Physics. — *The dependence of the susceptibility of diamagnetic metals upon the field.* By W. J. DE HAAS and P. M. VAN ALPHEN. (Communication N⁰. 212*a* from the Physical Laboratory, Leiden.)

(Communicated at the meeting of December 20, 1930).

Introduction. To explain the diamagnetism of metals we have to take into account three factors:

1st The diamagnetism of the electrons bound within the atom.

2nd The influence of the so-called free electrons on the whole diamagnetic effect.

3rd The influence on the bindings of the crystal lattice.

Under 2.

H. A. LORENTZ has shown that the free electrons do not contribute to the diamagnetism. In the classic calculation the conduction electron has been assumed to be absolutely free, which assumption however is not valid.

On the contrary, the great susceptibilities of some metals, bismuth, antimony etc. seem to make it probable that also the conduction electrons contribute to the diamagnetism.

It is possible that the classical theory of the conduction electrons may be able to let them contribute to the diamagnetism; but then these electrons must be assumed to be more or less bound.

In our opinion it seems probable, that a great diamagnetism may be expected there where the binding of the conduction electron is rather strong, so that during some time this electron is strongly under the influence of *two neighbouring atoms.*

Under 3.

The crystal lattice has a very great influence on the phenomena of diamagnetism.

For example this is very evident for tin. White tin is paramagnetic and grey tin diamagnetic. See also the results for copper by HONDA, Nature vol. 126, p. 990, 1930.

In general the problem of the influence of the crystal lattice is closely connected with the question whether the free electrons are bound more or less loosely. For high diamagnetism at least these two questions cannot be separated in our opinion.

Literature.

See for the theoretical treatment of the diamagnetism: LANGEVIN [1]). PAULI [2]), LANDAU [3]), P. EHRENFEST [4]).

---

[1]) P. LANGEVIN, Ann. de chim. et phys. (8) **5**, p. 70, 1905.

[2]) W. PAULI, Rapports Solvay 1930.

[3]) LANDAU. Zeits. f. Phys. Bd. **64**, p. 629, 1930.

[4]) P. EHRENFEST, Zeit. f. Phys, Bd **58**, p. 719, 1929.

For the explanation of the high diamagnetic values of some metals: P. EHRENFEST [1]); for the group of metals: bismuth, antimony and gallium. See also the summary of H. J. SEEMANN [2]). Detailed experimental investigations have been made by K. HONDA [3]), M. OWEN [4]) and others. The latter determined the temperature dependency of the susceptibility of most elements down to —190°.

§ 1. *Previous considerations.*

We investigated lead, tin and bismuth, the latter also in the form of single-crystals.

The most detailed investigation was that of the bismuth single-crystals.

1st because we had at our disposal a single crystal of extremely pure bismuth;

2nd because of the desirability of the examination of bismuth single-crystals in connexion with the anomalous results of the resistance measurements by L. SCHUBNIKOW and W. J. DE HAAS [5]) with these crystals. Because of the evident correlation [6]) of the diamagnetic susceptibility with the change of resistance we were inclined to expect a dependance of the susceptibility on the field analogous to that found for the resistance. Further on we shall see that our expectation was fulfilled.

§ 2. *General difficulties in measurements of the diamagnetic susceptibility.*

The general difficulty in the measurement of diamagnetic forces is their smallness. This makes the use either of the torsion balance or of the ordinary balance inevitable. At low temperatures the torsion balance is of no practical use. So we had to choose a balance method, which will be described in § 3.

Besides, a high degree of purity of the specimen used was required. The slightest traces of iron or of other ferromagnetic substances might spoil the results; even the occurrence of paramagnetic substances may be dangerous at low temperatures.

From the phenomena we can conclude however with great surety whether the substances are sufficiently pure. In high fields the ferromagnetic substances certainly become saturated.

Moreover a *strong* diamagnetism is always a sign of purity, both ferro- and paramagnetic substances having the other sign.

---

1) P. EHRENFEST, Zeits. f. Phys. Bd. **58**, p. 719, 1929.

2) H. J. SEEMANN, Zeits. f. Techn. Phys. **10**, p. 399, 1929.

