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## Investigations on Paramagnetism at Low Temperatures

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# PHILOSOPHICAL TRANSACTIONS.

## I.—*Investigations on Paramagnetism at Low Temperatures.*\*

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*Communicated by Prof. H. KAMERLINGH ONNES, For. Mem. R. S.*

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### INTRODUCTION.

THE investigations described in the present paper have already been the subject of two short preliminary notes published in collaboration with Prof. KAMERLINGH ONNES.† It was intended that this communication should also be a joint paper, but, as it has been used by the author in an amplified and somewhat altered form as his doctoral dissertation (Leiden 1923), it was decided, with the concurrence of Prof. ONNES, to present it for publication in its present form.

The work is intended as a contribution to the study of the paramagnetism of solids at low temperatures in continuation of the previous investigations already carried out at Leiden‡. It falls naturally into two parts, the first dealing with measurements of the susceptibilities of powdered substances and the second in which measurements on crystals are described. It was decided to investigate the following series of compounds in the powder form, viz. : the anhydrous and heptahydrated sulphates and the ammonium double sulphates of ferrous iron, nickel and cobalt. Of these compounds, data for the anhydrous and heptahydrated ferrous sulphates have already been published.§ They are considered here for the sake of completion in the series.

The choice of the substances was regulated by the following considerations. These substances form three series of compounds of precisely similar constitution for the three strongly ferro-magnetic metals. It would thus be expected that results of interest might be obtained in thus being able to determine the effect on the general behaviour of these paramagnetic substances, as the paramagnetic atom is changed from iron through nickel to cobalt. Again, the substances form three series of compounds of increasing “magnetic dilution”||. As a result of the previous work at Leiden it was considered that the deviation from the law of CURIE, at least as concerns the relatively higher temperatures,

\* Communication No. 163. “Magnetic Researches XX of the Communications from the Physical Laboratory of the University of Leiden.”

† ‘Roy. Soc. Proc.,’ A., vol. 102, pp. 678 and 680 (1923).

‡ ‘Leiden Comm.,’ Nos. 116, 122, 124, 129, 132, 139, 140.

§ *Ibid.*, Nos. 122, 124, 129, 139.

|| *Ibid.*, No. 139.

was smaller the greater the "magnetic dilution" of the substance under consideration. The above series of compounds was chosen with a view to further testing this idea.

In Part II will be found an account of the measurement of the principal susceptibilities of two crystals, cobalt ammonium sulphate and nickel sulphate heptahydrate, down to the lowest temperature obtainable with liquid hydrogen. These measurements constitute the first data available concerning the principal susceptibilities of crystals at these very low temperatures. The substances were chosen as representatives of different classes of crystals. Thus, cobalt ammonium sulphate belongs to the monoclinic system and has a considerable "magnetic dilution." Nickel sulphate heptahydrate is a rhombic crystal; its "magnetic dilution" is rather less than that of cobalt ammonium sulphate. It was chosen also partly on account of the interesting deviations from the WEISS law  $\chi (T + \Delta) = C$ , which were shown by its mean susceptibility as determined from measurements on the powdered material.

I desire to mention that some of the work here described had been previously undertaken at Leiden, conjointly with Prof. KAMERLINGH ONNES, by Dr. K. HOF in 1915-16, but owing to most of the notes of the observations having been lost during the return of Dr. HOF to Switzerland, and to the fact that the measurements could not at that time be made over the intermediate range of temperature between room temperature and hydrogen temperatures, the work was entirely repeated by me. Where the notes are still available, I have added the results obtained by Dr. HOF to those obtained later, so that a comparison may be made between the two. The apparatus for the measurement of the crystals was made at Leiden for the research of Prof. KAMERLINGH ONNES and Dr. HOF and a series of measurements with it on various crystals was carried out, but unfortunately none of the notes containing the final observations and results are now available. The work was therefore begun once more quite independently of the previous work. I wish, however, to make my acknowledgments for the considerable assistance which such of the notes as still remained afforded during the early stages of the work.

I desire further to express my thanks to Prof. H. KAMERLINGH ONNES, in whose laboratory these investigations were carried out, for the great interest which he has taken throughout in the work and for his kindness in placing all the facilities of the laboratory at my disposal.

## PART I. MEASUREMENTS ON POWDERED MATERIALS.

### METHOD OF MEASUREMENT AND MATERIALS.

#### §1. *Measurement of Susceptibility.*

The method adopted for the measurements of the susceptibilities of the powdered substances was that which may be termed the rod method. In this method a rod of the substance to be investigated is placed in the field of an electromagnet in such a manner

that one end of the rod is situated in a strong magnetic field (that on the axis of the interferrum of the magnet), while the other end is outside the field or in only a very weak field. A force then acts on the rod given by the expression

$$F = \frac{1}{2}\chi \frac{m}{l} (H_1^2 - H_2^2)$$

in which  $F$  = force on rod,  $\chi$  = specific susceptibility,  $m$  = mass of substance,  $l$  = length of rod,  $H_1$ ,  $H_2$  = fields at ends of rod.

The actual apparatus used in the measurements has been described in detail in 'Leiden Comm.,' Nos. 139A and 139B, the former giving the description of the apparatus and method of working and the latter the modification of the apparatus introduced by OOSTERHUIS. A very brief description will therefore suffice here. The powdered material is contained in a cylindrical glass tube of uniform cross-section, the lower half of which is filled with the substance, while the upper half is evacuated or contains helium at a low pressure, the latter being introduced to assist in the unification of the temperature over the specimen. To the upper end of the tube is attached a glass rod, this in turn being fastened to a system floating in mercury in such a way that the upper end of the cylinder of powder is situated on the axis of the poles of the magnet. The floating system carries a scale-pan on which weights can be put. The values of  $F$ ,  $H_1$  and  $H_2$  in the expression given above are then determined as follows. A known weight is placed on the scale-pan and the current through the magnet coils is then switched on and increased until the floating system, owing to the upward force acting on it due to the magnetic field, is brought back into the position it occupied in the absence of the field before the weight had been placed on the scale-pan. The values of  $F$  and  $H_1$  (and  $H_2$ ) are then given immediately by the weight added and the current through the magnet coils respectively. When making the measurements at low temperatures the tube containing the powder is, of course, surrounded by a Dewar vessel containing a suitable liquefied gas.

### § 2. *Measurement of Field Strength.*

The electromagnet used in the present work was a small-size WEISS magnet. It was mounted on a turn-table so that it could be turned into any position about a vertical axis, as was required in making the measurements on the crystals described later. The positions of the magnet could be read on a circular scale divided into degrees and attached to the magnet proper. The field strengths on the axis of the pole pieces, *i.e.*, the  $H_1$  of the above formula, had previously been determined with great care for a large number of current strengths, by both the ballistic method and that of the magnetic balance of Cotton. A table had then been prepared from the observations giving the field strength on the axis for the particular pole distance used (16·8 mms.) as a function of the current in the magnet coils. Further, the ratio of the strength of the field at any point in an equatorial plane to that on the axis of the magnet had also been determined, thus giving the value of  $H_2$ . In general with the lengths of tube used in the



present work the value of  $H_2^2$  was small compared with  $H_1^2$  and could be neglected altogether or introduced as a small correction. In the present work the values of  $H_1$  were determined by reading the value of the current in the magnet coils and referring to the table mentioned above.

### § 3. *Measurement and Control of the Temperature.*

The measurements of the atmospheric temperatures were made with a mercury thermometer which had been compared with a standard mercury thermometer calibrated at the Physikalisch-Technische Reichsanstalt. The lower temperatures were controlled and measured as follows. The temperatures were obtained by means of baths of the various liquefied gases boiling under constant known pressures. For temperatures lower than the boiling point of any of the liquefied gases, the pressure under which the gas was boiling was reduced by means of a pump and could be kept constant by means of a valve. The pressure was determined by the aid of an open mercury manometer, an auxiliary oil manometer being employed to show any small changes in the pressure. This oil manometer could be maintained at a definite pressure to within a few millimetres, thus ensuring that the liquefied gas, which was always kept well stirred by moving the floating system up and down, was boiling at a temperature which did not vary by so much as one-tenth of a degree absolute. The temperatures were obtained by measuring the pressure under which the liquefied gases were boiling and then referring to the vapour pressure curves previously obtained by measurements in the laboratory. The temperatures were thus known to within one-tenth of a degree, which was sufficiently accurate for the present purpose.

### § 4. *Materials.*

The substances used were, with the exception of cobalt ammonium sulphate,\* MERCK'S guaranteed pure reagents. The heptahydrated sulphates and the double sulphates were recrystallized before use, dried on filter paper and powdered. The anhydrous sulphates were prepared from MERCK'S pure samples of the corresponding heptahydrated sulphates by careful heating until all the water of crystallization had been driven out as shown by the constancy of the weight of the material and the agreement of the loss in weight with that corresponding to the loss of seven molecules of water.

## OBSERVATIONS AND RESULTS.

### § 1. *Specimen Observations.*

The following set of observations may serve to show the nature of the results obtained in the present investigation :—

Cobalt Sulphate Heptahydrate.

Mass of substance used = 5.565 gm.

Length of column of substance = 8.85 cm.

\* Supplied by H. TROMMSDORFF, 'Chemische Fabrik,' Erfurt.

Observations with bath of liquid nitrogen at 764·5 mms. pressure.

Hence temperature = 77°·3 K.

I. Mass in Scale-Pan = 3·1624 gm.

Current in magnet coils to balance above mass = 9·61 amps.

Field Strength = 8846 Gauss.

Susceptibility =  $126·1 \times 10^{-6}$ .

II. Mass in Scale-Pan = 4·4877 gm.

Current in magnet coils to balance above mass = 11·41 amps.

Field Strength = 10490 Gauss.

Susceptibility =  $127·2 \times 10^{-6}$ .

III. Mass in Scale-Pan = 4·4460 gm.

Current in magnet coils to balance above mass = 11·38 amps.

Field Strength = 10463 Gauss.

Susceptibility =  $126·7 \times 10^{-6}$ .

IV. Mass in Scale-Pan = 6·5762 gm.

Current in magnet coils to balance above mass = 14·16 amps.

Field Strength = 12700 Gauss.

Susceptibility =  $127·2 \times 10^{-6}$ .

V. Mass in Scale-Pan = 7·6501 gm.

Current in magnet coils to balance above mass = 15·81 amps.

Field Strength = 13701 Gauss.

Susceptibility =  $127·1 \times 10^{-6}$ .

Mean Susceptibility =  $126·9 \times 10^{-6}$ .

Range of Field Strengths = 8846 — 13701 Gauss.

#### *Final Results.*

##### *I. Anhydrous Cobalt Sulphate.*

The results of the measurements on anhydrous cobalt sulphate are given in the table below.

T	$\chi \times 10^6$	$\chi_m$	$1/\chi_m$	$\chi_m (T + 44·9)$
289·5	62·2 <sub>1</sub>	0·00964	103·7	3·22 <sub>4</sub>
286·5	62·7 <sub>8</sub>	0·00973	102·8	3·22 <sub>4</sub>
169·65	96·9 <sub>6</sub>	0·0150 <sub>3</sub>	66·5 <sub>2</sub>	3·22 <sub>5</sub>
77·27	169·7	0·0263 <sub>1</sub>	38·0 <sub>1</sub>	3·21 <sub>5</sub>
64·95	194·1	0·0300 <sub>9</sub>	33·2 <sub>2</sub>	3·30 <sub>5</sub>
20·45	378·8	0·0587 <sub>3</sub>	17·0 <sub>3</sub>	3·84 <sub>6</sub>
17·44	420·7	0·0652 <sub>2</sub>	15·3 <sub>3</sub>	4·06 <sub>5</sub>
14·77	461·8	0·0716 <sub>0</sub>	13·9 <sub>7</sub>	4·27 <sub>2</sub>

In the above table  $\chi$  denotes the specific susceptibility,  $\chi_m$  the molecular susceptibility,  $T$  the absolute temperature. The values of the reciprocals of the molecular susceptibilities given in column 4 are plotted against the absolute temperature in graph 1, fig. 1. The numbers in column 5 are intended as a test for the WEISS law  $\chi_m (T + \Delta) = C$  and will be discussed in the next section.

Before comparing the experimental results with any theory of paramagnetism, a correction must be applied to them on account of the diamagnetic properties of the anion, the water of crystallization, etc. The correction is, however, negligibly small in the present case and has been left out of account. It is applied to all the results given later for the cases in which it has an appreciable value.

From the above data we may calculate the number of magnetons present in the substance from the expressions given by WEISS, viz. :—

$$n = \sigma_m / 1123 \cdot 5. \quad \sigma_m^2 = 3\chi_m (T + \Delta) \cdot R = 3CR,$$

in which  $n$  = magneton number  $\sigma_m$  = magnetic moment per gramme molecule,  $R$  = gas constant per gramme molecule. We then find for  $n$  the value 25·2.

We may now compare the above given values with the data already to be found in the literature. This substance has been measured by ISHIWARA (*loc. cit.*) from atmospheric temperatures down to about 95°K. and by THEODORIDES (*loc. cit.*) from atmospheric temperatures up to about 500° C. The value for the susceptibility at 25° C. found by THEODORIDES is  $62 \cdot 25 \times 10^{-6}$ , while the data given by ISHIWARA are to be found below.

T	$\chi \times 10^6$	T	$\chi \times 10^6$	T	$\chi \times 10^6$
° C.		° C.		° C.	
22·4	59·6	— 69·2	85·1	— 145·8	127·3
— 1·1	65·1	— 86·6	91·6	— 161·9	145·1
— 22·0	70·3	— 106·8	100·6	— 179·3	170·3
— 45·4	77·4	— 127·2	113·2	—	—

The value given by THEODORIDES for atmospheric temperatures is somewhat higher than that found in the present work, but the present values are in good agreement with the data of ISHIWARA except for his lowest temperatures.

## II. Cobalt Sulphate Heptahydrate.

The values of the specific susceptibility of this substance found in the present work are given in the table below.

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T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m(T + 13.7)$
° K.					
292.0	37.0	0.0104 <sub>0</sub>	0.0105 <sub>0</sub>	95.2 <sub>2</sub>	3.210
291.4	36.9	0.0103 <sub>7</sub>	0.0104 <sub>7</sub>	95.4 <sub>6</sub>	3.196
288.2	37.0	0.0104 <sub>1</sub>	0.0105 <sub>1</sub>	95.1 <sub>7</sub>	3.172
169.5	61.6	0.0173 <sub>3</sub>	0.0174 <sub>3</sub>	57.3 <sub>7</sub>	3.193
77.48	126.5	0.0355 <sub>7</sub>	0.0356 <sub>7</sub>	28.0 <sub>3</sub>	3.252
77.3	126.9	0.0356 <sub>8</sub>	0.0357 <sub>8</sub>	27.9 <sub>5</sub>	3.256
63.85	146.2	0.0411	0.0412	24.2 <sub>7</sub>	3.195
63.8	144.6	0.0406 <sub>7</sub>	0.0407 <sub>7</sub>	24.5 <sub>3</sub>	3.160
20.4	403.0	0.113 <sub>3</sub>	0.113 <sub>4</sub>	8.81 <sub>8</sub>	3.779
20.32	404.4	0.113 <sub>7</sub>	0.113 <sub>8</sub>	8.78 <sub>7</sub>	3.783
17.47	464.4	0.130 <sub>6</sub>	0.130 <sub>7</sub>	7.65 <sub>3</sub>	4.084
14.76	535.9	0.150 <sub>7</sub>	0.150 <sub>8</sub>	6.63 <sub>3</sub>	4.292

In the above table  $\chi'_m$  denotes the molecular susceptibility corrected for the diamagnetism of the anion and the water of crystallization. The values of the corrections used were those derived principally from the work of PASCAL. The values required for the present case will be found collected together in a paper by WEISS and BRUINS

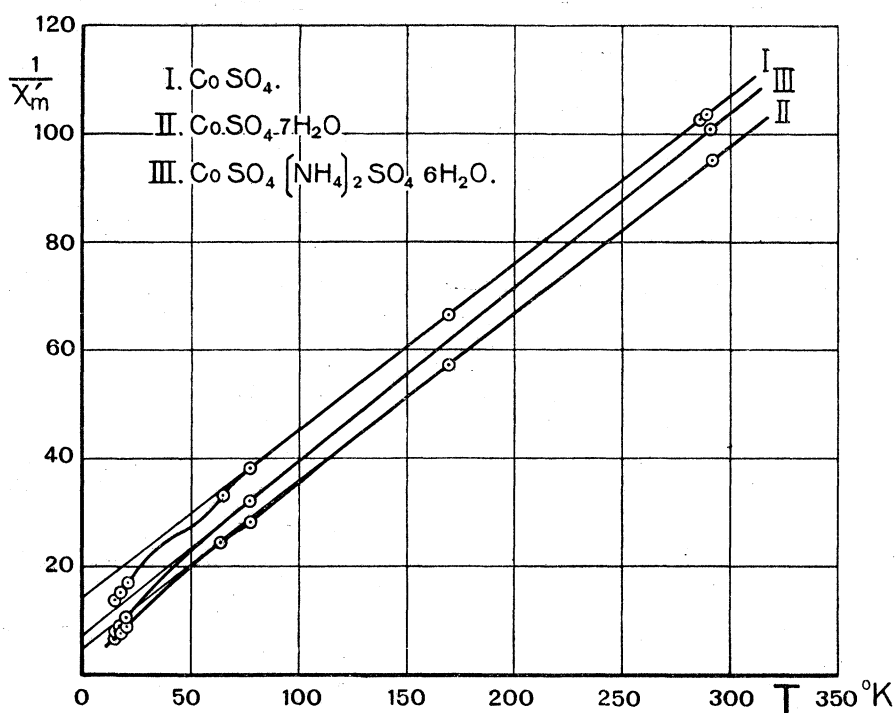


Fig. 1.

