

**Physics.** — *On the assumed paramagnetic anomaly of nickelsulphate-heptahydrate at low temperatures and on the types of deviation from the law of CURIE-WEISS at low temperatures.* By C. J. GORTER, W. J. DE HAAS and J. VAN DEN HANDEL. (Communication N<sup>o</sup>. 218d from the physical laboratory of Leiden.)

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§ 1. *Introduction.*

Previously the paramagnetic behaviour of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  has been examined in this laboratory by JACKSON<sup>1)</sup>. By the usual rod method the susceptibility of the powdered substance was measured at room temperature, at the boiling temperature of aethylen and in the temperature regions of liquid nitrogen and of liquid hydrogen.

The susceptibilities at room temperature and at the temperatures of liquid hydrogen are in rather good agreement with the results of unpublished measurements of KAMERLINGH ONNES and HOF.

The differences between the three principal susceptibilities of the rhombic crystal were determined on the WEISS-method. They were found not to exceed 1 % of the susceptibility at room temperature or 7 % of the susceptibility at the lowest hydrogen temperature.

From his measurements JACKSON derived for the powder a value of  $59^\circ$  for  $\theta$  and of 14.62 for the magneton number; for the principal directions of the crystal values of 59.9, 58.0 and 59.7 for the  $\theta$ 's.

Several reasons made it desirable to repeat and to extend these measurements.

1<sup>st</sup>. The magneton number does not agree with the value of 16.0—16.5 found for most substances<sup>2)</sup>.

2<sup>nd</sup>. The high value of  $\theta$  is remarkable compared with the usually small values of  $|\theta|$  for the hydrated salts of the iron group.

For  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ <sup>3)</sup> e.g.  $\theta = -4$ , for  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ <sup>3)</sup>  $\theta = -1$ . And  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ <sup>3)</sup>, which shows the characteristic anomaly of all Co-salts of having in the  $1/\chi'-T$ -diagram a curve convex at low temperatures, has  $\theta = -13.7$ .

We may remark however, that the exceptional values of  $\theta$  and  $p$  were determined by drawing a straight line through two points in the  $1/\chi'-T$ -

<sup>1)</sup> L. C. JACKSON, Phil. Trans. Roy. Soc. A 224, 1, 1923. Comm. Leiden 163.

<sup>2)</sup> See e.g. W. J. DE HAAS and C. J. GORTER, These Proc. 33, 1101, 1930. Comm Leiden 210d.

<sup>3)</sup> L. C. JACKSON, loc. cit.

diagram only, viz. through those belonging to room temperature and to the boiling point of aethylene.

By the anomalous behaviour of the susceptibility we might also expect important changes in the intensity of the absorption bands, when the temperature is lowered. That is why Dr. FREED investigated the absorption spectrum of a  $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$  crystal at different temperatures. He greatly obliged us by telling us as his provisional impression, that no changes of the magnitude expected occur.

So we decided to repeat the measurements and to extend them to more temperatures between room temperature and the boiling point of liquid nitrogen.

### § 2. *Material and method.*

The measurements were made with cobalt-free nickelsulphate kindly put at our disposal by the anorg. chem. laboratory.

Dr. C. GROENEVELD controlled the crystal water content.

The measurements were made by the "rod method", described in Comm. N<sup>o</sup>. 208c<sup>1</sup>). The magnet used was of a smaller type than the one used in our former investigations.

It was a small CARPENTIER magnet, which gave a central field of 11.5 K Gauss with 11 Ampères and for a polar distance of 24.5 mm. It was calibrated by the ballistic method.

### § 3. *Results.*

$T$	$\chi \cdot 10^6$	$\chi' \cdot 10^6$	$1/\chi' \cdot 10^{-4}$	$\chi' T \cdot 10^{-4}$	$\chi'(T+3.0) \cdot 10^4$
288.0	15.61	16.06	6.227	46.25	46.73
249.6 <sup>5</sup>	17.84	18.29	5.467	45.66	46.21
201.6 <sup>5</sup>	21.93	22.38	4.468	45.13	45.80
170.0	26.11	26.56	3.765	45.15	45.95
137.5	32.17	32.62	3.066	44.85	45.83
77.52	57.15	57.60	1.736	44.65	46.38
64.16	68.97	69.42	1.441	44.59	46.62
20.41	217.7	218.2	0.4583	44.53	51.08
17.29	258.0	258.2	0.3870	44.69	52.45
14.35	312.1	312.6	0.3199	45.86	54.24

The high susceptibilities have been corrected for demagnetisation. In the fig.  $1/\chi'$  has been plotted against  $T$ .