3) K. HONDA, Ann. de Phys. **32**, p. 1027, 1910.

4) M. OWEN, Ann. d. Phys. **37**, p. 657, 1912.

5) L. SCHUBNIKOW and W. J. DE HAAS, These Proc. **33**, pp. 130, 363, 1930, Comm. Leiden No. 207.

6) W. J. DE HAAS, These Proc. **16** p. 1110, 1914.

§ 3. *Description of the apparatus.*

Principle:

By means of a balance the substance is weighed with and without magnetic field.

In the case of a long rod with transverse section d, the extremities of

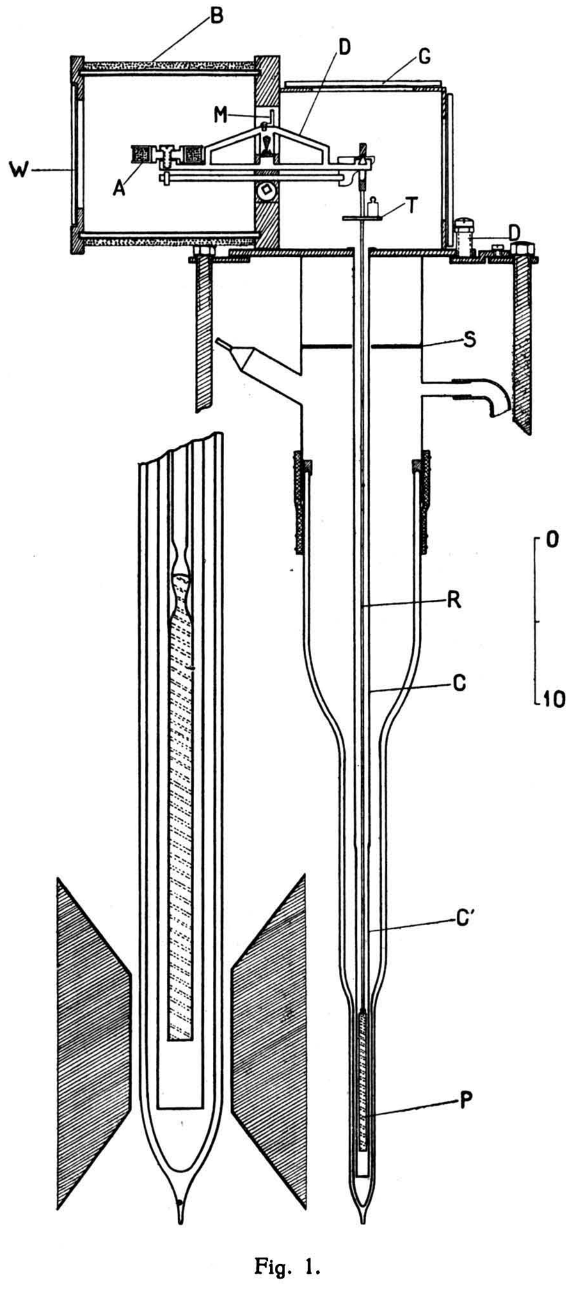

Fig. 1.

which are hanging in the fields H and H' respectively the change in weight is given by

$$p = \frac{2\,Kd}{g}(H^2 - H'^2),$$

where K is the volume susceptibility.

The field changing from H' to H in the space occupied by the substance this method cannot be used when the susceptibility is a function of the intensity of the field.

In that case the Faraday method is preferable, which makes use of a small quantity of matter placed there where $H\frac{dH}{dx}$ has its maximum value

The change in weight is now given by

$$p = \frac{m\chi}{g} H \frac{dH}{dx}$$

or

$$p = \frac{m\sigma}{g} \cdot \frac{dH}{dx},$$

where σ is the magnetic moment belonging to the intensity of the field H.

Performance.

The substance is suspended on a glass rod R at one arm of a balance. The other arm carries a coil A through which an electric current can be passed, by means of two thin springs at the side of the balance. The same current passes through the large coil B, the axis of which is perpendicular to that of A. The couple of forces which acts on the coil A is used to compensate the couple of forces cause by the change in weight of the substance.