(‘Proc. Acad. Amst.’, vol. 18, p. 246 (1915)). It must be noted, however, that the values of the corrections mentioned above were determined at atmospheric temperatures, but that they are here applied to all the readings at whatever temperature. This is probably quite justifiable, as the susceptibilities of diamagnetic substances are in general



independent of the temperature, although exceptions to this rule are known. It cannot thus be stated with certainty that the values of the corrections determined at atmospheric temperatures will be valid at the lower temperatures, but, in the present state of our knowledge, the best thing we can do is to assume that they are valid.

The values of  $1/\chi'_m$  are plotted against T in graph 2, fig. 1.

The magneton number calculated from the above data is found to be 25.04.

In the following table are given the observations made on cobalt sulphate heptahydrate taken from the unpublished researches of Prof. KAMERLINGH ONNES and Dr. HOF and kindly placed at my disposal.

T	$\chi \times 10^6$	$\chi_m$
° K.		
290	37.0 <sub>1</sub>	0.0104 <sub>1</sub>
20.33	400.7	0.112 <sub>7</sub>
15.5	478.9	0.134 <sub>6</sub>
14.8	540.0	0.151 <sub>8</sub>

The above data may be compared with the results found by previous investigators:—

MESLIN (1906) =  $34.5 \times 10^{-6}$  (atmospheric temperature — value not stated).

WEISS and FOËX (1911) =  $31.9 \times 10^{-6}$  (20° C.).

### III. Cobalt Ammonium Sulphate.

The observations on cobalt ammonium sulphate are given in the table below.

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m(T + 22)$
°					
290.8	24.61	0.0097 <sub>3</sub>	0.0099 <sub>1</sub>	100.9	3.100
77.28	78.4	0.0309 <sub>9</sub>	0.0311 <sub>7</sub>	32.0 <sub>8</sub>	3.095
20.3	241.2	0.0953 <sub>4</sub>	0.0955 <sub>2</sub>	10.4 <sub>7</sub>	4.040
16.71	287.8	0.113 <sub>8</sub>	0.113 <sub>9</sub>	8.77 <sub>6</sub>	4.409
14.78	321.6	0.127 <sub>1</sub>	0.127 <sub>3</sub>	7.85 <sub>5</sub>	4.682

The values of  $1/\chi'_m$  are plotted against T in graph 3, fig. 1.

The value of the magneton number calculated from the above data is 24.75.

### IV. Anhydrous Nickel Sulphate.

The measurements on anhydrous nickel sulphate gave the results to be found in the following table:—

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T	$\chi \times 10^6$	$\chi_m$	$1/\chi_m$	$\chi_m (T + 79.4)$
°				
289.0	26.7	0.0041 <sub>3</sub>	242.0	1.525
169.2	39.9	0.0061 <sub>7</sub>	161.9	1.535
77.4	62.8	0.0097 <sub>2</sub>	102.9	1.524
20.33	81.7	0.0126 <sub>4</sub>	79.1	1.261
20.33	82.1	0.0127 <sub>0</sub>	78.7	1.267
16.77	79.7	0.0123 <sub>3</sub>	81.1	1.186
16.63	79.6	0.0123 <sub>2</sub>	81.2	1.183
14.7	80.6	0.0124 <sub>7</sub>	80.2	1.173
14.5	80.9	0.0125 <sub>2</sub>	79.9	1.175

The values of  $1/\chi_m$  are plotted against T in graph 1, fig. 2.

The value of the magneton number calculated from the above data is 16.9.

To the above results may be added those taken from the unpublished researches of Prof. KAMERLINGH ONNES and Dr. HOF as below.

T	$\chi \times 10^6$	$\chi_m$
°		
290.0	25.8	0.0039 <sub>9</sub>
20.33	82.1	0.0127 <sub>0</sub>
14.8	82.1	0.0127 <sub>0</sub>

Anhydrous nickel sulphate has been measured by ISHIWARA with the following results:—

T	$\chi \times 10^6$	T	$\chi \times 10^6$	T	$\chi \times 10^6$
° C.		° C.		° C.	
24.3	27.1	— 52.5	34.8	— 122.6	46.3
6.1	28.5	— 72.7	38.3	— 144.1	52.1
— 11.7	30.5	— 86.7	39.9	— 162.7	58.0
— 27.5	32.0	— 105.8	42.7	— 182.8	68.4

The values of ISHIWARA are throughout somewhat higher than the present observations, but the dependence on temperature is exactly the same in the two cases in the range of temperature common to both.

It may also be mentioned that the following values have been found by various investigators as a result of measurements on solutions of nickel sulphate:—

QUINCKE*	.. .. .	$29.9 \times 10^{-6}$	(19° C.).
JAEGER and MEYER†	.. .. .	$27.9 \times 10^{-6}$	(17.5° C.).
LIEBKNECHT and WILLS‡	.. .. .	$27.0 \times 10^{-6}$	(18° C.).

\* 'Wied. Ann.,' vol. 24, p. 347 (1885).

† 'Wien. Ber.,' vol. 106, p. 594 and 623 (1897); vol. 107, p. 5 (1898).

‡ 'Ann. der. Phys.' (4), vol. 1, p. 178 (1900).

V. *Nickel Sulphate Heptahydrate.*

The results of the measurements on nickel sulphate heptahydrate are given in the following table:—

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m (T - 59)$
292.2	16.0	0.0045	0.0046	218.0	1.073
169.6	34.8	0.0097 <sub>7</sub>	0.0098 <sub>7</sub>	102.3	1.092
77.29	77.3	0.0217	0.0218	45.9	0.399
64.65	91.5	0.0257	0.0258	38.8	0.146
20.33	222.0	0.0624	0.0625	38.8	— 2.417
16.65	270.0	0.0757 <sub>5</sub>	0.0758 <sub>5</sub>	16.0	— 3.212
14.6	294.0	0.0826	0.0827	12.1	— 3.672

The values of  $1/\chi'_m$  are plotted against T in graph 2, fig. 2.

The value of the magneton number calculated from the above data is 14.62.

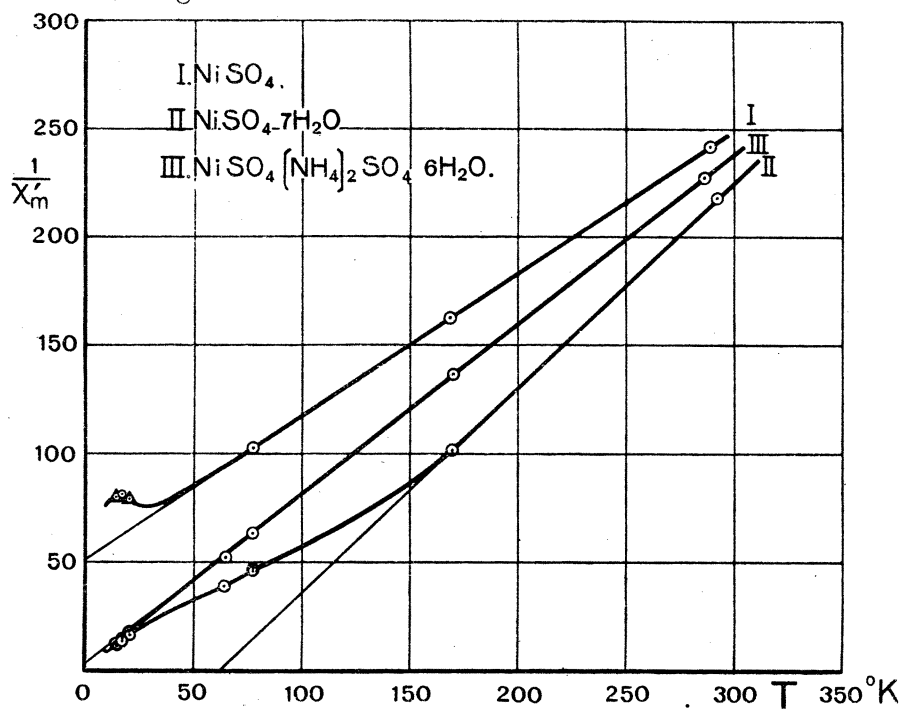


Fig. 2.

The following table gives the values taken from the unpublished researches of Prof. KAMERLINGH ONNES and Dr. HOF.

T	$\chi \times 10^6$	$\chi_m$
290.0	15.8	0.0044 <sub>5</sub>
20.33	218.0	0.0612 <sub>0</sub>
15.17	286.5	0.0804 <sub>3</sub>
14.8	294.1	0.0825 <sub>7</sub>

Nickel sulphate heptahydrate has been measured by MESLIN (*loc. cit.*), who found the following value:— $17.0 \times 10^{-6}$  at atmospheric temperature (precise value of temperature not stated).

#### VI. Nickel Ammonium Sulphate.

The results of the measurements on nickel ammonium sulphate are given in the following table:—

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m (T + 4)$
°					
286.5	10.6 <sub>8</sub>	0.0042 <sub>2</sub>	0.0044 <sub>0</sub>	227.3	1.278
169.5	18.0 <sub>3</sub>	0.0071 <sub>2</sub>	0.0073 <sub>0</sub>	137.0	1.270
77.15	39.5 <sub>5</sub>	0.0156 <sub>2</sub>	0.0158 <sub>0</sub>	63.2 <sub>9</sub>	1.282
64.6	48.0 <sub>6</sub>	0.0189 <sub>8</sub>	0.0191 <sub>6</sub>	52.1 <sub>9</sub>	1.314
20.3	150.4	0.0594 <sub>2</sub>	0.0596 <sub>0</sub>	16.7 <sub>8</sub>	1.448
16.8	179.2	0.0707 <sub>8</sub>	0.0709 <sub>6</sub>	14.0 <sub>9</sub>	1.476
14.5	207.5	0.081 <sub>6</sub>	0.0821 <sub>4</sub>	12.1 <sub>7</sub>	1.520

The values of  $1/\chi'_m$  are plotted against T in graph 3, fig. 2.

The value of the magneton number calculated from the above data is 15.9.

#### VII. Anhydrous Ferrous Sulphate.

The results of the measurements on this substance have been already published (see 'Leiden Comm.' No. 129B), but are given here for the sake of completion of the series.

T	$\chi \times 10^6$	$\chi_m$	$1/\chi_m$	$\chi_m (T + 31)$
°				
290.2	67.6	0.0102 <sub>7</sub>	97.3 <sub>6</sub>	3.299
169.6	107.2	0.0163 <sub>9</sub>	61.4 <sub>0</sub>	3.267
77.3	200.4	0.0304 <sub>5</sub>	32.8 <sub>4</sub>	3.298
70.4	215.1	0.0326 <sub>8</sub>	30.6 <sub>0</sub>	3.347
64.8	227.3	0.0345 <sub>4</sub>	28.9 <sub>5</sub>	3.309
20.1	402.0	0.0610 <sub>8</sub>	16.3 <sub>7</sub>	3.121
17.8	379.0	0.0575 <sub>9</sub>	17.3 <sub>6</sub>	2.810
14.4	335.0	0.0509 <sub>0</sub>	19.6 <sub>5</sub>	2.311

The values of  $1/\chi_m$  are plotted against T in graph 1, fig. 3.

The value of the magneton number calculated from the above data is 25.53.

The results given above may again be compared with the values found by other investigators. Thus we find the following values given for the susceptibility at atmospheric temperatures, as derived from measurements on solutions of ferrous sulphate.

QUINCKE ( <i>loc. cit.</i> )	..	..	..	..	75.8 $\times 10^{-6}$ (19° C.).
JAEGER and MEYER ( <i>loc. cit.</i> )	..	..	..	..	91.0 $\times 10^{-6}$ (17.5° C.).

KOENIGSBERGER*	.. .. .	69.9 × 10 <sup>-6</sup>	(22° C.).
LIEBKNECHT and WILLS ( <i>loc. cit.</i> )	.. .. .	80.4 × 10 <sup>-6</sup>	(18° C.).
TOWNSEND†	.. .. .	70.1 × 10 <sup>-6</sup>	(10° C.).
CABRERA, MOLES and MARQUINA‡	.. .. .	78.2 × 10 <sup>-6</sup>	(22.4° C.).

ISHIWARA has measured anhydrous ferrous sulphate in the powder form with the following results:—

T	$\chi \times 10^6$	T	$\chi \times 10^6$	T	$\chi \times 10^6$
° C		°		°	
33.3	71.0	- 56.3	97.5	- 146.1	153.9
8.5	76.9	- 78.4	107.3	- 162.8	177.0
- 17.0	83.8	- 102.2	120.1	—	—
- 41.0	92.5	- 128.8	139.5	—	—

#### VIII. Ferrous Sulphate Heptahydrate.

Data for this substance have also been published from Leiden (see 'Leiden Comm.', No. 122A). They are to be found in the table below.

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m (T + 1)$
°					
289.6	41.4 <sub>6</sub>	0.0115 <sub>3</sub>	0.0116 <sub>3</sub>	85.9 <sub>7</sub>	3.380
77.45	154.5	0.0429 <sub>5</sub>	0.0430 <sub>5</sub>	23.2 <sub>3</sub>	3.378
64.24	186.1	0.0517 <sub>4</sub>	0.0518 <sub>4</sub>	19.2 <sub>9</sub>	3.382
20.33	555.4	0.154 <sub>4</sub>	0.154 <sub>5</sub>	6.47 <sub>3</sub>	3.295
18.73	589.7	0.163 <sub>9</sub>	0.164 <sub>0</sub>	6.09 <sub>9</sub>	3.236
17.01	641.6	0.178 <sub>4</sub>	0.178 <sub>5</sub>	5.60 <sub>2</sub>	3.214
15.47	695.5	0.193 <sub>4</sub>	0.193 <sub>5</sub>	5.16 <sub>8</sub>	3.186
13.93	757.2	0.210 <sub>5</sub>	0.210 <sub>6</sub>	4.74 <sub>9</sub>	3.144

The values of  $1/\chi'_m$  are plotted against T in graph 2, fig. 3.

The value of the magneton number calculated from the above data is 25.84.

Ferrous sulphate heptahydrate has also been investigated by KOENIGSBERGER, MESLIN and ISHIWARA. The values found are given below.

KOENIGSBERGER	.. .. .	34.5 × 10 <sup>-6</sup>	(22° C.).
MESLIN	.. .. .	46.2 × 10 <sup>-6</sup>	(temperature not stated).

The data given by ISHIWARA are to be found in the table below.

\* 'Wied. Ann.,' vol. 66, p. 698 (1898).

† 'Roy. Soc. Proc.,' vol. 60, p. 186 (1896).

‡ 'Ann. Fis. Quim.,' vol. 13, p. 256 (1915).