<sup>1</sup>) W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 676, 1930. Comm. Leiden 208c.

Down to the temperatures of liquid nitrogen the paramagnetic behaviour can roughly be described by the law of CURIE-WEISS with:  $\chi(T + 3.0) = 46.2^2$ , which gives the magneton number  $p = 16.01$ .

From column 6 it is however evident, that at higher temperatures systematic deviations occur from this law. The curve in the  $1/\chi'-T$ -diagram becomes slightly convex there.

The deviations from our curve of the values found by KAMERLINGH ONNES and HOF are + 2 %, - 0.2 %, - 3 % and - 3 % at 290°, 20°.33, 15°.17 and 14°.8.

The deviations of JACKSONS values are much larger viz. + 4 %, + 33 %, + 35 %, + 34 %, + 2 %, + 0.6 % and - 4 % at 292°.3, 169°.6, 77°.29, 64°.65, 20°.33, 16°.65 and 14°.6.

We must certainly conclude, that the errors in JACKSONS values for the aethylene point and for the two nitrogen points amount to about 34 %.

#### § 4. Discussion of the results.

The magnetic behaviour of  $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$  was found analogous to that of  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  and of  $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$ , the magneton number is normal. The slight curvature of the curve in the  $1/\chi'-T$ -diagram is not yet explained. It may be due perhaps to a weak paramagnetism independent of the temperature. Possibly a similar curvature will be observed for the Co-salt, when the measurements will be made with the utmost care.

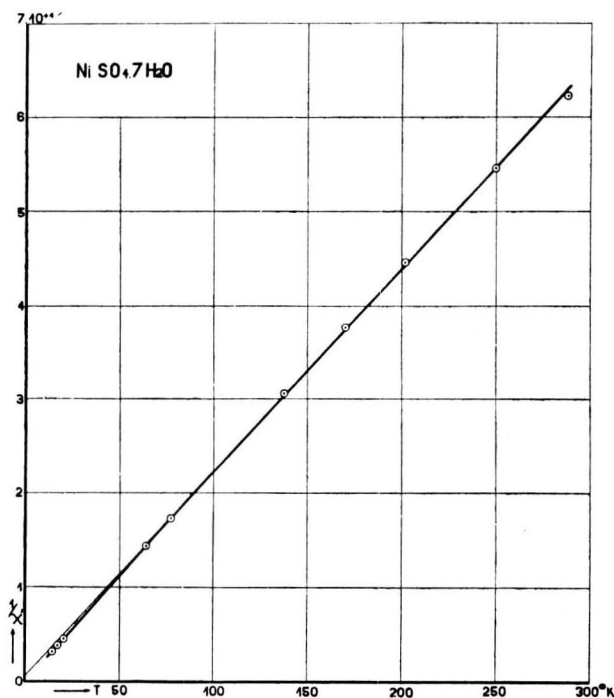


Fig. 1.

So the type of cryomagnetic anomaly, of which  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  constituted the only representant, has now vanished.

We can distinguish three types of deviation from the CURIE-WEISS law for paramagnetic salts at low temperatures.

1<sup>0</sup>. The curve in the  $1/\chi'-T$ -diagram is convex at low temperatures,  $\theta$  is negative: Co-salts<sup>1)</sup>,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , chromic sulphates<sup>2)</sup>,  $\text{CeF}_3$ <sup>3)</sup>,  $\text{CeCl}_3$ <sup>4)</sup>,  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ <sup>5)</sup>,  $\text{Pr}_2(\text{SO}_4)_3$ <sup>4)</sup>.

2<sup>0</sup>. The curve in the  $1/\chi'-T$ -diagram is concave at low temperatures,  $\theta$  is negative:  $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ <sup>5)</sup>,  $\text{MnSO}_4$ <sup>6)</sup> (non-degenerated fundamental term).