By commutating the current in A or in B we can change the sign of the couple of forces. The deflexions of the balance are read with the aid of a telescope, a scale and the mirror M.

The substance P can not hang immediately in the refrigerating liquid. In this case the boiling of the liquid would have too disturbing an influence. Therefore the substance is suspended within a copper tube C' This tube, closed at the bottom, is suspended by a German silver tube in order to reduce the conduction of head as much as possible, and filled with helium gas.

Experiments with a thermo-element showed that the temperatures inside and outside the copper tube differed less than 0.1°, over a range in vertical direction of about 20 cm.

The apparatus was calibrated by means of weights placed on the table T.

After the rod R has been introduced the apparatus is shut with the glass plate G. Through a side-tube the balance space is then evacuated and afterwards filled with helium gas.

The screen S protects the upper part against the cold vapours of the liquid.

The cryostat glass has three narrow places, of which the lowest one is fitted between the pole-pieces, the middle one between the windings of the magnet.

The oscillations of the balance are aperiodic and strongly damped by the FOUCAULT currents. The zero position is however well reproduced.

§ 4. *Measurements with a lead rod.*

To control whether the apparatus works satisfactorily the susceptibilities of lead and tin were determined at low temperatures. For this purpose rods

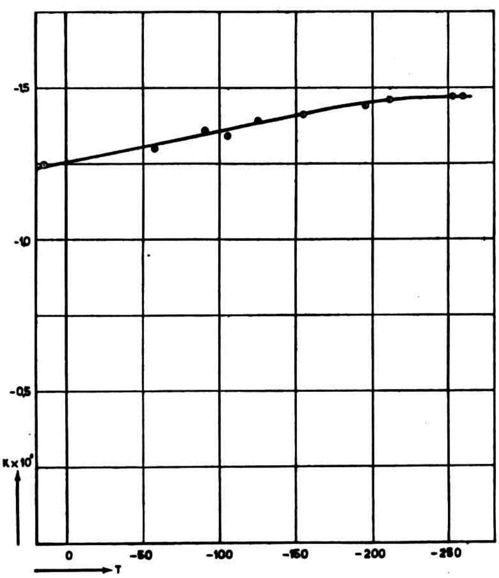

Fig. 2.

TABLE I (lead).

T	$-K \times 10^6$
+ 16° C.	1.25
— 57°.9	1.30
— 90°.5	1.36
—105°.5	1.34
—125°.7	1.39
—154°.8	1.41
—195°.9	1.44
—211°.1	1.46
—252°.7	1.47
—259°.4	1.47

of about 10 cm. length were made from the metal obtained from KAHLBAUM. First the impure surface was removed by etching and the metal was melted in vacuo and poured into a glass tube. After cooling down the lower part of the glass tube could easily be removed. The upper part was left intact, so that it could be used to fuse the rod to the glass tube.

The measurements from 0° to —154° are made with a vapour cryostat, so that the temperatures were not so constant as during the measurements in liquid nitrogen and hydrogen.

The diamagnetism of lead is found to increase about 15 %.

§ 5. *Measurements with a paramagnetic tin rod.*

TABLE II (tin).

T	$-K \times 10^6$
$+16°$ C.	0.187
$-252°.7$	0.173

§ 6. *Measurements with a poly-crystalline bismuth rod.* (Table III.) Already before the resistance measurements of L. SCHUBNIKOW and W. J. DE HAAS with bismuth single-crystals we examined a bismuth rod obtained from HILGER. This rod was made by melting the metal in vacuo, and letting it cool down in a glass tube. This cooling down had to be slow in order not to spring the glass.

This caused however the formation of rather large crystals the crystal directions of which strongly depend on the temperature gradient.

For most rods investigated by us (lead and bismuth at room temperature) an increase of the diamagnetic susceptibility with the field intensity was caused by traces of iron. For bismuth at hydrogen temperatures this was found to be no longer the case ; even the opposite effect was observed.

The results of these measurements are given in table III.

TABLE III (Bismuth).