T	$\chi \times 10^6$	T	$\chi \times 10^6$	T	$\chi \times 10^6$
° C.					
23.0	41.9	- 42.0	53.6	- 120.4	81.8
12.6	43.0	- 53.5	56.8	- 143.4	96.1
2.3	44.5	- 66.1	61.2	- 159.6	108.6
- 7.6	46.3	- 97.4	72.0	- 173.6	122.7
- 31.7	50.4	- 109.7	76.6	—	—

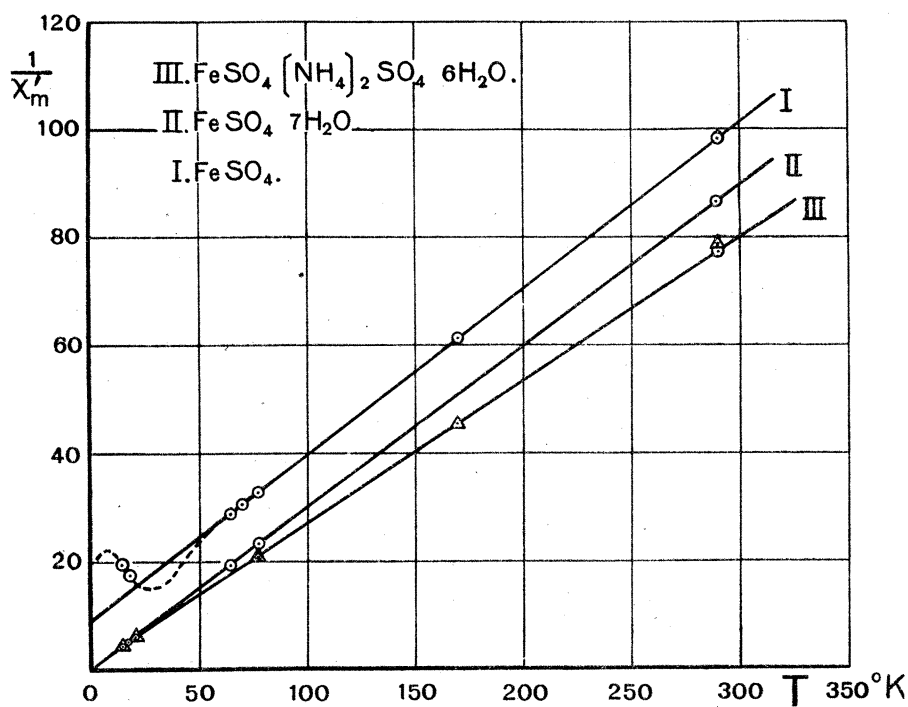


Fig. 3.

IX. *Ferrous Ammonium Sulphate.*

The results of the measurements on ferrous ammonium sulphate are given in the table below :—

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m (T + 3)$
290.3	32.5 <sub>7</sub>	0.0127 <sub>7</sub>	0.0129 <sub>5</sub>	77.2 <sub>2</sub>	3.798
77.1	121.6	0.0476 <sub>8</sub>	0.0478 <sub>6</sub>	20.8 <sub>9</sub>	3.833
20.3	413.1	0.0162 <sub>0</sub>	0.162 <sub>2</sub>	6.16 <sub>6</sub>	3.779
16.74	488.1	0.191 <sub>4</sub>	0.191 <sub>6</sub>	5.22 <sub>0</sub>	3.782
14.5	547.0	0.214 <sub>5</sub>	0.214 <sub>7</sub>	4.65 <sub>7</sub>	3.757

The value of the magneton number calculated from the above data is 27.5.

To the above measurements may be added some observations on ferrous ammonium sulphate taken from unpublished researches of Prof. KAMERLINGH ONNES and

Dr. OOSTERHUIS, and kindly put at my disposal. They are given in the following table:—

T	$\chi \times 10^6$	$\chi_m$	$\chi'_m$	$1/\chi'_m$	$\chi'_m (T + 3)$
°					
290.0	31.9	0.0125 <sub>1</sub>	0.0126 <sub>9</sub>	78.8 <sub>0</sub>	3.718
169.0	55.5	0.0217 <sub>6</sub>	0.0219 <sub>4</sub>	45.5 <sub>8</sub>	3.774
77.2	121.5	0.0476 <sub>5</sub>	0.0478 <sub>3</sub>	20.9 <sub>1</sub>	3.836
64.6	144.0	0.0564 <sub>7</sub>	0.0566 <sub>5</sub>	17.6 <sub>5</sub>	3.829
20.2	419.8	0.164 <sub>3</sub>	0.164 <sub>5</sub>	6.08 <sub>0</sub>	3.816
14.7	549.0	0.215 <sub>3</sub>	0.215 <sub>5</sub>	4.64 <sub>1</sub>	3.814

Both the above sets of observations are plotted in graph 3, fig. 3.

It will be seen that the present values (circles) and those of OOSTERHUIS (triangles) are in very good agreement, with the exception of the observations at atmospheric temperature, for which, as seen from the graph, the value in the first table would seem to be the more nearly correct.

Ferrous ammonium sulphate has also been investigated by FINKE\*, who determined the principal susceptibilities of a crystal of the substance and by FOËX†, who carried out measurements on the powdered substance.

For the principal susceptibilities (per unit volume) at atmospheric temperature, FINKE gives the following values:—

$$\chi_1 = 84.3_2 \times 10^{-6}, \quad \chi_2 = 78.7_4 \times 10^{-6}, \quad \chi_3 = 76.2_0 \times 10^{-6}.$$

Calculating the specific susceptibilities (density = 1.899) and taking the mean we find  $\chi = 42.0 \times 10^{-6}$ .

FOËX gives the following two series of observations of the molecular susceptibility, corrected for the diamagnetic properties of the molecule.

T	$\chi_m$	$\chi_m (T - 22)$
°		
288.9	0.01278	3.411
275.9	0.01346	3.417
223.4	0.01695	3.414
200.5	0.01903	3.397
88.0	0.0529	4.66
86.0	0.0693	5.96
288.1	0.01283	3.414
290.7	0.01271	—
89.0	0.0404	—
88.0	0.0420	—
87.0	0.0432	—
86.0	0.0480	—

\* 'Ann. der Phys.,' vol. 31, p. 149 (1910).

† THÈSE, Strasbourg, 1921; 'Ann. de Phys.' (9), vol. 16, p. 174 (1921).

Although the values for atmospheric temperature are in good agreement with the present observations, the values at lower temperatures are very different in the first series. Again, in the present measurements, no trace was found of a great deviation from the WEISS law at the lower temperatures as found by FOËX, neither was the  $\Delta$  negative. It may be observed that of the two series of measurements by FOËX, which differ from each other by a very considerable amount, the present observations agree better with the second than with the first.\*

#### DISCUSSION OF RESULTS.

##### § 1. *Examination for the law $\chi_m(T + \Delta) = C$ .*

In the tables of the results given in the previous chapter will be found columns giving the values of  $\chi_m(T + \Delta)$  in which  $\Delta$  is a constant characteristic of the substance. It will be seen that in all cases but that of nickel sulphate heptahydrate, the values in these columns are constant to within the experimental error down to the temperatures obtainable with liquid nitrogen (*i.e.*, about 70° K.). Hence it may be stated that these substances follow the WEISS law  $\chi_m(T + \Delta) = C$  over this range of temperatures. In the case of ferrous ammonium sulphate it will be seen that this law holds with the same accuracy down to still lower temperatures, and indeed to the lowest temperature investigated. This is brought out by an examination of the graph given in fig. 3. This graph shows that the observations for this substance fall on a straight line when  $1/\chi_m$  is plotted against  $T$ .

It may also be noted that, with the exception of nickel sulphate heptahydrate, all the substances, for which  $\Delta$  is not zero, have a positive value of  $\Delta$ . The value of  $\Delta$  for nickel sulphate heptahydrate is, however, negative ( $= -59$ ). This substance is therefore of considerable interest since, according to WEISS'S theory, it should become ferromagnetic at temperatures below that corresponding to  $\Delta$  (CURIE point), provided that the WEISS law is obeyed down to this temperature. It was, however, found that this substance did not become ferromagnetic at the lowest temperatures, since it ceased to obey the WEISS law, showing very large and interesting deviations therefrom.

On examining the present data in the light of the suggestion of KAMERLINGH ONNES and OOSTERHUIS as to the possible connection between "magnetic dilution" and the value of the  $\Delta$  in the WEISS law, we find that they are not altogether in agreement with this idea. Taking first the case of the cobalt compounds, we see that the  $\Delta$ 's for  $\text{CoSO}_4$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  are 44.9, 13.7 and 22 respectively. Thus, while it is true that for  $\text{CoSO}_4$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  the  $\Delta$  is smaller in the substance with the greater magnetic dilution, the value of  $\Delta$  for  $\text{CoSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  is greater than that for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , although one would expect that the former substance could be considered as the more dilute magnetically, since it is derived from the latter by the substitution of one molecule of ammonium sulphate for one molecule of water of crystallization.

\* FOËX has discussed this discrepancy in a recent paper. See 'Bull. Soc. Franç. de Physique,' No. 188, June 1, 1923.

In the case of the nickel compounds we find that the  $\Delta$ 's have the following values :—  
 $\text{NiSO}_4$ , 79·4,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , — 59,  $\text{NiSO}_4$ ,  $(\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ , 4. The heptahydrated sulphate here appears to be exceptional.

For the ferrous compounds we find the values  $\text{FeSO}_4$ , 31,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 1,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ , 3. In the case of the two sulphates the  $\Delta$  is, of course, the smaller for the substance of the greater magnetic dilution, since this was one of the cases considered by KAMERLINGH ONNES and OOSTERHUIS in making the suggestion referred to above, but here again the double sulphate has a larger  $\Delta$  than the heptahydrated sulphate. The values of  $\Delta$  are, however, very small, and hence they are not determinable with any great accuracy from the observations.

It would thus seem that while the values of  $\Delta$  are frequently greater, the smaller the magnetic dilution of the substance, more especially in the case of the hydrated and the corresponding anhydrous compounds, this rule does not always hold.

### § 2. *Deviations from the WEISS Law.*

An examination of the tables and the graphs will make it immediately obvious that, with the exception of ferrous sulphate heptahydrate and ferrous ammonium sulphate, all the substances show deviations from the WEISS law at low temperatures, and that these deviations are of various types.

We will now examine in detail the deviations from the law  $\chi_m (T + \Delta) = C$  which occur at low temperatures, considering first the double sulphates, then the heptahydrated sulphates, and finally the anhydrous sulphates, this order being chosen here, as then the type of deviation becomes progressively more complex.

Considering first the double sulphates and referring to the tables and the graphs, we see that the deviations from the WEISS law are such that *the susceptibility increases more rapidly with fall in temperature than is given by this law*. The deviation is considerable in the case of cobalt ammonium sulphate, less with nickel ammonium sulphate and too small for measurement with ferrous ammonium sulphate. It will be seen that at about 14° K. the susceptibility of cobalt ammonium sulphate is 1·4 times greater than the value calculated for this temperature from the law  $\chi_m (T + 22) = C$ . This type of deviation from the WEISS law is thus *the exact counterpart of the type previously found*, for example, with anhydrous manganese sulphate, and *now known as the cryomagnetic anomaly*.

Turning now to the heptahydrated sulphates, and taking first the case of the nickel compound, we find here a more complicated type of deviation. Thus, as the temperature falls, the susceptibility first increases *less* rapidly with fall in temperature than is given by the WEISS law, later the susceptibility begins to increase more rapidly. Hence the curve of  $1/\chi_m$  against  $T$  shows an inflection, the curvature changing sign at about 120° K. The susceptibility remains throughout, however, less than the value for any particular temperature below about 160° K. as calculated from the WEISS law. Cobalt



sulphate heptahydrate shows somewhat similar phenomena but on a much smaller scale ; also the susceptibility at the lowest temperatures is greater than the value given by the law  $\chi_m (T + 13.7) = C$ , which is obeyed at relatively high temperatures. On the other hand, ferrous sulphate heptahydrate shows a small deviation from the WEISS law of the older type, *i.e.*, the “ cryomagnetic anomaly.”

Considering now the anhydrous sulphates and taking first the case of the nickel compound, we see that (1) the susceptibility for temperatures below about  $75^\circ$  K. has a value throughout which is less than that given by the WEISS law and (2) there are a distinct maximum and minimum of susceptibility. The minimum, which is very sharp, occurs in the region of temperature obtainable with liquid hydrogen. In the case of anhydrous ferrous sulphate the points actually measured are shown on the full curve. It is immediately obvious that a maximum value of the susceptibility occurs between hydrogen and nitrogen temperatures. Nothing can be said with certainty of the shape of the curve in the region between the lowest nitrogen temperature (about  $64^\circ$  K.) and the highest hydrogen temperature (about  $20.3^\circ$  K.), as it is almost impossible to make accurate magnetic measurements in this region on account of the cryogenic difficulties, but it is probable, in the light of the phenomena shown by anhydrous nickel sulphate, that the curve runs something as shown in the dotted portion. It will be observed that in this case no minimum of susceptibility has been found. It would be of the greatest interest to continue the measurements down to helium temperatures so as to determine whether a minimum occurs or whether the susceptibility continues to decrease steadily.

Anhydrous cobalt sulphate also shows some indications of a maximum and a minimum value of the susceptibility at the lowest temperatures, but the phenomena are on a much smaller scale than in the case of the corresponding nickel and iron compounds.

### § 3. *Comparison of Results with Existing Theories.*

The theories of paramagnetism can be divided into two classes, those based on the classical electrodynamics and those based on the quantum theory. A short account will be given here of these theories in so far as they concern the phenomena shown by paramagnetic substances at low temperatures.

The theories of paramagnetism based on the classical electrodynamics are all more or less intimately connected with the theory of LANGEVIN. According to this theory the susceptibility should be independent of the field strength except for very great fields, and should be inversely proportional to the absolute temperature, that is, it should follow CURIE'S law. It is now known that in general this is not the case with solid substances. WEISS later showed that the introduction of a molecular field into the theory of paramagnetism leads to the law  $\chi (T + \Delta) = C$ , in which the symbols have their usual signification. It has been found that this law is almost invariably obeyed at relatively high temperatures, but in general it does not hold at low temperatures.



Other writers have proposed various modifications of the theory, in particular, GANS\* allowed for the effect of the mutual interactions of the molecules. He found that if the molecule possesses a figure axis the substance will be paramagnetic, but the dependence on temperature of the susceptibility at low temperatures given by the theory is not in good agreement with the experimental facts.

FOËX† has extended the theory of WEISS by considering the effect of the introduction of the following ideas (1) a molecular field equal to  $n\sigma$  ( $\sigma$  = magnetisation), in which  $n$  has in general different values along the principal axes of the crystal and (2) there exists a potential energy which is a function of the direction in the crystal. An account of this theory, as far as it concerns the principal susceptibilities of crystals, will be found in Part II. FOËX also considers in considerable detail the possible phenomena shown by the mean of the principal susceptibilities, *i.e.*, the quantity determined by measurements on powdered materials. He shows that the theory predicts the existence of the following phenomena: (1) At the higher temperatures the WEISS law holds, (2) at the lower temperatures the susceptibility may increase either *more* rapidly or *less* rapidly with fall in temperature than is given by the WEISS law, (3) the curve of the reciprocal of the susceptibility against the absolute temperature may possess a point of inflection so that the curve changes from concave towards the temperature axis to convex and *vice versa*, (4) a maximum and a minimum of susceptibility may occur at the lowest temperatures. It will thus be seen that the theory covers all the phenomena found as yet, including those announced in the previous pages. FOËX's theory is, however, purely qualitative, so that it cannot be asserted with any certainty that the theory is really a true representation of the facts.

The earliest of the theories of paramagnetism based on the quantum theory is that of OOSTERHUIS‡. The susceptibility according to LANGEVIN's is inversely proportional to the kinetic energy of rotation of the molecules. OOSTERHUIS replaces the classical expression for this energy by the quantum expression given by EINSTEIN and STERN§ *viz.* :—

$$U = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{1}{2}h\nu,$$

and obtains finally a formula which degenerates into the WEISS law at relatively high temperatures and which is capable of reproducing the experimental results for the anhydrous and hydrated manganese sulphates with a good accuracy over the whole temperature range investigated. The theory was later extended by KEESOM.||

Theories which are more in accordance with the later developments of the quantum

\* GANS, 'Ann. der Phys.,' vol. 49, p. 149 (1916).

† THÈSE, Strasbourg, 1921; 'Ann. de Physique' (9), vol. 16, p. 174 (1921).

‡ 'Leiden Comm.,' Suppl. No. 31.

§ 'Ann. der Phys.,' vol. 40, p. 551 (1913).

|| 'Leiden Comm.,' Suppl. No. 32.

theory have been given by REICHE\* and SMEKAL† as extensions to two degrees of freedom of an earlier work by WEYSSENHOFF‡ which dealt only with one degree of freedom.

