

**Physics.** — *Measurement of the piezo-electric modulus of zincblende.*

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§ 1. In connection with an investigation of the influence of polarity on the intensity of X-ray reflection in the case of zincblende, a qualitative determination of the piezo-electric modulus for this substance has been made in this laboratory<sup>1)</sup>. For this constant one finds quoted in the german literature the following value<sup>2)</sup> :

$$\delta_{14} = -5.24 \cdot 10^{-8} \text{ c. g. s. units,}$$

which has been taken from the thesis of L. W. E. VAN DER VEEN<sup>3)</sup>. We have already pointed to the fact that apparently the above number is due to a misunderstanding of VAN DER VEEN's thesis, and that the real value taken from VAN DER VEEN ought to be  $\sqrt{3}$  times as large :

$$\delta_{14} = 9.08 \cdot 10^{-8} \text{ c. g. s. units, } ^4)$$

whereas the negative sign has no meaning at all, as long as no definite agreement has been made about the positive direction in the crystal (Compare § 4).

It seemed worth while to make an absolute redetermination of the piezo-electric modulus of zincblende, in order to make sure in how far the correction proposed by us to the ordinarily quoted value is trustworthy.

From new measurements, which will be discussed below, it follows that the piezo-electric modulus for zincblende is :

$$\delta_{14} = 9.70 \pm 0.15 \cdot 10^{-8} \text{ c. g. s. units.}$$

At the same time I have made a remeasurement of the piezo-electric constant of quartz. For this I find a value about 1 per cent less than the best known values of CURIE and RÖNTGEN. If this discrepancy has to be ascribed to some error in the apparatus (e.g. too small a value, assumed for the electrostatic capacity used in my measurements), then we have to assume that the best value for zincblende is probably :

$$\delta_{14} = 9.80 \cdot 10^{-8} \text{ c. g. s. units,}$$

which is nearly two times as large as the value hitherto quoted.

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<sup>1)</sup> D. COSTER, K. S. KNOL and J. A. PRINS, *Zs. f. Phys.* **63**, 345, 1930. Further on quoted as l. c.

<sup>2)</sup> See e. g. *Handb. d. Phys.* (GEIGER u. SCHEEL) XIII page 312.

<sup>3)</sup> L. W. E. VAN DER VEEN, doctor dissertation, Delft 1911.

<sup>4)</sup> From VAN DER VEEN's numbers, as a matter of fact, a value 10 per cent smaller is obtained, but he made his measurements relative to the piezo-electric constant of quartz for which an old value of CURIE, 10 per cent less than the best value of to-day, was taken.

§ 2. The measurements were made with a very simple apparatus, an idea of which may be obtained from figure 1. The crystal was put between two flat polished copperplates of about 3 mm thickness. These plates as well as the crystal itself were cleaned with the utmost care and dried in the exsiccator before they were put together in the box *B* (See figure 1).