	$T = 14.2$ K.	$T = 16°$ C.
H_{max}	$-K \times 10^6$	$-K \times 10^6$
6.4 K.G.	14.9	11.7
8.4	15.1	11.8
10.4	15.0	11.8
12.0	15.0	11.8
13.1	15.0	11.8
14.0	14.9	11.8
14.6	14.9	11.8^5
15.1	14.9	11.8^5
15.6	14.8^5	11.9

§ 7. *Measurements with a long single-crystal of bismuth.*

The first research on bismuth single-crystals was made with a long crystal (22 mm.). The principal axis coincided with the longitudinal direction of the crystal.

The results of this investigation have already been published [1]). As was expected the susceptibility proved to depend on the field, so that another method should be applied.

§ 8. *Measurements with a small bismuth single-crystal.*

For the above reason Dr. L. SCHUBNIKOW prepared for us a small single-crystal ($5 \times 5 \times 5$ mm.). With this crystal the measurements were repeated in a known field, in which $H \frac{dH}{dx}$ was constant within a range of 8 mm. The material for this crystal was chemically pure bismuth which was further recrystalised 12 times. The bismuth was therefore extremely pure.

The principal crystal axis was parallel with an edge of the crystal, so that the plane through the binary axes was parallel with a side of the cube.

The direction of the binary axes was derived from the line system on a cleavage plane.

§ 9. *Adjustment of the crystal.*

By means of a very thin strip of copper the crystal was suspended from a ground glass rod in such a way that the principal axis was directed vertically, that is to say perpendicular to the magnetic lines of force.

The correction for the carrier was determined for each temperature separately by taking the crystal each time out of the strip.

The glass becoming paramagnetic at low temperatures the lower part was later replaced by a zinc rod which was diamagnetic. The upper part remained of glass to prevent heat conduction. As this part was not in the magnetic field it had no considerable influence.

§ 10. *The magnets.*

For the low fields a CARPENTIER magnet was used, for the high fields a large type WEISS magnet.

Both magnets could be turned round a vertical axis and the angle of rotation could be read.

In both cases the field intensity was measured at different points and for different currents by means of a small coil and a ballistic galvanometer.

In this way the place of the maximum of $H \frac{dH}{dx}$ was determined as well as its maximum value.

---

1) W. J. DE HAAS and P. M. VAN ALPHEN, These Proc. Vol. **33**, N⁰. 7 p. 680, 1930; Comm. Leiden N⁰. 208*d*.

The corresponding value of H was 12.9 K.G. with the first magnet, 20.4 K.G. with the second one.

§ 11. *Results at 16° C.*

As might be expected the susceptibility was found to be independent of the position of the magnet. Nor did the values for the different fields differ more than $\pm$ 1 % and these deviations were not systematic.

For low field we found $\chi = 1.47^{8} \,.\, 10^{-6}$,

for high fields $\chi = 1.48^{2} \,.\, 10^{-6}$,

the mean value of which is $1.48 \,.\, 10^{-6}$,

which is in good agreement with the measurements of FOCKE [1]) and MC LENNAN [2]), who found respectively $\chi = 1.487 \,.\, 10^{-6}$ and $1.50 \,.\, 10^{-6}$.

§ 12. *Measurements at the temperatures of liquid hydrogen.* (20°.4 K. and 14°.2 K.).

Dependency of the magnetisation on the field intensity and on the direction of the magnetic field.

The principal axis of the crystal was again perpendicular to the lines of force. By rotating the magnet about the vertical axis all values could be given to the angles between the field and the binary axes.

In tables IV and V the value of the specific magnetisation has been given, together with the intensity of the field for different field directions.

As might be expected the magnetisation does not only change with the

TABLE IV. (Fig. 3 and 4). $-\sigma \times 10^{3}$.