In these theories the HAMILTON-JACOBIAN differential equation of motion is developed for the rotations of a molecule with two degrees of freedom, a permanent magnetic moment  $m$  and a moment of inertia  $J$  in a magnetic field  $H$ . The rotations are then quantised according to the conditions laid down by SOMMERFELD and WILSON. The distribution of the molecules in the "phase space" is then considered by REICHE from the point of view of the so-called PLANCK'S second quantum theory and by SMEKAL from that of the first quantum theory. REICHE thus arrives at the following formula for the susceptibility—

$$\chi = \frac{5\pi^2 m^2 J N}{4h^2} \cdot \frac{e^{-\sigma} + \frac{4}{15} S_0}{S},$$

in which

$$S_0 = \sum_2^{\infty} \frac{e^{-\sigma n^2}}{n(n^2 - 1)}; \quad S = \sum_1^{\infty} n e^{-\sigma n^2};$$

$N$  = AVOGADRO number;  $h$  = PLANCK'S constant;  $\sigma = \frac{h^2}{8\pi^2 J k T}$ ;  $k$  = gas constant.

The values calculated from this formula are in good agreement with the experimental data for the anhydrous and hydrated manganese sulphates, anhydrous ferric sulphate and hydrated ferrous sulphate. The formula derived by SMEKAL does not, however, reproduce the observed results with the same accuracy.

REICHE'S theory can thus give a quantitative explanation of the phenomena shown by several substances, but is open to several serious objections. Firstly, the value for the magnetic moment required to secure the agreement of the calculated and the observed values is altogether different from that found from measurements on solutions by applying the CURIE formula, although this formula is the limiting expression for  $T = \infty$  according to REICHE'S theory. Secondly, the theory explains only the type of deviation from the WEISS law in which the "cryomagnetic anomaly" occurs and not the other types of deviation shown to exist in the present work. It may also be objected that no account is taken in the theory of the possible intramolecular actions, but REICHE himself acknowledges this and notices it as a point requiring improvement.

An almost identical theory was published almost at the same time as that of REICHE, but quite independently of the latter by ROTSZAJN.§

GANS|| has also published a theory of paramagnetism based on the quantum theory.

\* 'Ann. der Phys.,' vol. 54, p. 401 (1917).

† *Ibid.*, vol. 57, p. 376 (1918).

‡ *Ibid.*, vol. 51, p. 285 (1916).

§ 'Ann. der Phys.,' vol. 57, p. 81 (1918).

|| *Ibid.*, vol. 50, p. 163 (1916).

In this theory the mutual interactions of the molecules is allowed for, and the quantum theory is introduced by equating the mean energy of the molecule to

$$\frac{2h\nu}{e^{h\nu/kT} - 1},$$

the value given by the original PLANCK theory for an oscillator with two degrees of freedom. He then arrives at a formula which reproduces quite well the observations on platinum, the anhydrous and hydrated manganese sulphates, hydrated ferrous sulphate, anhydrous ferric sulphate, and liquid oxygen-nitrogen mixtures. It must be observed, however, that the method of the introduction of the quantum theory is not very satisfactory theoretically, and that the theory does not explain the newer types of deviation from the WEISS law at low temperatures.

In reviewing the present position of the theory of paramagnetism, it may be said that no satisfactory quantitative theory embracing all the known facts exists at present. Thus, though FOËX's theory explains the existence of the various types of deviation, it is in no wise quantitative, while the quantitative theories such as that of REICHE, which may be considered as fairly satisfactory theoretically, give no explanation of the other types of deviations from the WEISS law than that known as the "cryomagnetic anomaly."

#### PART II.—MEASUREMENTS OF THE PRINCIPAL SUSCEPTIBILITIES OF CRYSTALS.

Very few instances of trustworthy quantitative measurements of the magnetic properties of crystals are to be found in the literature and still fewer data on the temperature dependence of the principal susceptibilities. The first reliable measurements of the principal susceptibilities of crystals are those of VOIGT and KINOSHITA,\* who investigated a large number of minerals at atmospheric temperature. Their work was later extended by FINKE†, who determined the susceptibilities of a number of paramagnetic and diamagnetic crystals belonging principally to the monoclinic system.

Of the investigations of the temperature dependence of the magnetic properties of crystals we may note the work of LUTTEROTH.‡ This investigator determined the influence of the temperature on the differences of the susceptibilities of a number of paramagnetic and diamagnetic crystals in two mutually perpendicular planes. It was found that in every case the results could be represented by the linear relation

$$d_t = d_0 (1 + a t)$$

in which

$d_t$  = difference in susceptibility at temp.  $t$ ,

$d_0$  = difference in susceptibility at temp. 0,

$t$  = temperature in degrees Centigrade.

The range of temperature employed was from 0° C. to 50° C. The coefficient  $a$  was

\* 'Ann. der Phys.,' vol. 24, p. 492 (1907).

† *Ibid.*, vol. 31, p. 149 (1910).

‡ 'Wied. Ann.,' vol. 66, p. 1080 (1898).

found to be different for the different directions in the crystal, to be either positive or negative dependent on the class of crystal used, and to be dependent on the crystal symmetry since the  $a$ 's arranged themselves into groups corresponding to the crystallographic systems of the substances.

The first instance of the determination of the principal susceptibilities of a crystal over any extended range of temperature to be found in the literature is the measurement of siderose by FOËX.\* This substance is a naturally occurring ferrous carbonate containing appreciable quantities of the carbonates of manganese and the alkaline earth metals, belonging to the tetragonal system. The principal susceptibilities were determined between 87° K. and 400° K., with the following results. The graphs of the reciprocals of these quantities against the absolute temperature are, for moderately high temperatures, parallel straight lines, *i.e.*, each of the susceptibilities obeys the WEISS law  $\chi (T + \Delta) = C$  with the same CURIE constant  $C$ . Again, the  $\Delta$ 's in the above formula are of opposite sign for the two susceptibilities  $\chi_1$  and  $\chi_2$  ( $\chi_3 = \chi_2$  since the crystal is tetragonal), the actual values being  $\Delta_1 = -60^\circ$  and  $\Delta_2 = +103^\circ$ . Finally, the curves show deviations from the straight-line law at lower temperatures, and these deviations are in opposite directions in the cases of  $\chi_1$  and  $\chi_2$ .

### § 1. *Theory of the Method of Observation.*

Two methods present themselves as suitable for the determination of the principal susceptibilities of a crystal at different temperatures, *viz.* :—(1) the CURIE method†, in which the attraction on a small body placed in a non-homogeneous magnetic field at the position of the maximum of  $H \cdot dH/dx$  ( $x$  being the co-ordinate at right angles to the direction of the field) is measured and (2) the WEISS‡ method, in which the maximum couple exerted on a small cylinder of the crystal suspended in a homogeneous field is measured. The first method has the advantage that the observations give directly the value of the susceptibility of the crystal in a direction parallel to the  $x$  co-ordinate, whereas the second method gives only the difference of the susceptibilities in the plane perpendicular to the direction of suspension of the crystal cylinder. The CURIE method, however, presents considerably greater difficulties from the cryogenic point of view than the WEISS method, so that it was decided to apply the latter method to the present measurements.

For each crystal the three principal susceptibilities  $\chi_1, \chi_2, \chi_3$  have to be determined and, for all crystals not belonging to one of the rectangular crystal systems (regular or cubic, tetragonal and rhombic), also the angles defining the orientation of the magnetic axes with respect to the crystallographic axes. To determine these  $n$  unknowns

\* THÈSE, Strasbourg, 1921; 'Ann. de Physique,' vol. 16, p. 174 (1921).

† P. CURIE, 'J. de Phys.' (3), vol. 4, pp. 197 and 263 (1895); see also 'C. R.,' vol. 116, p. 136 (1893).

‡ P. WEISS, 'J. de Phys.' (4), vol. 6, p. 655 (1907); see also P. WEISS and H. KAMERLINGH ONNES, 'Leiden Comm.,' No. 114.



we must have, of course,  $n$  independent equations involving them. Of these  $n$  equations we may obtain  $n - 1$  equations by measuring the differences of susceptibilities of crystal sections orientated in  $n - 1$  different directions with respect to the crystallographic axes. The final equation must involve some absolute value of the susceptibilities in order to make it possible to calculate the values of the  $n$  unknowns, since the other  $n - 1$  equations involve only differences of susceptibility. This last requirement could not, of course, be obtained with the WEISS method, but it did not involve further measurements, since the value of the mean of the three principal susceptibilities of the crystals under consideration had already been determined by the measurements on the powders described in the previous section of the present work, and this quantity could be used in the calculations.

The theory underlying the WEISS method as applied to the measurements of the susceptibilities of crystals will now be given. Let  $\chi_1, \chi_2, \chi_3$  be the principal susceptibilities of the crystal. Then the formula for the induction ellipsoid gives immediately

$$\chi_1 X^2 + \chi_2 Y^2 + \chi_3 Z^2 = 1$$

Let  $a, b, c$  be the principal axes of the induction ellipsoid; then we have

$$\chi_1 = 1/a^2, \quad \chi_2 = 1/b^2, \quad \chi_3 = 1/c^2$$

The susceptibility  $\chi_r$  corresponding to a definite direction  $r$ , of which the direction cosines are  $\alpha, \beta, \gamma$ , is then given by

$$\frac{\alpha^2}{a^2} + \frac{\beta^2}{b^2} + \frac{\gamma^2}{c^2} = \frac{1}{r^2};$$

or

$$\chi_1 \alpha^2 + \chi_2 \beta^2 + \chi_3 \gamma^2 = \frac{1}{r^2} = \chi_r \dots \dots \dots (1)$$

Let the crystal now be brought into the magnetic field and let the direction  $r$  be parallel to the field; then the energy resulting from the introduction of the crystal into the field is equal to

$$E = \frac{1}{2} \chi_r H^2.$$

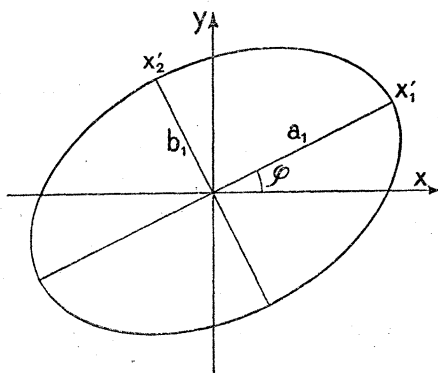


Fig. 4.

If now the crystal is suspended about a vertical axis and the magnetic field is in a horizontal plane, then the crystal will tend to turn into such a position that the energy is a minimum. In this connection only the susceptibilities, which lie in that ellipse, which is the section of the induction ellipsoid by the horizontal plane, are to be taken into consideration.

In fig. 4 let  $a$  and  $b$  be the axes of this ellipse, and  $\chi'_1$  and  $\chi'_2$  the corresponding susceptibilities. From considerations of symmetry it follows that equilibrium occurs



for  $r = a$  and  $r = b$ . For every other direction there occurs a couple, which is determined by

$$\frac{dE}{d\phi} = \frac{d(\frac{1}{2}\chi H^2)}{d\phi} \dots \dots \dots (2)$$

Since  $H$  is constant, this gives

$$\begin{aligned} \frac{d\chi}{d\phi} &= \frac{d\left(\frac{1}{r^2}\right)}{d\phi}; \quad \frac{1}{r^2} = \frac{\cos^2 \phi}{a^2} + \frac{\sin^2 \phi}{b^2}, \\ \frac{d\left(\frac{1}{r^2}\right)}{d\phi} &= \frac{-2 \cos \phi \sin \phi}{a^2} + \frac{2 \cos \phi \sin \phi}{b^2} \\ &= \sin 2\phi \left(\frac{1}{b^2} - \frac{1}{a^2}\right) = (\chi'_2 - \chi'_1) \sin 2\phi, \\ \frac{dE}{d\phi} &= \frac{1}{2} (\chi'_2 - \chi'_1) \cdot \sin 2\phi \cdot H^2 = \text{couple} = C. \dots \dots \dots (3) \end{aligned}$$

We will now describe how the susceptibilities along the principal magnetic axes and the positions of the latter for the two substances as yet investigated (nickel sulphate heptahydrate and cobalt ammonium sulphate) can be obtained by observations of the couple, whose value is given by equation (3). This couple is measured for various section plates cut in different and definitely known directions from the crystal.

We will consider first the case of nickel sulphate,  $\text{Ni SO}_4 \cdot 7 \text{H}_2\text{O}$ . As the heptahydrated form crystallizes in the rhombic system, the positions of the magnetic axes are fixed *a priori*, since they must be parallel to the crystallographic axes. We thus have to determine  $\chi_1, \chi_2, \chi_3$ . For this purpose we require two cylinders cut from the crystal in known directions. Nickel sulphate heptahydrate crystallizes in the form shown

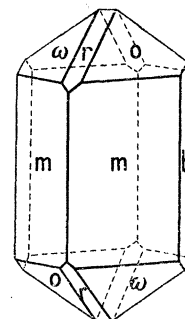


Fig. 5.

in fig. 5. The crystals are elongated along the direction of the crystallographic  $c$  axis and are also sometimes tabular parallel to the  $m$  face (110). It was therefore decided to cut the crystal sections in the following manner, viz.:—(1) axis of cylinder parallel to the  $c$  axis and (2) axis of cylinder perpendicular to the  $m$  face.

Then a measurement of the couple exerted on cylinder (1) will give the value of  $\chi_a - \chi_b = c$ , and the cylinder (2) will give  $\chi_c - \chi_m = m$ , where  $\chi_a, \chi_b, \chi_c, \chi_m$  are the susceptibilities parallel to the directions  $a, b, c, m$  respectively, *i.e.*, perpendicular to the planes (100), (010), (001), (110). Now  $\chi_a, \chi_b, \chi_c$  are respectively equal to  $\chi_1, \chi_2, \chi_3$  and  $\chi_m$  is given by

$$\chi_m = \chi_1 \cos^2 \phi + \chi_2 \sin^2 \phi \text{ (see fig. 6),}$$

in which  $\phi$  is equal to  $\tan^{-1}(b/a) = \tan^{-1}(1/0.9815) = 45^\circ 32'$ .\*

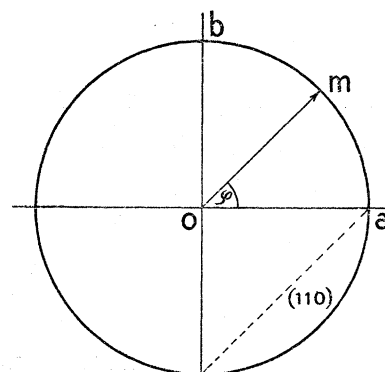


Fig. 6.

\* See GROTH, 'Chem. Kryst.,' vol. 2, p. 434.

Rewriting the above relations and adding the value of the mean susceptibilities derived from the measurements on the powdered material, we have the following equations from which to determine  $\chi_1$ ,  $\chi_2$  and  $\chi_3$ .

$$\chi_1 - \chi_2 = c \quad \dots \quad (1)$$

$$\chi_3 - (\chi_1 \cos^2 \phi + \chi_2 \sin^2 \phi) = m \quad \dots \quad (2)$$

$$\chi_1 + \chi_2 + \chi_3 = 3a \quad \dots \quad (3)$$

Solving these equations, we find for the principal susceptibilities the following values:—

$$\left. \begin{aligned} \chi_1 &= 1/3 (3a + 2c - m - c \cos^2 \phi). \\ \chi_2 &= 1/3 (3a - c - m - c \cos^2 \phi) \\ \chi_3 &= 1/3 (3a - c + 2m + 2c \cos^2 \phi). \end{aligned} \right\} \dots \quad (4)$$

*Cobalt ammonium sulphate*:  $\text{CoSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ .—This substance belongs crystallographically to the monoclinic system. In such a system we only know *a priori* that one of the magnetic axes, let us say  $\chi_3$ , lies along the direction of the symmetry axis of the crystal, *i.e.*, the *b* axis, and that the other two magnetic axes lie in the symmetry plane, *i.e.*, the plane containing the crystallographic *a* and *c* axes. We have thus to determine the positions of the magnetic axes in the symmetry plane in addition to the values of the principal susceptibilities. For the former purpose it will be sufficient to determine the angle  $\psi$ , which  $\chi_1$ , the axis of greatest susceptibility, makes with the *c* axis (see fig. 7).\*

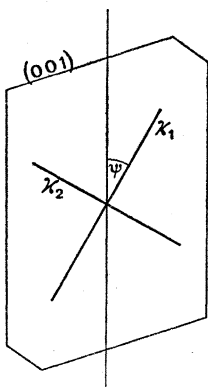


Fig. 7.

