 1,202$ . The value found by BÄCKSTRÖM and ANGSTRÖM for their mineral with the aid of CHRISTIANSEN'S method was 1,12. In this case the deviation also occurs in the above sense.

From the experiments communicated we find for the quotient  $\kappa_a : \kappa_c$  in both crystal phases, if by this is meant  $\left(\frac{\lambda}{\sigma}\right)_a : \left(\frac{\lambda}{\sigma}\right)_c$  the values:

$$\text{With } \textit{Bismuth} : \frac{\kappa_a}{\kappa_c} = 1,128.$$

$$\text{With } \textit{Haematite} : \frac{\kappa_a}{\kappa_c} = 1,480.$$

In this my measurements of  $\frac{\lambda_a}{\lambda_c}$  are combined with the best value



found by VAN EVERDINGEN<sup>1)</sup> with PERROT'S prism, namely  $\frac{\sigma_a}{\sigma_c} = 1,68$ , and with the value found by the Swedish investigators for haematite 1,78 at 50° C.

7. If there were a perfect concordance between theory and observation, we should have in both cases  $\frac{\kappa_a}{\kappa_c} = 1$ . The said values 1,128 and 1,480 are, therefore, in a certain sense a measure for the extent of the divergence between the observation and the conclusion which is rendered probable by the electron theory.

In the first place it will be observed that the agreement is much better with *bismuth* than with *haematite*. However, this may be expected if we consider that the theory has been proposed, in the first instance, for *metallic* conductors. The influence of the peculiar nature of the *oxide* when compared with the true *metal* is shown very plainly in this case.

The question may be raised whether, perhaps, there may be shown to exist some connection between the crystal structure and the chemical nature on one side, and the given values of  $\frac{\kappa_a}{\kappa_c}$  on the other side.

Such a connection would have some significance because it may be, probably, a guide for the detection of special factors situated in the crystalline structure, which stand in the way of a complete agreement of electron theory and observations.

§ 8. First of all, it must be observed that we are easily led to compare the structures of the two phases. Both substances investigated crystallise ditrigonally and have an analogous axial quotient; for *bismuth*:  $a : c = 1 : 1,3035$  (G. ROSE); for *haematite*  $a : c = 1 : 1,3654$  (MELCZER). In both substances, the habit is that of the rhomboid, which in each of them approaches very closely to the regular hexahedron. The characteristic angle  $\alpha$  is 87°34' for *bismuth* for *haematite* 85°42'. Particularly in bismuth the pseudo-cubic construction is very distinct, the planes of complete cleavage which answer the forms  $\{111\}$  and  $\{11\bar{1}\}$  approach by their combination the regular octahedron in a high degree. Although haematite does not

<sup>1)</sup> VAN EVERDINGEN, Archives Neerland. (1901) 371; Versl. Akad. v. Wet. (1895—1900); Comm. Phys. Lab. Leiden, 19, 26, 37, 40 and 61. See Archiv. Néerl. p 452; 10ds No. 1 and No. 5.

possess a perfect plane of cleavage, it may be cleaved in any case along {111} with testaceous plane of separation. It admits of no doubt that the elementary parallelepipeds of the two crystal structures are in both phases pseudo-cubic rhombohedral configurations and the question then rises in what proportion are the molecular dimensions of those cells in both crystals?

If, in all crystal-phases, we imagine the whole space divided into volume-units in such a manner that each of those, everywhere joined, mutually congruent, for instance cubic elements, just contains a single chemical molecule, it then follows that in different crystals

the size of those volume elements is proportionate to  $\frac{M}{d}$ , in which

$M$  represents the molecular weight of the substances and  $d$  the sp. gr. of the crystals. If, now, in each crystal phase the content of the elementary cells of the structure is supposed to be equal to

this equivalent-volume  $\frac{M}{d}$ , the dimensions of those cells will be reduced