$H \times 10^{6}$ G.	$T = 20°.4$ K.		$T = 14°.2$ K.	
	H // Bin. Axis	$H \perp$ Bin. Axis	H // Bin. Axis	$H \perp$ Bin. Axis
3.4	5.3	5.4	5.8	5.9
5.1	8.7	9.0	9.1	9.5
6.7	12.5	11.8	13.5	11.7
8.3	13.9	15.1	13.4	15 6
9.6	17.7	18.8	18.7	20.2
10.5	20.9	20.8	22.6	22.3
11.3	23.0	21.9	24.9	22.9
11.9	24.5	22.3	26.4	22.9
12.5	24.9	22.3	26.6	22.1
12.9	25.2	22.2	26.6	21.5

[1]) A. B. FOCKE, Phys. Rev. **36**, p. 316, 1930.

[2]) J. C. MC LENNAN and E. COHEN, Trans. Roy. Soc. Canada 23 sect. 3 p. 159, 1929.

intensity of the field but also with the direction of the latter. This latter change has a period of 60°. Extreme values are reached for those positions of the magnet for which the lines of force are either parallel or perpendicular to the binary axes.

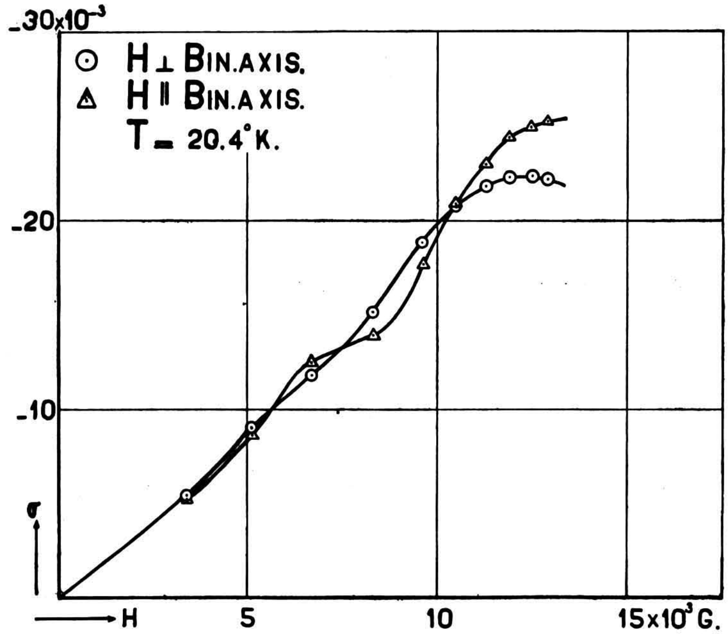

Fig. 3.

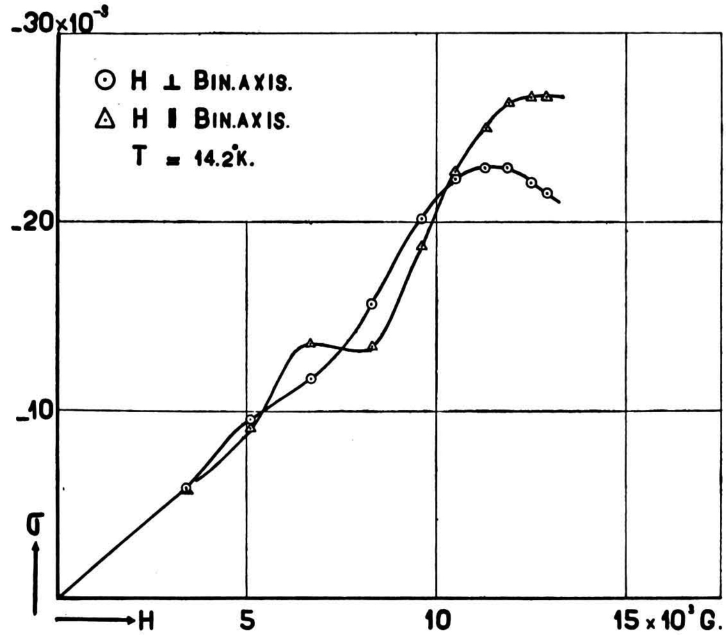

Fig. 4.

TABLE V. (Fig. 5). $-\sigma \, . \, 10^3$.