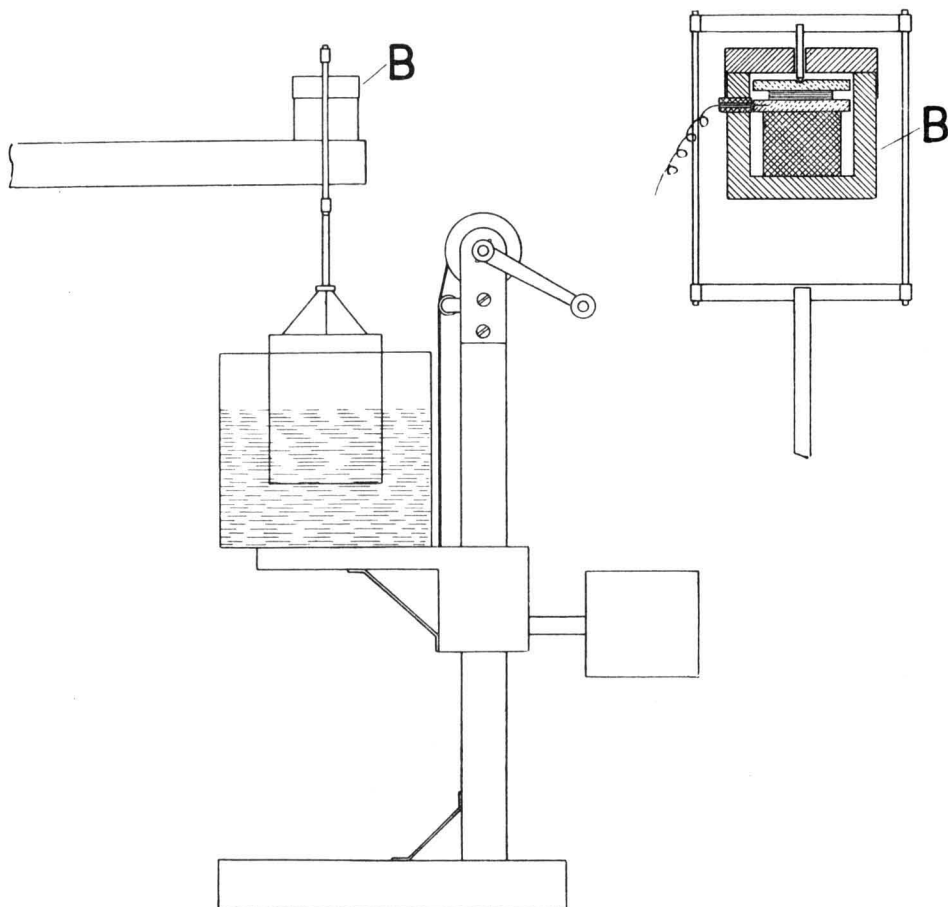


Fig. 1. Apparatus for piezo-electric measurements.

Of this box an enlargement is shown in the upper right hand corner of the figure. It is made of tinned iron. On the bottom lies first a piece of ambroid for insulation, then follows the undermost copperplate of which the electric potential has to be measured with the electrometer, then the piezo-electric crystal and finally the uppermost copperplate. To avoid an eventual pyro-electric effect, care was taken that during the course of one experiment the temperature did not change noticeably. Therefore the box was put in a second one, the space between them being filled with cotton wool.

Furthermore care was taken that all the metal parts of the apparatus with the exception of the undermost copperplate, of which the changes in

potential had to be measured, were constantly grounded. An insulated copperwire connected the undermost copperplate with the string electrometer and (eventually) a capacity of known magnitude. The pressure was furnished by a known weight which pressed through a hole in the cover of the box on the upper copperplate. The difficulty with such a procedure is to bring the pressure *continuously* on the plate. If the pressing weight meets the plate with some impulse then the pressure is much higher at first and will gradually (eventually oscillating) come down to the amount of the weight. Accordingly the changes in potential will also be too high at first and afterwards diminish. It will be very difficult to distinguish this decrease of potential from the natural electrostatic leakage. I have tried to avoid this difficulty in the following manner: The pressing weight was a cylindrical vessel attached to a frame work which pressed with a metal point on the upper copperplate in the box *B*. This vessel, when no weight was pressing, floated in a basin with water standing on a disk which could be moved upwards and downwards. Moving the disk continuously downwards the pressure was brought nearly continuously on the crystal.

The string electrometer of the WULF type was kindly put at the disposal of the laboratory by Professor D. VAN GULIK at Wageningen. This electrometer was put in a metal box to prevent electrostatic induction. This metal box as well as the frame of the electrometer itself were connected to earth. With the aid of a storage battery the one field plate was put at  $+80$  Volts, the other at  $-80$  Volts. The string was a platinum wire of 0.002 mm thickness. In the ordinary manner the field plates were placed symmetrically with regard to the string. The sensitivity of the electrometer was such that one part of the scale corresponded to about 0.05 Volt.

Before and after a series of measurements, which took place in about an hour, the scale of the electrometer was empirically calibrated in Volts. One measurement of the piezo-electric modulus consists of the following manipulations:

1. The electrometer string connected to the one side of the crystal is connected to earth and then insulated. If the string, when insulated, gets spontaneously an increasing deviation, this is a proof that the crystal or the copperplates are not sufficiently cleaned. (The deviation is caused by an electric polarisation).
2. The pressure is put on the crystal by moving the water basin downwards, and the deviation is read. Afterwards the natural leakage is determined. In most cases, when the room was sufficiently heated to avoid moisture this leakage was so small that no correction had to be made for it.
3. The electrometer is again connected to earth and then insulated.
4. By moving the water basin upwards the pressure is taken away, the electrometer gets a deviation in the opposite direction, which is read.