for all crystals to a same length unit, namely all to the length of a cubic-side belonging to the volume-element of a crystal phase, whose density is expressed by the same number as its molecular

weight, then in that particular case  $V = \frac{M}{d} = 1$ . If we now calculate

the dimensions of such an elementary parallelepiped of a BRAVAIS structure whose content equals the quotient  $\frac{M}{d}$  and whose sides are

in proportion to the crystal parameters  $a : b : c$ , the dimensions  $\chi$ ,  $\psi$  and  $\omega$  thus found will be the so-called *topic parameters* of the phase which, after having been introduced by BECKE and MUTHMANN independently of each other, have already rendered great services in the mutual comparison of chemically-different crystal-phases. In the particular case, that the elementary cells of the crystal-structure possess a rhombohedral form, as is the case with ditrigonal crystals, the parameters  $\chi$ ,  $\psi$  and  $\omega$  become equal to each other ( $= \varrho$ ). The relations applying in this case are

$$\varrho = \left( \frac{V}{\sin^2 \alpha \cdot \sin A} \right)^{\frac{1}{3}}, \quad \text{with} \quad \sin \frac{A}{2} = \frac{\sin \frac{\alpha}{2}}{\sin \alpha}.$$

If now these calculations are executed with the values holding here:  $B_i = 207,5$ ;  $F_{e_2}O_3 = 159,64$ ;  $d_{B_i} = 9,851$  (PERROT);  $d_{F_{e_2}O_3} = 4,98$ , then

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$$V_{Bi} = 21,064 \text{ and } V_{Fe_2O_3} = 32,06,$$

and with the aid of the given relations and the values for  $\alpha$  and  $A$  we find for each phase: <sup>1)</sup>

$$\frac{Q_{Bi}}{Q_{Fe_2O_3}} = \frac{2,7641}{3,1853}.$$

If now we just compare these values for the sides of the rhombohedral elementary cells of the crystal structure with those of the quotients  $\frac{\kappa_a}{\kappa_c}$  in the two phases, they curiously enough show the following relation:

$$\left(\frac{\kappa_a}{\kappa_c}\right)_{Fe_2O_3} : \left(\frac{\kappa_a}{\kappa_c}\right)_{Bi} = Q_{Fe_2O_3}^2 : Q_{Bi}^2 = 1,32.$$

Allowing for experimental errors, the agreement is all that can be desired: in the first term of the equation the value is exactly: 1.312, in the last term: 1,328.

In our case the quotient  $\frac{\kappa_a}{\kappa_c}$  may therefore be written for both phases in the form:  $C \cdot Q^2$ , in which  $C$  is a constant independent of the particular chemical nature of the phase.

Instead of the relation

$$Q_1^2 : Q_2^2, \text{ perhaps } Q_1^2 \sin \alpha_1 : Q_2^2 \sin \alpha_2 = 1.305$$

is still more satisfactory. These expressions, however, represent nothing else *but the surface of the elementary mazes of the three chief planes of the trigonal molecule structure*, for these are in our case squares whose flat axis =  $a$ . The quotient  $\frac{\kappa_a}{\kappa_c}$  in the two phases should then be directly proportional to the reticular density of the main net-planes of BRAVAIS's structures.

A choice between this and the above conception cannot yet be made, because  $\alpha_1$  and  $\alpha_2$  differ too little from  $90^\circ$ . Moreover, a further investigation of other crystals will show whether we have to do here with something more than a mere accidental agreement. Similar investigations also with lower-symmetric conductors are at this moment in process and will, I hope, be shortly the subject of further communications.

Zaandam, May 1906.

<sup>1)</sup> For bismuth  $\alpha = 87^\circ 34'$  and  $A = 87^\circ 40'$ ; for haematite  $\alpha = 85^\circ 42'$  and  $A = 86^\circ 0'$ . The angle  $A$  is the supplement of the right angle on the polar axes of the rhombohedral cells and  $\alpha$  is the flat angle enclosed between the polar axes.