$H \times 10^6$ G.	$T = 20°.4$ K.		$T = 14°.2$ K.	
	$H//$ Bin. Axis	$H\perp$ Bin. Axis	$H//$ Bin. Axis	$H\perp$ Bin. Axis
2.4	4.0	4.2	4.6	4.8
4.9	8.6	8.5	8.0	9.2
6.2			11.5	10.4
7.4	13.0	12.7	11.9	12.3
8.6			13.7	16.2
9.8	18.8	19.1	18.8	20.0
11.0			22.6	21.4
11.9	23.1	20.6	23.9	20.4
12.8			24.3	19.2
13.7	24.4	21.4	23.9	19.3
15.7	24.6	24.9	22.6	23.6
16.9			23.0	28.0
17.8	26.3	30.7	24.2	30.8
18.8	28.0	32.9	26.6	33.8
19.6			29.4	35.7
20.4	33.5	36.3	32.8	37.6

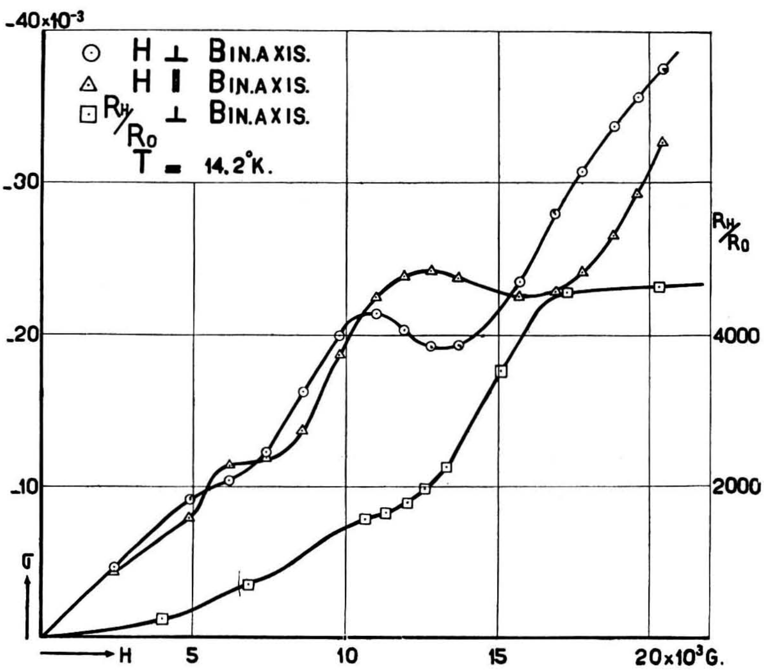

Fig. 5.

From the figures 3, 4, 5 it is evident that between 5 and 7.5 K.G. and between 10 and 15 K.G. the specific magnetisation does not increase much and in the second interval even diminishes with increasing intensity of the field.

TABLE VI. (Fig. 6). $-\chi \times 10^6$.

H	$H //$ Bin. Axis	$H \perp$ Bin. Axis
4.9	1.59	1.82
6.2	1.88	1.70
7.4	1.57	1.63
8.6	1.55	1.82
9.8	1.87	2.00
11.0	2.04	1.94
11.9	1.95	1.66
12.8	1.84	1.46
13.7	1.71	1.38
15.7	1.41	1.47
16.9	1.34	1.63
17.8	1.34	1.70
18.8	1.39	1.77
19.6	1.49	1.81
20.4	1.58	1.80