Cylinders were ground from the crystal with their axes respectively perpendicular to the planes (100), (010), (001). Then measurements of the couples exerted on these crystal cylinders will give the values of

$$(1) \chi_3 - \chi_c = a;$$

$$(2) \chi_3 - \chi_a = b;$$

$$(3) \chi_1 - \chi_2 = c.$$

From these quantities and adding the value of the mean susceptibility derived from measurements with the powdered material, we obtain the following equations for  $\chi_1$ ,  $\chi_2$ ,  $\chi_3$ , and  $\psi$ .

$$\chi_3 - (\chi_1 \cos^2 \psi + \chi_2 \sin^2 \psi) = a \quad \dots \quad (1)$$

$$\chi_3 - (\chi_1 \cos^2 (\psi + \beta) + \chi_2 \sin^2 (\psi + \beta)) = b \quad \dots \quad (2)$$

$$\chi_1 - \chi_2 = c \quad \dots \quad (3)$$

$$\chi_1 + \chi_2 + \chi_3 = 3m \quad \dots \quad (4)$$

in which  $\beta$  is the known crystallographic angle between the *a* and *c* axes.

\* This mode of defining the positions of the magnetic axes is adopted so that the results may be directly comparable with those of FINKE, *loc. cit.*

From (1) with (3) and (4) we obtain

$$\chi_3 - c \cos^2 \psi - \chi_2 = a;$$

and from (2)

$$\chi_3 - c \cos^2 (\psi + \beta) - \chi_2 = b.$$

Subtracting we have

$$c \{ \cos^2 (\psi + \beta) - \cos^2 \psi \} = a - b$$

This may be transformed into

$$c \{ (l \cos \psi - n \sin \psi)^2 - \cos^2 \psi \} = a - b,$$

in which

$$l = \cos \beta, \quad n = \sin \beta, \quad l^2 + n^2 = 1.$$

From this we obtain

$$\{ (l^2 - n^2 - 1) \cos^2 \psi - 2ln \cos \psi \sqrt{1 - \cos^2 \psi} \} \\ = (a - b)/c - n^2 = k.$$

$$4l^2n^2 \cos^2 \psi (1 - \cos^2 \psi) = k^2 + 4n^4 \cos^4 \psi \\ + 4n^2k \cos^2 \psi.$$

Solving for  $\cos^2 \psi$  we find

$$\cos^2 \psi = \frac{(l^2n^2 - n^2k) \pm \sqrt{\{(l^2n^2 - n^2k)^2 - (n^4 - l^2n^2)k^2\}}}{2(n^4 + l^2n^2)}.$$

Treating  $\psi$  now as known we obtain from equations (1), (3) and (4)

$$\left. \begin{aligned} \chi_1 &= \frac{1}{3} (3m + 2c - a - c \cos^2 \psi) \\ \chi_2 &= \frac{1}{3} (3m - c - a - c \cos^2 \psi) \\ \chi_3 &= \frac{1}{3} (3m - c + 2a + 2c \cos^2 \psi) \end{aligned} \right\} \quad (5)$$

*Apparatus and Materials.*—The apparatus,\* by means of which the method theoretically described in the previous pages was applied to the measurement of the principal susceptibilities of crystals at low temperatures, will now be described. As it was necessary to shut off from the air the space in which the crystal was suspended and which also contained the liquefied gas and its vapour, a fairly complicated cryogenic apparatus had to be employed. This is shown in section in fig. 8. It consists principally of three tubular portions

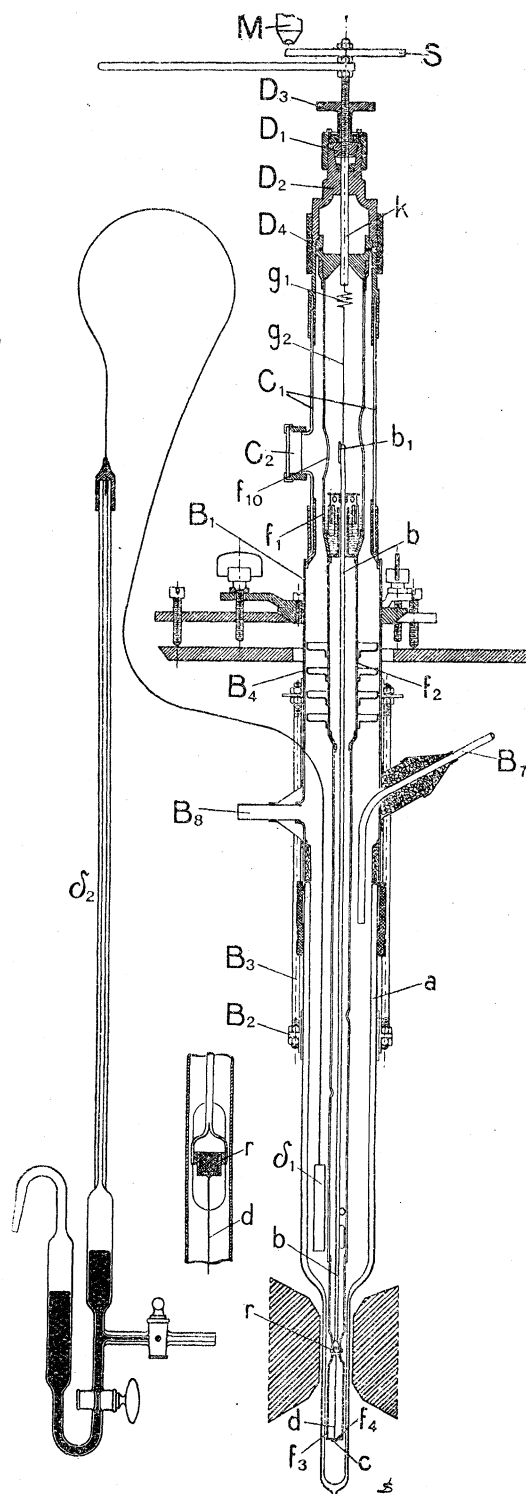


Fig. 8.

\* The apparatus is, in fact, the one referred to "depending on the use of couples *b*, apparatus for crystals (to be constructed)" in 'Leiden Comm.,' No. 139A, p. 6, in which the programme of the laboratory as regards magnetic researches is outlined.

which, naming from the outside inwards, we may call the *cover*, the *adjusting tube*  $f$  and the *holder*  $b$ . The cover consists of a silvered vacuum tube  $a$ , a brass tube B, a glass tube C, and a cap D, which closes the apparatus.

The crystal holder  $b$  is made from a long thin brass tube  $bb$ . At the lower end of this tube a copper ring  $r$  is fastened. A small copper cylindrical cup fits into this ring with considerable friction and holds the crystal, which is fastened into the cup with the smallest possible amount of wax or Canada balsam. The whole holder is very light and is constructed of practically non-magnetic material, in order to make the corrections which must be applied to the observations for the inherent magnetism of the apparatus as small as possible. The holder is connected to the rod  $k$  by the wire  $g_2$ , and the spring  $g_1$ . In order to make the equilibrium of the suspended system stable and to prevent the crystal from being attracted to the poles of the magnet the holder is held fast underneath by a thin wire  $d$ , fastened to a small projection on the lower side of the crystal holder; the other end of this wire is held in place by a small cone of brass which fits into a hole in the bottom of the adjusting tube. By means of the spring  $g_1$  a small tension can be put on the wires  $g_2$  and  $d$  without risk of breaking them. For this purpose the spring  $g_1$  is so constructed that it can be easily elongated in the direction of  $g_2$ , but serves, with all the accuracy necessary, as an immovable connection as far as torsion is concerned.

The turning of the crystal in the magnetic field is brought by the tube  $bb$  to the mirror  $b_1$ , by means of which the deflections of the crystal holder can be read through the opening  $f_{10}$  and the window  $C_2$  on a glass scale divided into millimetres, placed at 2·2 metres distance and illuminated by means of spherical mirror strips.

The tension on the wires can be regulated by the rod  $k$  which passes through the packing-gland  $D_1$  in the cap  $D_2$ . The rod  $k$  may be moved up and down by turning the nut  $D_3$  and at the same time preventing the rotation of  $k$ .

As the holder is very light and under tension, it has a great tendency to vibrate under the influence of small shocks. In some preliminary experiments this tendency was found to be so great as to make it impossible to read the scale when machinery was in motion in the building. A damping arrangement, similar to that used by KAMERLINGH ONNES and PERRIER\*, was therefore attached to the upper end of the tube  $bb$ . It consists of a small cylinder to which are attached four vanes which dip into an annular oil-bath. The vanes must be entirely immersed in the oil in order to prevent the occurrence of capillary actions, which lead to couples on the suspended system which are not negligible. As WEISS and KAMERLINGH ONNES† have observed, it is also necessary to free the oil from all volatile substances and to prevent the occurrence of bubbles of air under the oil, since the apparatus has to be evacuated after it has been completely mounted. With this damping arrangement (supplemented in strong magnetic fields by the damping

\* 'Leiden Communication,' No. 116.

† *Ibid.*, No. 114, p. 20.



due to the Foucault currents induced in the well conducting holder), the deflections of the suspended system were easily and accurately readable.

The whole holder and the wires hang in the adjusting tube  $f$ , the upper end of which is screwed to the cap  $D_2$ , which also carries the rod  $k$  and itself rests on the glass tube  $C_1$ . The cross-section of the adjusting tube, which consists of three parts  $f_1 - f_3$ , decreases three times; the narrowest lower part  $f_3$  surrounds the crystal holder as closely as possible. Against the bottom  $f_4$  rests the small cone  $c$ , to which the lower wire  $d$  is soldered and which serves to maintain the tension on the suspended system. A small slot in the bottom allows the small cone to be placed in position. In order to mount the adjusting tube, already containing the crystal holder, in position in the cover, the cap  $D_2$  is fitted into the bronze ring, which is fastened to the glass tube  $C_1$  of the cover, and the joint is made air-tight by means of the rubber ring  $D_4$ . This latter is smeared with rubber solution and bound tight with wire. The lower end of the glass tube  $C_1$  is fastened to a second tube  $B_1$  of the cover, the middle part of which carries a ring, in which the rods  $B_3$  holding the vacuum glass terminate.

The Dewar glass itself consists of a lower narrow part, which is completely silvered, and an upper wider part, which is silvered as far as  $a$ ; the upper part is left transparent so that it may be possible to ascertain that too much of the liquefied gas is not allowed to enter the vacuum-glass. The latter fits into the brass tube  $B_1$  and is protected by a wooden ring. The rods  $B_3$  hold the glass in its place and at such a height that it is just free of the wooden ring. The connection between the vacuum-glass and the cover is made air-tight by means of a rubber ring, smeared with rubber solution and fastened with copper wires. The upper part of the vacuum-glass has an outer diameter of 4.9 cm. and an inner diameter of 3.8 cm.; the lower part has an outer diameter of 1.85 cm. and an inner diameter of 1.45 cm.

Into the tube  $B_1$  is soldered the steel capillary of a helium thermometer with a german-silver reservoir  $\delta_1$  and a glass stem  $\delta_2$ . The quantity of helium is so chosen that at the boiling point of nitrogen the mercury stands at a mark in the lower portion of the stem and at the melting point of hydrogen at one in the upper portion. The thermometer is not used to measure the temperature of the liquefied gas, but to indicate the level of the latter in the vacuum-glass. As soon as the level sinks below the upper end of the reservoir of the thermometer, the mercury sinks in the stem  $\delta_2$ .

The liquefied gas is introduced into the apparatus through the german-silver tube  $B_7$ . The gas formed by evaporation escapes through  $B_8$  and through valves to a gas-holder or to a vacuum pump. By means of the valves the vapour pressure is regulated and its value is read off on a manometer. Before introducing the liquefied gas through the tube  $B_7$ , which is closed by a rubber tube with a glass stopper, the air is pumped out of the apparatus through  $B_8$ .

To prevent the cooling of the upper portion of the apparatus containing the torsion wire by the escaping vapours, a number of large openings are made in the tube  $f_3$  arranged in such a way that its resistance to torsion is not impaired. In addition to this, copper



baffle-plates surrounding  $f_2$  and soldered to  $B_3$  are arranged so that the tube can move with slight friction in them. The refilling of the apparatus with liquefied gas takes place in the same manner as the first filling. Generally, several series of observations can be carried out with a single filling.

*The Electromagnet.*—This is the same as was used in the measurements of the susceptibilities of the powders described in the previous section of this work. It was mounted on a turntable so that it could be rotated into any position about a vertical axis. The azimuth of the magnet, and hence the direction of the magnetic field, can be read on a circular scale, divided into degrees and attached to the turntable. The pole distance used in the present measurements was 30 mm.

*The Crystals.*—The crystals, from which the cylindrical sections used in the measurements were ground, were prepared by the slow evaporation of a saturated solution at atmospheric temperature, according to the method described by TUTTON ('Crystallography and Practical Crystal Measurement,' Part. I, p. 14). By this means large crystals of excellent quality can easily be obtained. The best crystals in a number of crops were chosen and employed in preparing the sections. Small cylinders had then to be ground from the crystals in such a way that the axes of the cylinders were orientated in known directions with regard to the crystallographic axes. As the accuracy, with which the measurements could be made with the cryomagnetic apparatus, was of the order one per cent., it was not thought necessary to employ an accurate grinding goniometer for the preparation of the crystal sections. A crystal was mounted on the end of a brass rod in such a manner that the direction in the crystal, in which the cylinder axis was to lie, was coaxial with the rod. This adjustment could be made with all the accuracy that was necessary in the present case by taking advantage of the well-developed faces of the crystal. The rod was then mounted in a lathe and the crystal carefully ground to a circular shape with fine emery. The crystal was then removed from the rod and the ends ground flat perpendicular to the length of the cylinder. No attempt was made to polish the cylinder, as this was quite unnecessary for the present purpose, and as the use of the usual polishing materials, since they themselves possess strongly magnetic properties, would render the measurements doubtful or even useless.

*Method of Observation.*—The course of the observations is very simple when once the apparatus has been set up in order. We have to determine the maximum value of the couple exerted on the crystal by the magnetic field. This couple is, by theory, connected with the azimuth of the magnetic field by the relation

$$C = 1/2 \cdot (\chi_1 - \chi_2) \cdot m \cdot H^2 \cdot \sin 2\theta.$$

in which  $\theta$  is the angle between one of the magnetic axes  $\chi_1$  or  $\chi_2$  and the direction of the field. The couple should then have a maximum value corresponding to the value of  $45^\circ$  of  $\theta$ , and hence as the azimuth of the magnet is turned through  $360^\circ$  we should obtain four positions of maximum value of the couple distant  $90^\circ$  from one another. A test of the accurate working of the apparatus and of the magnitude of the corrections

to be applied to the actual readings may thus be made by measuring the couple exerted on the crystal for a number of azimuths of the magnet and comparing the resultant curve connecting the observations with a true sine curve. Such an example is given in the next section.

As, however, it is the maximum value of the couple that is required, this maximum may be determined directly and not by interpolation on the experimental curve obtained connecting the magnitude of the couple and the azimuth of the magnetic field. Those azimuths of the electromagnet are first determined tentatively, for which the couple is a maximum on either side of the zero. It is sufficient to perform these trials two or three times with a suitably chosen field strength, since the azimuth of the maximum couple changes but little with the field, and for other values of the field we can, without risk of error, have recourse to interpolation. These positions of the magnet can be determined quite easily to within  $0^{\circ}\cdot 5$  or  $1^{\circ}$ , which is sufficiently accurate, as the value of the couple changes but little with the azimuth in the immediate neighbourhood of the maximum.

After this has been effected, the observations are taken in the following manner. The magnet is set in one of the positions of maximum couple, the current through the coils is switched on and adjusted to a definite value. Before any readings are taken, however, the current is reversed several times to ensure a well-defined field, for, as a couple proportional to the square of the field has to be measured, any inaccuracies in the value of the field strength, which might be obtained notwithstanding the fact that the iron of the electromagnet core was extremely soft, would have considerable influence on the results. Having adjusted the current finally to a definite amount, the value of the couple was estimated as given below; the current was then reversed and the couple determined again. The same observations were then repeated with the magnet in one of the other positions of maximum couple. The whole process was carried out every time for a whole series of different values of the field strength.

*Measurement of Couple.*—When small values of the field strength were employed at atmospheric temperatures, the deflection of the suspended system was generally of such a magnitude as to be accurately readable on the scale. In this case, then, the couple was estimated by measuring the deflection, both torsion wires thus contributing to the opposing torsional couple. For greater values of the field, however, and for the lower temperatures at which the susceptibilities of the crystals are much greater, the deflection of the suspended system was too great to be read on the scale. The constant of the suspension wires had been purposely chosen so that this might occur and hence make possible the application of the method of observation now to be described.