The deviations read in case 2 and 4 were sensibly the same, as can be seen from table 1. As an example in this table the deviations are given for crystal II negative (See also table 2).

TABLE 1.  
Deviations of the electrometer in volts.

Pressure on	Pressure off
1.280	1.275
1.265	1.275
1.285	1.275
1.225	1.250
1.250	1.260
1.285	1.270

Besides, in order to eliminate the unknown capacity of the system, the same four manipulations were repeated when an additional capacity of known magnitude was connected to it. If the deviation first is  $V_1$  (measured in units of tension) and after the capacity of magnitude  $C$  was connected to the system  $V_2$ , then it is easily seen that the charge set free is :

$$e = \frac{C}{\frac{1}{V_2} - \frac{1}{V_1}}$$

If the pressing weight is  $G$ , then the charge set free per unit of force is :

$$k = \frac{1}{G} \frac{C}{\frac{1}{V_2} - \frac{1}{V_1}}$$

§ 3. The zincblende crystals used were the crystals called I and II in our former work <sup>1)</sup>, cut by STEEG and REUTER parallel to the 111-planes. They have a surface of about 2 cm<sup>2</sup> and are about 3 mm thick. They gave good X-ray reflection on their whole surface so that we may assume that the formation of twins, such a common phenomenon with polar crystals and especially with zincblende, in these cases does not play an important part. The pressing weight was 1632 grams. The capacity of known magnitude was a condensor of HARMS <sup>2)</sup>, made by GÜNTHER and TEGETMAYER. It was used for a capacity of 43.21 cm. The values obtained are inserted in Table 2, they are given as charge in electrostatic c.g.s. units per kg pressure. For each crystal two sets of measurements were made, one set of measurements when the electrometer is getting a *positive* charge by putting the pressure on (1<sup>st</sup> and 3<sup>d</sup> column of table 2) the other with

<sup>1)</sup> l. c.

<sup>2)</sup> F. HARMS, Physik. Zs. 5, 47, 1904.

TABLE 2.

Charge set free in electrostatic c. g. s. units per kg pressure.

Crystal I		Crystal II	
Positive	Negative	Positive	Negative
0.0553	0.0547	0.0538	0.0575
0.0538	0.0569	0.0535	0.0573
0.0533	0.0572	0.0537	0.0555
0.0540	0.0556	0.0548	0.0553
0.0532	0.0568	0.0534	0.0555
0.0535	0.0565	0.0541	0.0542
0.0539	0.0570		
0.0545	0.0553		
0.0545	0.0564		
	0.0560		
Mean value	0.0562	0.0539	0.0559

the crystal inverted when it gets a *negative* charge in the same way (2<sup>d</sup> and 4<sup>th</sup> column of table 2). The mean of all the values obtained is 0.0550 electrostatic units per kg.

The agreement between the different values is sufficiently good. It is a curious fact that for both crystals the first set gives a mean value nearly 4 per cent smaller than the second set. This cannot be due to an asymmetry of the electrometer deviation because for both sets (compare § 2) deviations of the electrometer to the left as well as to the right were used. For the moment we cannot explain this small discrepancy.

As this discrepancy-though it is a rather small one- as long as its cause is not understood, gives an uncertainty as to the reliability of the results, we thought it desirable to have a control by measuring with the same apparatus a piezo-electric constant which is already well known. Now the best known piezo-electric constant is undoubtedly the modulus  $\delta_{11}$  of quartz which has been measured repeatedly by such skilled experimenters as CURIE and RÖNTGEN. It is a happy circumstance, indeed, that the values they finally obtained converged to nearly the same number: CURIE<sup>1)</sup> found  $\delta_{11}=0.0677$  (per kg), whereas RÖNTGEN<sup>2)</sup> got  $\delta_{11}=0.0681$  (per kg).

We used for our measurements with quartz a commercial piezo-quartz

<sup>1)</sup> J. P. CURIE, See Mme CURIE, *Traité de radioactivité*, Paris 1910.