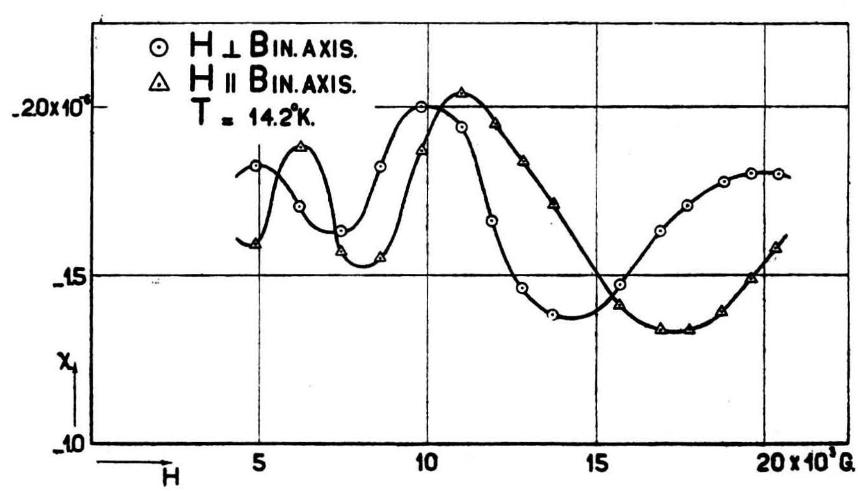

Fig. 6.

$T = 14^{\circ}.2$ K.

TABLE VII. (Fig. 7). $-\sigma \times 10^3$.

	$H = 11.9$	13.7	15.7	17.4	18.8
0°	19.9	20.6	24.0	28.8	32.3
5°	20.2	19.8	23.5	29.7	34.0
10°	20.0	20.7	24.2	28.8	31.9
15°	20.3	21.6	25.2	27.8	29.2
20°	21.7	23.0	24.6	26.2	28.4
25°	22.9	23.6	23.5	24.9	27.0
30°	23.9	23.7	22.4	23.6	26.1
35°	24.0	23.7	22.2	23.3	26.0
40°	23.6	23.5	22.5	23.6	26.1

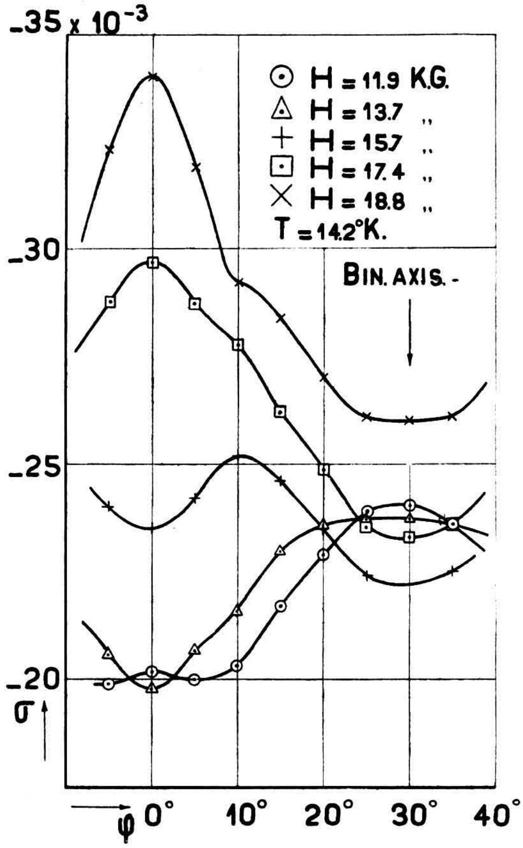

Fig. 7.

These regions of slightly increasing magnetisation are displaced towards the higher fields in the case $H \parallel$ binary axis.

In fig. 5 the change in resistance of *Bi* (for the case binary axis perpendicular to the field, bisectrix parallel and the current vector perpendicular to the field) has been plotted beside the magnetisation. It is evident that a connexion exists between this resistance change and the magnetisation perpendical to it.

The resistance change for the case H parallel with the binary axis shows at 14°.2 a character too weakly pronounced to allow comparison.

In fact the determination of the susceptibility generally offers a more refined means of research than the change of resistance.

Table VII and fig. 7 give the change of the susceptibility with the direction of the field for different field intensities.

It is evident that still other periods occur beside that of 30°. Fourier analysis may reveal the details.

§ 13. *Summary.*

The susceptibility of bismuth at low temperatures (hydrogen) is found to be a periodical function of the field.

The susceptibility in directions perpendicular to the principal axes are complicated functions of the field and of the angle between the binary axes and the field.

The *Bi* atoms that are very near to each other are subjected to their mutual influences.

Finally we wish to express our best thanks to Messrs T. JURRIAANSE, J. W. BLOM and J. DE BOER for their valuable help during the measurements.