When working at the low temperatures obtainable with the various liquefied gases, the upper part of the apparatus, on account of the presence of the baffle-plates at  $f_3$ , remains throughout at atmospheric temperature; hence of the two wires  $g_2$  and  $d$ ,  $g_2$  is always at atmospheric temperature and  $d$  takes up the temperature of the bath. If, therefore, both wires were used in the observations at low temperatures by allowing

the suspended system to be deflected, we should require a knowledge of the elastic properties of the wire at the low temperatures, so that a correction might be applied to the value of the constant of the wire for its change with temperature. This, however, may be eliminated by the following procedure.

After the current in the magnet has been switched on and the suspended system has suffered a deflection, the graduated head S attached to the top of the rod  $k$  is turned until the suspended system returns to nearly its original position in the absence of the magnetic field as shown by the scale and telescope. The angle through which the torsion head has been turned is then read by means of the small reading microscope M. No attempt is made to bring the crystal holder exactly into its original position, but the torsion head is turned through an exact number of divisions of the scale engraved on S, until the deflection has been reduced to not more than one or two centimetres on the glass scale. This was done because the accuracy with which the deflections could be read was thereby much increased, for, as the scale on the torsion head was not very finely divided, readings obtained by estimating parts of a division might contain considerable errors. Then the value of the couple could be obtained as follows. Let  $2\alpha$  be the angle through which the torsion head had to be turned,  $x_1 - x_2$  the difference in scale readings respectively in the presence and in the absence of the magnetic field,  $d$  the distance of the scale from the mirror on the suspended system, and  $C_1$  and  $C_2$  the constants of the upper wire and the combined upper and lower wires respectively (both being the values corresponding to ordinary temperatures). Then the couple exerted on the crystal is given by

$$C_1\alpha + C_2 \tan^{-1}\left(\frac{x_1 - x_2}{2d}\right), \dots \dots \dots (1)$$

which was used for the calculations in the form

$$C_1 \left\{ \alpha + \left(\frac{l_1 + l_2}{l_1}\right) \tan^{-1}\left(\frac{x_1 - x_2}{2d}\right) \right\} \dots \dots \dots (1A)$$

in which  $l_1$  and  $l_2$  are the lengths of the upper and lower suspension wires respectively.

In employing (1) (actually in the form (1A)) to calculate the couples obtained at low temperatures, it will be noticed that the value  $C_2$  of the constant of the suspensions wires used is actually the value holding at atmospheric temperatures, although the lower wire, which contributes a part of the couple, is at the low temperature. This is permissible, as it was found that the correction to be applied on account of the low temperature of the lower wire was small and was well within the limits of the experimental error.

*Measurement of Temperature.*—For the low temperatures this was carried out as described above in Part I (p. 4), by determining the pressure under which the particular liquefied gas was boiling at the time of the experiment.

*Measurement of Magnetic Field.*—The field was as before characterized by the strength

of the current in the coils of the electromagnet, reference then being made to a table of field strengths compiled as a result of previous calibrations.

*Sources of Error and Corrections.*—We will now examine the sources of error incidental to the method of experiment and any corrections which must be applied to the actual readings. As possible sources of uncertainty we may note

- (1) Inhomogeneity of the field.
- (2) Influence of the crystal holder.
- (3) Asymmetries in the apparatus and its mounting.

We will deal with these in turn.

(1) An inhomogeneity of the magnetic field will bring with it an additional couple dependent on the lack of homogeneity of the field in a plane perpendicular to the axis of suspension of the crystal. As the inhomogeneity in the present case was such that the change of the field strength over a volume of one cubic centimetre did not amount to more than one part in a thousand, the correction to be applied to the observations fell within the limits of accuracy of the experiments and hence might be neglected.

(2) Although the crystal holder was made of material which was free from ferromagnetic substances and was but weakly magnetic itself, the apparatus showed certain deflections when mounted precisely as when the actual observations were taken, but without any crystal in the holder. At atmospheric temperatures these deflections were systematic, but quite small; so that a small correction could be applied to the observations, to allow for the effect of the holder itself. At low temperatures, however, the deflections due to the holder itself were quite unsystematic, being on opposite sides of the zero for opposite directions of the current in the magnetic coils for the same position of the magnet and were not proportional to the square of the field. The effect was thus to bring in certain (small) asymmetries into the readings at low temperatures. It was, however, found that the effect on the results of these asymmetries could be eliminated by employing the method of observation previously described.

(3) Asymmetries in the apparatus and in its mounting also cause asymmetries in the deflections, which are also eliminated by the method of observation.

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## OBSERVATIONS AND RESULTS.

### § 1. *Observations.*

*Calibration of Torsion Wires.*—The torsion wires were calibrated in the following manner. A small metal body of suitable moment of inertia was attached to an accurately measured length of wire cut from the same reel as that used for the torsion wires. The system was then suspended from the free end of the wire and caused to perform torsional oscillations, the period of which was then determined. A body of known moment of inertia in the shape of a ring was then added to the system and the period of the torsional oscillations again determined. The constant of the wire per unit length per radian angular displacement was then calculated from the above-mentioned data by the aid of the well-



known formula. The process was repeated for a number of lengths of the wire and in this manner its uniformity was tested. The wire was found to be satisfactorily uniform, so that the mean value of the constant of the wire derived from the above determinations could safely be used in calculating the value of the constant of the actual torsion wires of the apparatus. The mean value thus found was  $D = 414.7$ .

*Preliminary Test of Apparatus.*—In order to test the good working of the apparatus when set up in the usual manner, a crystal was mounted and the deflections determined as a function of the azimuth of the magnet for a number of field strengths. The theory indicates that the observations should lie on a sine curve. An examination of the results showed that the theory and observation were in satisfactory agreement, and hence that the apparatus was working well. An example of such a series of observations selected at random is given below.

*Cobalt Ammonium Sulphate. Crystal c.*—Mass of crystal = 0.1250 gm. Temperature =  $16^{\circ}.0$  C. Length of upper wire = 8.5 cm. Pole distance = 21.4 mm. Length of lower wire = 5.52 cm. Current in magnet coils = 4 amps. Distance of mirror from scale = 227 cm.

Magnet.	Scale readings.			
	Current off.	On direct.	Off.	On reverse.
90	38.65	37.62	38.68	37.70
80	38.66	38.70	38.80	38.70
70	38.80	39.50	38.75	39.51
60	38.80	40.35	38.80	40.30
50	38.80	40.90	38.80	40.85
40	38.80	41.15	38.80	41.10
30	38.70	40.89	38.70	40.70
20	38.73	40.45	38.70	40.50
10	38.40	40.22	38.53	40.35
0	38.53	39.60	38.53	39.43
350	38.30	38.75	38.30	38.68
340	38.20	37.80	38.10	37.70
330	38.16	36.86	37.95	36.95
320	37.90	35.90	38.00	35.91
310	38.00	35.70	37.95	35.75
300	38.00	35.70	38.00	35.35
290	38.10	35.50	38.10	35.62
280	38.20	36.10	38.10	36.00
270	38.16	36.93	38.04	36.87
260	38.10	37.92	38.10	37.89
250	38.10	38.70	38.20	38.80
240	38.20	39.70	38.30	39.75
230	38.20	40.35	38.20	40.40
220	38.20	40.80	38.20	40.78
210	38.25	40.70	38.20	40.80
200	38.40	40.80	38.30	40.50
190	38.40	40.38	38.40	40.30
180	38.40	39.80	38.40	39.70



The numbers under the heading "magnet" denote the positions of the magnet in degrees as shown on the scale attached to the turntable. The figures in the other columns denote the readings of the glass scale expressed in centimetres. The observations are exhibited graphically in fig. 9.

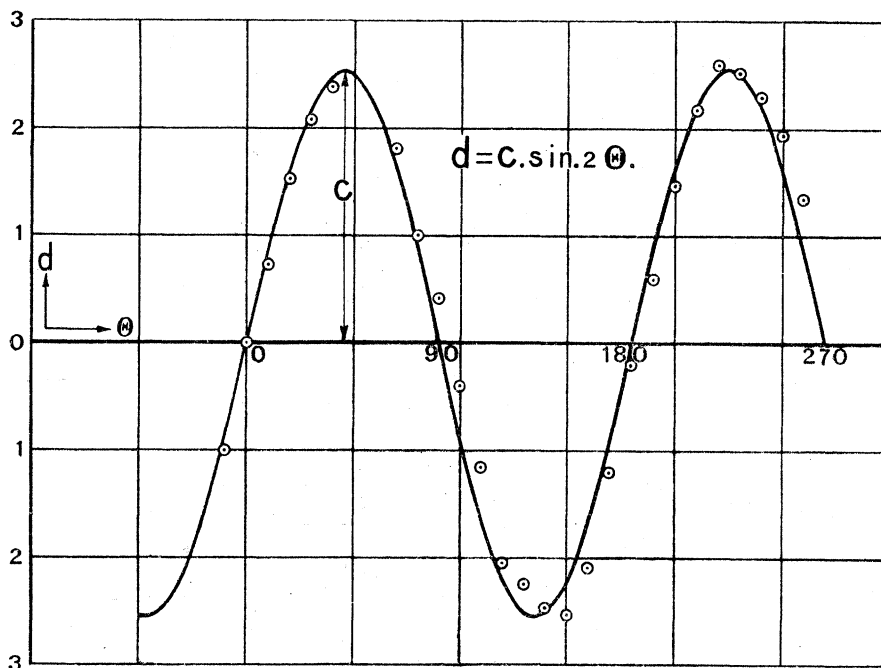


Fig. 9.

*Specimen Set of Observations.*—The set of observations given below may serve as a specimen of the results obtained in the measurements.

*Cobalt Ammonium Sulphate.*—Crystal  $c_2$  (crystal cut with axis of cylinder perpendicular to  $c$  face). Mass of crystal = 0.087 gm. Distance of mirror from scale = 220.7 cm. Length of upper torsion wire = 8.37 cm. Length of lower torsion wire = 5.90 cm. Pole distance = 30 mm.

Measurements in liquid nitrogen at 756.2 mm. pressure.

Hence temperature = 77° 3 K. Zero at 125 and 43.5 cm.

Magnet.	Readings.
°	Magnet current = 8 amps.
13.0	(l) 116 and 46.68 cm.
	(h) 116 and 42.80 cm.
283.0	(h) 134 and 35.80 cm.
	(l) 134 and 40.50 cm.
	Magnet current = 10 amps.
283.0	(l) 141 and 41.10 cm.
	(h) 141 and 54.50 cm.
13.0	(h) 109 and 35.5 cm.
	(l) 109 and 35.7 cm.

Zero after experiments = 125 and 43.3 cm.

Further observations = data as before.

Zero at 125 and 43·1 cm.

Magnet	Readings.
13·0	Magnet current = 14 amps. ( <i>l</i> ) 96·1 and 40·8 cm. ( <i>h</i> ) 96·1 and 37·4 cm. ( <i>h</i> ) 96 and 36·5 cm.
283·0	(repeated at end of experiment) ( <i>h</i> ) 154·0 and 48·2 cm. ( <i>l</i> ) 154·0 and 53·6 cm.
283·0	Magnet current = 12 amps. ( <i>l</i> ) 146·0 and 41·3 cm. ( <i>h</i> ) 146·0 and 45·2 cm.
13·0	( <i>h</i> ) 102·0 and 38·1 cm. ( <i>l</i> ) 102·0 and 29·4 cm.
13·0	(last observations repeated) ( <i>h</i> ) 102·0 and 34·3 cm. ( <i>l</i> ) 102·0 and 29·3 cm.
13·0	Magnet current = 10 amps. ( <i>l</i> ) 110·0 and 45·2 cm. ( <i>h</i> ) 110·0 and 39·9 cm.
283·0	( <i>h</i> ) 140·0 and 47·5 cm. ( <i>l</i> ) 140·0 and 46·6 cm.
283·0	Magnet current = 8 amps. ( <i>l</i> ) 135·0 and 46·5 cm. ( <i>h</i> ) 135·0 and 51·0 cm.
13·0	( <i>h</i> ) 114·0 and 35·7 cm. ( <i>l</i> ) 114·0 and 37·0 cm.

The figures in the first column under the heading "Readings" denote the readings on the scale attached to the torsion head; the numbers followed by "cm." denote the readings on the glass scale expressed in centimetres. The letters *l* and *h* in brackets indicate the positions low and high of the reversing switch and hence the directions of the current in the magnet coil.

From the above data we may calculate, first, the angles corresponding to the difference in scale readings and, secondly, the values of the deflections, *i.e.*, the quantities which, when multiplied by  $C_1$  (see (1a), p. 30), give the values of the couple acting on the crystal.

Angles from scale readings.

Current.	Angle.			
8 amps.	(1) 0·825,	(2) 0·182,	(3) 2·154,	(4) 0·779.
10 amps.	(1) 0·629,	(2) 2·850,	(3) 2·077,	(4) 2·026.
14 amps.	(1) 0·596,	(2) 1·480,	(3) 1·323,	(4) 2·710.
12 amps.	(1) 0·467,	(2) 0·535,	(3) 1·298,	(4) 1·932.
10 amps.	(1) 0·535,	(2) 0·830,	(3a) 2·284,	(4a) 3·580.
8 amps.	(1) 0·895,	(2) 2·048,	(3) 1·141,	(4) 0·908.
			(3) 1·905,	(4) 1·584.

## Angles from scale readings (continued).

Current.	Deflections.			
8 amps.	(1) 19·996,	(2) 17·560,	(3) 21·211,	(4) 17·881.
10 amps.	(1) 33·523,	(2) 25·106,	(3) 26·977,	(4) 27·098.
14 amps.	(1) 56·325,	(2) 54·106,	(3) 54·800,	(4) 51·446.
		(2a) 53·856		
12 amps.	(1) 43·130,	(2) 40·705,	(3) 42·860,	(4) 41·326.
			(3a) 40·475,	(4a) 37·340.
10 amps.	(1) 31·294,	(2) 27·993,	(3) 27·238,	(4) 27·803.
8 amps.	(1) 17·834,	(2) 15·158,	(3) 17·393,	(4) 18·169.

From the above data we can calculate the values of the differences of susceptibility as given by the various series of observations. The results of the calculation are given below.

Magnet Current.	Difference of susceptibility.
8 amps.	$11·34 \times 10^{-6}$
10 amps.	$10·67 \times 10^{-6}$
14 amps.	$10·54 \times 10^{-6}$
	mean = $10·73 \times 10^{-6}$
12 amps.	$10·85 \times 10^{-6}$
10 amps.	$10·84 \times 10^{-6}$
8 amps.	$10·16 \times 10^{-6}$

*Final Observations.*—In the present section are given the final observations of the differences of susceptibility of the crystal sections of cobalt ammonium sulphate and nickel sulphate at the different temperatures investigated. The figures are throughout mean values derived from observations with various field strengths, no systematic dependence of the differences of susceptibility on the field strength being observed.

*Cobalt Ammonium Sulphate.*I. *Crystal c* — axis perpendicular to (001) plane.

Temperature.	Difference of susceptibility.
290·0	$1·11 \times 10^{-6}$
77·2	$10·7 \times 10^{-6}$
20·3	$46·8 \times 10^{-6}$
16·7	$56·8 \times 10^{-6}$
14·5	$65·7 \times 10^{-6}$

II. *Crystal a* — axis perpendicular to (100) plane.

Temperature.	Difference of susceptibility.
280.5	$0.403 \times 10^{-6}$
77.18	$1.88 \times 10^{-6}$
20.33	$9.59 \times 10^{-6}$
16.75	$12.10 \times 10^{-6}$
14.8	$14.07 \times 10^{-6}$

III. *Crystal b* — axis perpendicular to (010) plane.

Temperature.	Difference of susceptibility.
289.7	$3.88 \times 10^{-6}$
77.4	$32.5 \times 10^{-6}$
20.3	$121.0 \times 10^{-6}$
17.0	$153.8 \times 10^{-6}$
14.6	$170.9 \times 10^{-6}$

*Nickel Sulphate Heptahydrate.*—The final results for one of the crystal sections of nickel sulphate are given below in full as an example of the measurements on this crystal.