<sup>2)</sup> W. C. RÖNTGEN, *Ann. d. Phys.* **41**, 449, 1913.

crystal as they are used for tuning high frequency oscillation circuits<sup>1)</sup>. The crystal had a surface of  $1.3 \times 2.8$  cm<sup>2</sup> and was 1.5 mm thick. It was cut perpendicularly to the electric axis. If compressed in this direction a charge comes free

$$e = \delta_{11} P$$

where  $P$  is the force applied in the direction of the electric axis and  $\delta_{11}$  is the piezo-electric modulus when the axes of reference are properly chosen.

The crystal was highly polished on both surfaces; these were coated with a thin layer of copper. The values obtained in the same way as described in the case of zincblende are inserted in table 3. We find for the modulus  $\delta_{11}$  of quartz in the mean 0.0671 electrostatic units per kg pres-

TABLE 3.  
Piezo-electric modulus  $\delta_{11}$  of quartz in  
electrostatic c.g.s. units per kg pressure

Positive	Negative
0.0654	0.0697
0.0646	0.0680
0.0634	0.0684
0.0664	0.0672
0.0682	0.0668
0.0690	0.0667
0.0662	0.0677
0.0666	0.0676
0.0666	0.0680
0.0663	0.0678

sure, which is only 1 per cent less than the mean value of CURIE and RÖNTGEN. If this difference should be due to some systematic error in our apparatus (e.g. too small a value assumed for the known capacity), then we had to correct our value for zincblende with 1 per cent and we thus find for the constant  $k$  defined in § 2:

$$k = 0.0555 \text{ electrostatic c. g. s. units per kg.}$$

§ 4. As has been mentioned in § 1 we succeeded formerly<sup>2)</sup> in determining the piezo-electric effect of zincblende in a qualitative way. A

<sup>1)</sup> Supplied by STEEG and REUTER, Homburg v. d. Höhe, Germany.

<sup>2)</sup> l. c.

summary of the results seems justified here. Zincblende belongs to the cubic system, the 111-planes are alternately occupied by zinc- or by sulphur-atoms. The sulphur planes divide the distance between the successive zinc planes in the ratio 1:3. Now there is a difference in intensity of reflection for X-rays for the two different 111-planes *A* and *B* (see figure 2), which shows some anomalies in the neighbourhood of the absorption edge of zinc. This afforded a means to make sure which of the 111-planes

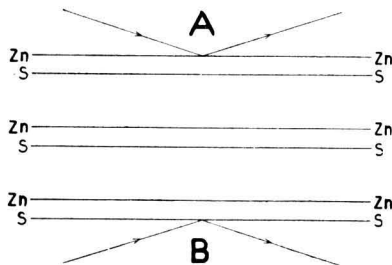


Fig. 2. Reflection of X-rays on the both 111-planes *A* and *B* of zincblende.

of the crystals I and II has to be identified with *A* (figure 2) and which with *B*. A piezo-electric determination showed at the same time, that if the crystal is compressed in a direction perpendicular to the 111-planes (i.e. in the direction *A—B* of figure 2), then the plane *A* gets a negative and the plane *B* a positive charge. As mentioned above, this charge is:

$$k = 0,0555 \text{ electrostatic c. g. s. units per kg.}$$

Now the question arises how we have to derive the piezo-electric modulus of zincblende from the value of *k*. The piezo-electric constants and moduli have to be referred to the common crystal axes i.e. the cubic axes in the regular system. VOIGT<sup>1)</sup> has shown that from the 18 piezo-electric constants in the case of the regular system only 3 may be different from zero. The same is true for the moduli. These moduli have the following meaning

$$-p_x = \delta_{14} Y_z$$

$$-p_y = \delta_{25} Z_x$$

$$-p_z = \delta_{36} X_y$$

Here  $p_x$ ,  $p_y$  and  $p_z$  are the components of the electric polarisation caused by the components of shearing stress  $Y_z$ ,  $Z_x$  and  $X_y$ . For cubic crystals these moduli are equal to one another, usually they are all denoted by  $\delta_{14}$ . The connection between  $\delta_{14}$  and the constant *k* determined in § 3 is easily seen with the help of figure 3.

The angle which the 111-plane makes with the three coordinate planes is

$$\arccos \frac{1}{3} \sqrt{3}.$$

<sup>1)</sup> W. VOIGT, Lehrbuch der Kristallphysik, Leipzig 1928.