*Crystal c.*

Temperature.	Magnet Current.	Difference of susceptibility.
287.5	10 amps.	$1.36 \times 10^{-7}$
	12 amps.	$1.29 \times 10^{-7}$
	14 amps.	$1.28 \times 10^{-7}$
		} mean = $1.29 \times 10^{-7}$
169.5	14 amps.	$5.79 \times 10^{-7}$
	16 amps.	$5.77 \times 10^{-7}$
		} mean = $5.78 \times 10^{-7}$
77.2	14 amps.	$1.65 \times 10^{-6}$
	16 amps.	$1.70 \times 10^{-6}$
	12 amps.	$1.72 \times 10^{-6}$
		} mean = $1.69 \times 10^{-6}$
65.6	14 amps.	$2.28 \times 10^{-6}$
	16 amps.	$2.20 \times 10^{-6}$
	12 amps.	$2.22 \times 10^{-6}$
		} mean = $2.23 \times 10^{-6}$
20.43	10 amps.	$12.04 \times 10^{-6}$
	12 amps.	$12.26 \times 10^{-6}$
	14 amps.	$12.26 \times 10^{-6}$
		} mean = $12.18 \times 10^{-6}$
17.07	10 amps.	$16.47 \times 10^{-6}$
	12 amps.	$17.02 \times 10^{-6}$
	14 amps.	$16.96 \times 10^{-6}$
		} mean = $16.81 \times 10^{-6}$
14.65	10 amps.	$21.29 \times 10^{-6}$
	12 amps.	$21.71 \times 10^{-6}$
		} mean = $21.50 \times 10^{-6}$

With the other crystal section of nickel sulphate heptahydrate the noteworthy result was obtained that the difference of susceptibility decreased with fall in temperature instead of increasing as is the case with the other crystal sections. This result is in agreement with the observations of LUTTEROTH\*. The final values for this crystal section are given below.

*Crystal m.*

Temperature.	Difference of susceptibility.
289.0	$3.1 \times 10^{-8}$
169.5	$2.6 \times 10^{-8}$
77.29	$2.2 \times 10^{-8}$
64.5	$2.1 \times 10^{-8}$
20.33	$2.0 \times 10^{-8}$
16.65	$2.0 \times 10^{-8}$
14.6	$1.95 \times 10^{-8}$

### § 2. Final Results.

*Cobalt Ammonium Sulphate.*—From the observations given in the previous section we may draw graphs, and with their aid read off a series of values of  $a$ ,  $b$  and  $c$  (see pages 35 and 36) in the immediate neighbourhood of the observations. The following are the values of  $a$ ,  $b$  and  $c$  finally adopted in the calculation of the principal susceptibilities.

T	$a \times 10^6$	$b \times 10^6$	$c \times 10^6$
°			
290.0	0.40	1.11	3.88
77.2	1.89	10.7	32.6
20.3	9.60	46.8	121.0
16.7	12.1 <sub>5</sub>	56.8	154.0
14.5	14.2	65.7 <sub>5</sub>	175.0

From the above data we may next calculate the values of  $\psi$ .  $\psi$  is, however, to be determined from the roots of a quadratic equation involving  $\cos^2 \psi$ . We thus obtain the following two series of alternative values for  $\cos^2 \psi$ .

T	$\cos^2 \psi$ .
°	
290.0	0.7340 or 0.4490
77.2	0.7756 or 0.4949
20.3	0.7920 or 0.5156
16.7	0.7843 or 0.5052
14.5	0.7845 or 0.5090

\* *Loc. cit.*



A calculation enables us to distinguish the applicable and inapplicable values (positive or negative) of the square roots to be used to determine  $\cos \psi$  and hence  $\psi$ . We thus arrive at two alternative values for the angle, viz.: about  $27^\circ 40'$  and  $135^\circ 31'$ . As the first value is in good agreement with the value  $27^\circ 31'$  given by FINKE\*, this value has been used in the further calculation of the results.

Then calculating the principal susceptibilities from the expressions (5) on page 25 we obtain the following final values for these quantities†:—

T	$\chi_1 \times 10^6$	$\chi_2 \times 10^6$	$\chi_3 \times 10^6$	$\chi_m \times 10^6$	$\psi$
°					
290·0	26·1	21·9	25·5	24·6	$31^\circ 18'$
77·2	91·2	58·6	85·6	78·5	$28^\circ 17'$
20·3	286·5	165·5	277·0	241·0	$27^\circ 8'$
16·7	346·0	192·0	325·0	288·0	$27^\circ 41'$
14·5	388·0	213·0	365·0	322·0	$27^\circ 40'$

It will be seen that with the exception of the value at atmospheric temperature, for which the precision of the determination is necessarily small, the values of  $\psi$  are fairly constant, showing that the magnetic axes preserve their orientation with regard to the crystallographic axes down to the lowest temperature investigated.

In the following table are given the values of the molecular susceptibilities:—

T	$\chi_{1m}$	$\chi_{2m}$	$\chi_{3m}$
°			
290·0	0·0103 <sub>2</sub>	0·0086 <sub>6</sub>	0·0100 <sub>8</sub>
77·2	0·0360 <sub>0</sub>	0·0231 <sub>7</sub>	0·0338 <sub>8</sub>
20·3	0·113 <sub>3</sub>	0·0654 <sub>2</sub>	0·109 <sub>5</sub>
16·7	0·136 <sub>8</sub>	0·0759 <sub>8</sub>	0·128 <sub>5</sub>
14·5	0·153 <sub>4</sub>	0·0842 <sub>0</sub>	0·144 <sub>3</sub>

For purposes of comparison with any theory of paramagnetism the above values must be corrected for the diamagnetic properties of the anion, ammonium sulphate and the water of crystallization. The corrected values are given below.

T	$\chi'_{1m}$	$\chi'_{2m}$	$\chi'_{3m}$	$1/\chi'_{1m}$	$1/\chi'_{2m}$	$1/\chi'_{3m}$
°						
290·0	0·0105 <sub>0</sub>	0·0088 <sub>4</sub>	0·0102 <sub>6</sub>	95·24	113·2	97·45
77·2	0·0361 <sub>8</sub>	0·0233 <sub>5</sub>	0·0340 <sub>6</sub>	27·64	42·83	29·36
20·3	0·113 <sub>5</sub>	0·0656 <sub>0</sub>	0·109 <sub>7</sub>	8·812	15·24	9·117
16·7	0·137 <sub>0</sub>	0·0761 <sub>6</sub>	0·128 <sub>7</sub>	7·300	13·13	7·771
14·5	0·153 <sub>6</sub>	0·0843 <sub>4</sub>	0·144 <sub>5</sub>	6·511	11·85	6·921

\* *loc. cit.*

† These values are calculated per unit mass. Hence the term "principal susceptibilities" should perhaps be more correctly "principal specific susceptibilities."

In the above table the values of the reciprocals of the corrected molecular susceptibilities are added for convenience. The latter values are plotted as functions of the absolute temperature in fig. 10.

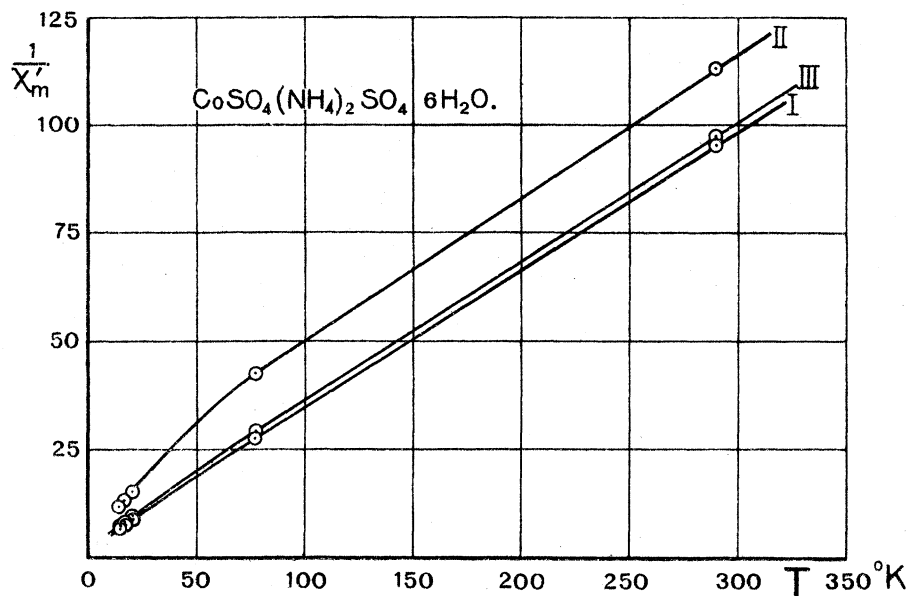


Fig. 10.

In testing the results for a WEISS law  $\chi (T + \Delta) = C$  we obtain the results given below.

T	$\chi'_{1m} (T + 9.8)$	$\chi'_{2m} (T + 52.4)$	$\chi'_{3m} (T + 14.6)$
290.0	3.129	3.026	3.125
77.2	3.148	3.026	3.127
20.3	3.416	4.769	3.827
16.7	3.629	5.263	4.028
14.5	3.732	5.645	4.205

Hence we have  $\Delta_1 = 9.8$ ,  $\Delta_2 = 52.4$ ,  $\Delta_3 = 14.6$ .

*Nickel Sulphate Heptahydrate.*—The results of the calculations of the principal susceptibilities of nickel sulphate heptahydrate will now be given. The final values for  $a$ ,  $c$  and  $m$  used in the calculations will be found in the table below.

T	$c$	$3a$	$m$
288.0	$1.29 \times 10^{-7}$	$49.83 \times 10^{-6}$	$3.10 \times 10^{-8}$
169.5	$5.78 \times 10^{-7}$	$104.3 \times 10^{-6}$	$2.6 \times 10^{-8}$
77.29	$1.69 \times 10^{-6}$	$231.9 \times 10^{-6}$	$2.2 \times 10^{-8}$
64.5	$2.30 \times 10^{-6}$	$274.5 \times 10^{-6}$	$2.1 \times 10^{-8}$
20.33	$12.32 \times 10^{-6}$	$666.0 \times 10^{-6}$	$2.0 \times 10^{-8}$
16.65	$17.41 \times 10^{-6}$	$810.0 \times 10^{-6}$	$2.0 \times 10^{-8}$
14.6	$21.57 \times 10^{-6}$	$882.0 \times 10^{-6}$	$1.95 \times 10^{-8}$

From the above data the following results were obtained in calculating  $\chi_1$ ,  $\chi_2$  and  $\chi_3$  from the expressions (4) on page 24:—

T	$\chi_1 \times 10^6$	$\chi_2 \times 10^6$	$\chi_3 \times 10^6$
288°	16.66	16.53	16.63
169.5	35.1	34.5	34.8
77.29	78.1	76.4 <sub>5</sub>	77.3
64.5	92.6 <sub>5</sub>	90.3 <sub>5</sub>	91.5
20.33	228.2	215.9	219.9
16.65	278.8	255.5	261.3
14.6	304.9	283.3	290.4

Calculating the molecular susceptibilities we obtain the following values:—

T	$\chi_{1m}$	$\chi_{2m}$	$\chi_{3m}$
288.0	0.0046 <sub>8</sub>	0.0046 <sub>4</sub>	0.0046 <sub>7</sub>
169.5	0.0098 <sub>5</sub>	0.0096 <sub>8</sub>	0.0097 <sub>7</sub>
77.29	0.0219	0.0215	0.0217
64.5	0.0260	0.0254	0.0257
20.33	0.0641	0.0606	0.0618
16.65	0.0783	0.0718	0.0734
14.6	0.0856	0.0796	0.0815

These values must now be corrected for the diamagnetic properties of the anion and the water of crystallization. The corrected figures are given below, together with the reciprocals of the corrected molecular susceptibilities.

T.	$\chi'_{1m}$	$\chi'_{2m}$	$\chi'_{3m}$	$1/\chi'_{1m}$	$1/\chi'_{2m}$	$1/\chi'_{3m}$
288°	0.0047 <sub>8</sub>	0.0047 <sub>4</sub>	0.0047 <sub>7</sub>	209.2	211.0	209.7
169.5	0.0099 <sub>5</sub>	0.0097 <sub>8</sub>	0.0098 <sub>7</sub>	100.5	102.2	101.3
77.29	0.0220	0.0216	0.0218	45.45	46.30	45.87
64.5	0.0261	0.0255	0.0258	38.31	39.22	38.80
20.33	0.0642	0.0607	0.0619	15.58	16.48	16.16
16.65	0.0784	0.0719	0.0735	12.75	13.91	13.61
14.6	0.0857	0.0797	0.0816	11.67	12.55	12.26

Testing now for a WEISS law we obtain the following results with  $\Delta_1 = -59.9$ ,  $\Delta_2 = -58.0$ ,  $\Delta_3 = -59.7$ .

T	$\chi'_{1m} (T - 59.9)$	$\chi'_{2m} (T - 58.0)$	$\chi'_{3m} (T - 59.7)$
288.0	1.090 <sub>3</sub>	1.090 <sub>2</sub>	1.09 <sub>0</sub>
169.5	1.090 <sub>5</sub>	1.090 <sub>4</sub>	1.08 <sub>6</sub>
77.29	0.382 <sub>6</sub>	0.416 <sub>6</sub>	0.383 <sub>4</sub>
64.5	0.120 <sub>1</sub>	0.165 <sub>7</sub>	0.123 <sub>8</sub>
20.33	-2.540	-2.287	-2.375
16.65	-3.391	-2.973	-3.16 <sub>4</sub>
14.6	-3.882	-3.459	-3.68 <sub>1</sub>

## DISCUSSION OF RESULTS.

§ 1. *Examination for the law  $\chi (T + \Delta) = C$ .*

A glance at the graph (fig. 10), which gives the reciprocals of the principal susceptibilities of cobalt ammonium sulphate as functions of the absolute temperature, will show immediately that down to about 80° K. the graphs consist of three approximately parallel straight lines, none of which pass through the zero. From this fact we may draw two important conclusions, viz. :—

(1) *That each of the principal susceptibilities follows the WEISS law  $\chi (T + \Delta) = C$  (and not the simpler CURIE law  $\chi (T) = C$ ) down to about nitrogen temperatures and*

(2) *the CURIE constant  $C$  is approximately the same in the three cases, since  $C$  is given by the slope of the curve.*

The similar result of FOËX\* thus receives confirmation from the present work.

In columns 2, 3 and 4 of the first table on p. 39 are given the values of  $\chi'_{1m} (T + \Delta_1)$ ,  $\chi'_{2m} (T + \Delta_2)$  and  $\chi'_{3m} (T + \Delta_3)$  derived from the observations. The values of  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$  are 9·8, 52·4 and 14·7 respectively, the greatest value belonging, of course, to the axis of smallest susceptibility. The values of  $C$  derived from the calculations will be seen to be equal within the limits of accuracy of the experiment.

An examination shows that similar phenomena are shown by nickel sulphate heptahydrate.† In this case also *each of the principal susceptibilities follows the law  $\chi (T + \Delta) = C$ , but only down to temperatures not lower than about 160° K. The CURIE constant obtained for the three principal directions is again the same in the three cases.* In columns 2, 3 and 4 of the last table on p. 40 are given the results obtained in testing for the WEISS law. It will be seen that the values of the  $\Delta$ 's are all negative,  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$  being respectively equal to  $-59\cdot9$ ,  $-58\cdot0$  and  $-59\cdot7$ .

From the above results it is immediately obvious that the CURIE constant is a quantity of great significance in connection with the magnetic properties of crystals, since it is a quantity which is equal along the principal magnetic axes. The CURIE constant is of special significance in the theory of WEISS, since from it the number of magnetons‡ present in a substance is to be calculated from the following expressions :—

$$n = \sigma/1123\cdot5, \quad \sigma^2 = \chi (T + \Delta) R = CR,$$

in which

$n$  = number of magnetons,

$\sigma$  = magnetic moment per gramme-molecule,

$R$  = gas constant per gramme-molecule.

Performing such calculations for the three principal susceptibilities of a crystal we

\* *Loc. cit.*

† No graph is given of the principal susceptibilities of nickel sulphate, as the differences of the susceptibilities are so small as not to show clearly on a graph on any reasonable scale. The shape of the curves may, however, be visualized by comparison with the "mean" curve, the individual curves being all similar to the latter.

‡ The experimental magneton of WEISS is, of course, meant here ; not the theoretical magneton of BOHR.

obtain, of course, the same number for the three cases, this number being, within the limits of accuracy of the knowledge of the  $\Delta$ 's, equal to the number obtained from similar calculations on the mean susceptibilities as determined from measurements with the powdered substance. This was to be expected, as the latter number is the mean of the already equal numbers relating to the crystal. It would, therefore, seem that the magnetic moments of the paramagnetic atoms in crystals are symmetrical with regard to the principal magnetic axes.

### § 2. *Deviations from the WEISS law.*

Considering first the case of cobalt ammonium sulphate, we will now examine in how far the law  $\chi (T + \Delta) = C$  holds for the lowest temperatures. It will be seen on examination of columns 2, 3 and 4 of the first table on p. 39 and of the graphs in fig. 10 that this law ceases to be valid at temperatures lower than about 75° K. Thus the values of  $\chi (T + \Delta)$ , instead of remaining constant, become gradually greater, showing that *the principal susceptibilities increase more rapidly with fall in temperature than is given by the WEISS law.* These deviations from the WEISS law appear to be the exact counterpart of the deviation shown by anhydrous manganese sulphate, in which the susceptibility increases less rapidly with fall in temperature than is given by the WEISS law.

Again the magnitudes of the deviations from the straight line law are in the inverse order of the magnitudes of the susceptibilities, the axis of smallest susceptibility showing the greatest deviation and *vice versa*.

Reference to the last table on p. 40 will show that the principal susceptibilities of nickel sulphate heptahydrate deviate in a particularly interesting manner from the law of WEISS at low temperatures. Thus this substance commences to deviate from this law at a temperature of about 160° K., the susceptibilities remaining throughout less than would be given by the WEISS law. The curves for  $1/\chi_m$  as functions of the absolute temperature are, however, somewhat complicated, as they possess a point of inflection such that, for temperatures above 70° K. and below 170° K., the curve is convex to the temperature axis, but at temperatures below 70° K. it is concave towards the temperature axis.

In each of the cases here considered the three principal susceptibilities, when plotted as in the figures given here, follow the same type of curve as the mean susceptibility derived from measurements on the powdered material.

Thus the principal susceptibilities do not show phenomena which are hidden when the mean is taken. This is, however, probably not a general phenomenon, for FOËX, from his measurements on siderose, concludes that the principal susceptibilities of this substance show different types of deviation from the WEISS law for the various axes (see p. 21).

### § 3. *Connection of $\Delta$ with Crystal Structure.*

As has been mentioned in Part I, KAMERLINGH ONNES and OOSTERHUIS\* have suggested that the constant  $\Delta$  is related in a simple manner to the distances between the

\* 'Leid. Comm.,' No. 139D.



paramagnetic atoms in a solid,  $\Delta$  being greater the smaller the distance between the atoms in question. They also suggested that the values of  $\Delta$  in the different directions in a crystal might be simply related to the corresponding linear concentrations of the paramagnetic atoms in these directions. In making this suggestion it was tacitly assumed that the diamagnetic atoms of the crystal exert no immediate magnetic action on the paramagnetic atoms, but act merely as diluents.

This latter suggestion has now been tested and extended, as will now be described. If the structure of either of the crystals investigated in the present work had been known as a result of X-ray analysis, it would have been a simple matter to test the above-mentioned suggestion and determine the actual relation, if one really exists, connecting the  $\Delta$ 's with the corresponding spacings. Unfortunately, we have no such data available for either of the crystals at present under consideration. The idea was, therefore, tested in the case of nickel sulphate heptahydrate in the following manner, which is avowedly of a provisional nature only. It was tried whether, in the light of the available crystallographic data, the nickel atoms could be arranged on a space lattice in agreement with the latter, in such a manner that the  $\Delta$ 's could be calculated immediately from a single simple law in terms of the spacings. If then the hypothetical space lattice could be tested by X-ray methods and found to be highly probable, some evidence would have been obtained for the correctness of the view that a simple relation exists between the  $\Delta$ 's and the corresponding spacings in a crystal. Should the hypothesis be verified by future measurements\* for the cases of other crystals, we should obtain a means of determining the structure of paramagnetic crystals, at least as far as the paramagnetic atoms are concerned. The method would be particularly useful in the case of the more complicated crystal systems, for which the X-ray analysis becomes very difficult, if not impossible.

We possess the following data concerning nickel sulphate heptahydrate of use for our present purpose :—

$$\Delta_1 = -59.9, \quad \Delta_2 = -58.0, \quad \Delta_3 = -59.7.$$

$$a : b : c = 0.9815 : 1 : 0.5656.$$

$$\text{Density} = 1.95 (1.953, 1.949, 1.955).$$

Now it was found that the values of  $\Delta$  could be calculated accurately by means of the following expressions :—

$$\Delta_1 = a - bd_1, \quad \Delta_2 = a - bd_2, \quad \Delta_3 = a - bd_3$$

provided that the nickel atoms were arranged on a space lattice as shown in fig. 10,†  $d_1, d_2, d_3$  are the distances

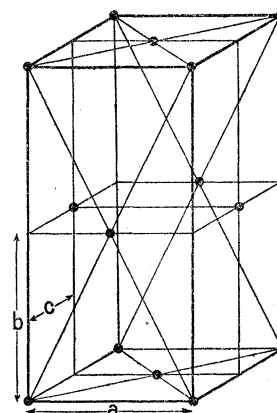


Fig. 11.

\* Unfortunately, the case of cobalt ammonium sulphate could not be tested in a similar manner on account of the difficulty of interpreting the results of X-ray analysis in the case of a monoclinic crystal.

† It will be noticed that the suggested structure is in every way analogous to that found by Ogg and Hopwood ('Phil. Mag.', vol. 32, p. 518 (1916)) for the case of the anhydrous alkali sulphates, which are also rhombic.

between the successive planes of nickel atoms along the axes  $a$ ,  $b$  and  $c$  respectively. An examination of the figure will show that the following relations hold between the  $d$ 's :—

$$d_1 : d_2 : d_3 = 0.4907 : 1 : 0.5656.$$

Then with  $a = -61.79$  and  $b = -3.77$ , the calculated values of the  $\Delta$ 's are as given below :—

$$\Delta_1 = -59.94, \quad \Delta_2 = -58.02, \quad \Delta_3 = -59.64.$$

It was not found possible to arrange the nickel atoms to fit the data assuming any other equally simple law, particularly that of the inverse proportionality of  $\Delta$  and spacing, which was more particularly in mind when the suggestion of KAMERLINGH ONNES and OOSTERHUIS, mentioned above, was made.

A specimen of the substance was then sent to Prof. KEESOM, of Utrecht, who had the goodness to test the correctness of the hypothetical space-lattice shown in the above figure, by the DEBYE-SCHERRER method of X-ray analysis. He reported that the tests succeeded well, a good photograph having been obtained, on which were twenty-four measurable lines. In making the test 326 lines, emanating from all the possible planes of the suggested structure, were calculated on the assumption that the remaining atoms of the crystal were arranged in the same manner as the nickel atoms and without taking into account the influence of the remaining atoms on the intensities of the lines. The observed and calculated lines were then compared as regards position and intensity. As a result of the comparison, Prof. KEESOM announces that *the hypothetical structure suggested for the crystal is in agreement with the photograph obtained.*\* It is, however, not possible to state definitely that the photograph leads necessarily to the suggested structure, on account of the difficulty of interpreting the experimental results in the case of a rhombic crystal. The test, however, furnishes considerable evidence of the correctness of the suggested structure.

It would seem, therefore, that the conception of a simple relation existing between the  $\Delta$ 's and the corresponding spacings in a crystal receives support from the present work, thus opening up a possible new field in the investigation of crystal structure. It remains for future work to test the point more fully.

#### § 4. Comparison with existing theories.

The great majority of the theories put forward to explain the phenomena of paramagnetism deal only with the mean value of the susceptibility and not with the principal susceptibilities of crystals. Thus the only theories actually relating to crystals at present

\* To give the actual words of the report :—“ *De conclusie moet luiden, dat de Röntgenphoto in overeenstemming is met de aangegeven structuur, maar wegens de moeilijkheid van dit onderzoek bij een rhombisch kristal (zeer speciale assenverhoudingen buitengesloten) kunnen wij niet zeggen, dat de Röntgenphoto ondubbelzinnig moet luiden tot die structuur.*”

in existence are those of WEISS\* and FOËX†. WEISS has considered independently the effect of introducing into the LANGEVIN theory of paramagnetism (1) a molecular field different in different directions in the crystal and (2) a potential energy which is a function of the direction in the crystal and is intended to represent the interaction of the atoms of the crystal lattice. FOËX has combined these two ideas and has developed them further. We will therefore confine ourselves here to the theory of FOËX.

This theory is based on the conceptions of the "classical" electrostatics and contains no reference to the quantum theory. It rests on the following three assumptions :—

- (1) The "classical" kinetic theory holds and the heat energy of the atoms is proportional to the absolute temperature.
- (2) There exists a molecular field equal to  $n\sigma$  ( $\sigma =$  magnetization) in which  $n$  is equal to  $n_1, n_2, n_3$  for the three principal directions in the crystal.
- (3) There are also forces due to the crystalline nature of the material such that there is a potential energy which is a function of the direction.

The assumption is also made, and pains are taken to justify it, that the two last named types of action are independent of one another.

It is then supposed that for each orientation of the atomic magnets there is a potential energy  $W$ ; then if  $\alpha$  is the angle between the direction of the magnetic moment of the atom and the field  $H$ ,  $d\omega$  the solid angle and  $R$  the gas constant as in the theory of LANGEVIN, we find the following value for  $\sigma$  the magnetization at the temperature  $T$  :—

$$\sigma = \frac{3CH}{T} \frac{\int e^{-W/RT} \cos^2 \alpha d\omega}{\int e^{-W/RT} d\omega} \dots \dots \dots (1)$$

in which  $C$  is the CURIE constant.

Generalizing now for the three principal directions in the crystal and denoting by  $y_1, y_2, y_3$  the quantities along the principal axes corresponding to the ratio of the integrals.

$$y = \frac{\int e^{-W/RT} \cos^2 \alpha d\omega}{\int e^{-W/RT} d\omega},$$

we find for the magnetizations along the principal axes

$$\sigma_1 = \frac{3CH}{T} \cdot y_1, \quad \sigma_2 = \frac{3CH}{T} \cdot y_2, \quad \sigma_3 = \frac{3CH}{T} \cdot y_3 \dots \dots \dots (2)$$

\* 'C.R.,' vol. 156, pp. 1674 and 1836 (1913).

† THÈSE, Strasbourg, 1921; 'Ann. de Physique,' vol. 16, p. 174 (1921).

Introducing now a molecular field with the three coefficients  $n_1, n_2, n_3$ , we obtain the three following equations in place of (2) :—

$$\sigma_1 = \frac{3CH}{T} (H + n_1\sigma_1) \cdot y_1, \quad \sigma_2 = \frac{3CH}{T} (H + n_2\sigma_2) \cdot y_2, \quad \sigma_3 = \frac{3CH}{T} (H + n_3\sigma_3) \cdot y_3. \quad (3)$$

From these expressions we can determine the principal susceptibilities as follows :—

$$\chi_1 = \frac{3Cy_1}{T - 3n_1Cy_1}, \quad \chi_2 = \frac{3Cy_2}{T - 3n_2Cy_2}, \quad \chi_3 = \frac{3Cy_3}{T - 3n_3Cy_3}. \quad (4)$$

In order to proceed any further with the theory, some definite assumption must be made as to the dependence of the  $y$ 's, which represent actually the mean value of  $\cos^2 \alpha$  taken over all atoms on the temperature. The assumption is made in the form of two alternative graphs. Thus it is known *a priori* that at high temperatures  $y$  must approximate to  $1/3$  and at low temperatures must have a value between zero and 1. The shape of the curve of the dependence of the  $y$ 's on the temperature between these points is then assumed to be given by one of two possible graphs, in the first of which the rate of change of the value of  $y$  is everywhere of the same sign, but in the second there is a point of inflection. On this basis the shape of the  $1/\chi \cdot T$  curves may be determined. It is shown that these curves are straight lines at the higher temperatures, but at the lower temperatures they may show any of the following types of deviation from the straight line law.

(1) The curves may show a gradual curvature, either concave or convex, towards the temperature axis.

(2) They may possess a point of inflection such that the curvature changes from concave towards the temperature axis to convex or *vice versa* and

(3) A maximum and a minimum of susceptibility may occur at the lowest temperatures.

The theory can be more precise on certain points without the necessity of introducing the above assumptions. Thus for a regular crystal we have

$$n_1 = n_2 = n_3, \quad y_1 = y_2 = y_3 = 1/3,$$

$$\chi_1 = \chi_2 = \chi_3 = \frac{C}{T - nC}.$$

Thus a regular crystal will obey the WEISS law or the CURIE law, depending on whether  $n$  is not or is equal to zero. This has been confirmed in the case of ferric alum,\* a regular crystal which follows the CURIE law.

It may also be noticed that the CURIE constant  $C$  is the same for each of the principal axes of the crystal, in agreement with the results of FOËX for siderose and the present work on cobalt ammonium sulphate and nickel sulphate heptahydrate.

\* 'Leiden Comm.,' No. 139e.



It will be seen thus that the theory can give a qualitative explanation of all the phenomena of the temperature dependence of the susceptibilities of paramagnetic substances, including those announced in the present work. The theory must, however, be regarded as empirical, and is from its very nature impossible of quantitative verification in its present form.

#### SUMMARY.

The work described in the previous pages is divided into two parts. In the first part is given an account of the investigation of the susceptibilities of the following paramagnetic substances as functions of the temperature down to the lowest temperature obtainable with liquid hydrogen (about 14° K.): the anhydrous sulphates, the heptahydrated sulphates and the ammonium double sulphates of cobalt, nickel and ferrous iron, all in the powder form.

Whilst all these substances follow the WEISS law,  $\chi (T + \Delta) = C$ , at relatively high temperatures, they show the following types of deviation from this law at the lower temperatures, not found in previous investigations at the lowest temperatures.

(1) The susceptibility *increases more rapidly with fall in temperature than is given by the WEISS law* (cobalt ammonium sulphate, nickel ammonium sulphate).

(2) The curve of  $1/\chi$  against  $T$  possesses a point of inflection (nickel sulphate heptahydrate).

(3) A maximum and a minimum value of the susceptibility occur in the region of the lowest temperatures (anhydrous nickel sulphate, anhydrous ferrous sulphate).

It has been found that the idea of the intimate connection between the "magnetic dilution" of a substance and the  $\Delta$  of the WEISS law suggested by KAMERLINGH ONNES and OOSTERHUIS is not of quite general application, exceptions to the rule having been found.

In the second part of the work an account is given of the determination of the principal susceptibilities of two crystals over a range of temperature from about 14° K. to 290° K. These are the only data yet available as regards the principal susceptibilities of crystals at the lowest temperatures. The substances chosen were cobalt ammonium sulphate and nickel sulphate heptahydrate. In both cases each of the principal susceptibilities follows the WEISS law at the higher temperatures, but deviates therefrom at the lower temperatures. It was found that in each case the CURIE constant is the same for each of the three principal susceptibilities.

The curves of  $1/\chi$  against  $T$  for cobalt ammonium sulphate, which consist of three parallel straight lines at the higher temperatures, become concave towards the temperature axis at the lower temperatures; the magnitudes of the deviations from the straight line law are in the inverse order of the magnitudes of the susceptibilities, as are also the  $\Delta$ 's of the WEISS laws  $\chi_1 (T + \Delta_1) = C$ , etc. Hence, each of the principal susceptibilities of this crystal *increases more rapidly with fall in temperature than is given by the WEISS law, which is obeyed at the higher temperature.*



In the case of nickel sulphate heptahydrate each of the curves of the reciprocals of the principal susceptibilities against the temperature possesses a point of inflection, the curvature changing from convex towards the temperature axis to concave as the temperature falls below  $70^{\circ}$  K.

Thus in each case the principal susceptibilities show the same type of dependence on temperature as the mean susceptibility, though this is probably not a general phenomenon, as FOËX found opposite types of deviation in two of the principal susceptibilities of siderose.

An attempt has been made to test the suggestion of KAMERLINGH ONNES and OOSTERHUIS that the  $\Delta$ 's along the principal axes should be intimately connected with corresponding spacings of the paramagnetic atoms, the  $\Delta$  being greater the smaller the spacing. As a result, a hypothetical space-lattice has been suggested for the positions of the nickel atoms in nickel sulphate heptahydrate, by using the magnetic data which have now been obtained. This hypothetical space-lattice has been tested by the DEBYE-SCHERRER method of X-ray analysis, and it has been found that the X-ray photograph obtained is in agreement with the lattice suggested. Should the idea be confirmed by further measurement, a new method will have been obtained for the investigation of the structure of paramagnetic crystals.