3<sup>0</sup>. At low temperatures the susceptibility is only slightly dependent on the temperature; it depends however on the intensity of the field,  $\theta$  has a high positive or negative value: anhydrous salts only e.g.  $\text{CrCl}_3$ <sup>7)</sup>,  $\text{FeCl}_2$ <sup>8)</sup>,  $\text{CoCl}_2$ <sup>7)</sup>,  $\text{NiCl}_2$ <sup>7)</sup>,  $\text{CuSO}_4$ <sup>9)</sup>.

Perhaps also  $\text{FeSO}_4$ <sup>10)</sup>,  $\text{NiSO}_4$ <sup>10)</sup>,  $\text{CuCl}_2$ <sup>9)</sup> and  $\text{MnSO}_4$ <sup>6)</sup> belong to this group. As however for these no dependence on the field has been recorded, they may also belong to group 2.

The other paramagnetic salts that have been examined (all containing much crystal water) show small deviations from the law of CURIE-WEISS and low values of  $|\theta|$ :  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ <sup>11)</sup>,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ <sup>12)</sup>,  $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ <sup>13)</sup>,  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ <sup>14)</sup>,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ <sup>14)</sup>,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ <sup>14)</sup>,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ <sup>14)</sup>,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ <sup>15)</sup>.

Using the differences between the principal susceptibilities found by JACKSON we find for these susceptibilities:

1) L. C. JACKSON, loc. cit.

L. C. JACKSON and H. KAMERLINGH ONNES, Proc. Roy. Soc. A **104**, 671, 1923. Comm. Leiden 168b.

2) W. J. DE HAAS and C. J. GORTER, unpublished measurements.

3) W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 949, 1930. Comm. Leiden 210c.

4) C. J. GORTER, W. J. DE HAAS and J. v. D. HANDEL, These Proc. **34**, 1249, 1931. Comm. Leiden 218c.

5) C. J. GORTER and W. J. DE HAAS, These Proc. **34**, 1243, 1931. Comm. Leiden 218b.

6) H. KAMERLINGH ONNES and E. OOSTERHUIS, These Proc. **21**, 322, 1932. Comm. Leiden 129b.

7) H. R. WOLTJER, Comm. Leiden 173b.

8) H. R. WOLTJER and E. C. WIERSMA, These Proc. **32**, 735, 1929. Comm. Leiden 201b.

9) W. J. DE HAAS and C. J. GORTER, These Proc. **34**, 317, 1931. Comm. Leiden 215a.

10) L. C. JACKSON, loc. cit.

11) W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 676, 1930. Comm. Leiden 208b.

12) H. KAMERLINGH ONNES, and E. OOSTERHUIS, loc. cit.

13) L. C. JACKSON and H. KAMERLINGH ONNES, loc. cit.

L. C. JACKSON and W. J. DE HAAS, These Proc. **31**, 346, 1928. Comm. Leiden 187c.  
[K. S. KRISHNAN, Z.S. f. Phys. **71**, 137, 1931.]

14) L. C. JACKSON, loc. cit.

15) W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 1101, 1930. Comm. Leiden 210d.

$T$	$\chi_1$	$\chi_2$	$\chi_3$
288	15.66	15.53	15.63
169.5	26.5	26.9	26.2
77.29	58.1 <sup>5</sup>	56.5	57.3 <sup>5</sup>
64.5	69.7 <sup>5</sup>	67.4 <sup>5</sup>	68.6
20.33	224	212	216
16.65	277	254	260
14.6	317	295	303

The corresponding values for  $\theta$  are:  $-2.0$ ,  $-4.0$  and  $-3.0$ , the corresponding magneton numbers: 16.03, 16.01 and 16.06<sup>1</sup>).

#### § 5. Summary.

Repetition and extension of the magnetic measurements of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  show no striking anomalies. Previous measurements at the temperatures of liquid aethylene and nitrogen must have been wrong.

At temperatures higher than those of liquid nitrogen the salt follows pretty well the law of CURIE-WEISS with  $\theta = -3.0$  and  $p = 16.01$ .

The principal susceptibilities given by JACKSON have been corrected for the new powder-measurements.

Finally the different types of anomalies at low temperatures have been described.

We wish to express our thanks to Mr. P. v. D. LEEDEN for his valuable help in the measurements.

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<sup>1</sup>) The rule of FOEX (G. FOEX, Ann. de Phys. 16, 174, 1921). that different  $\theta$ 's but no different  $p$ 's belong to the principal susceptibilities is thus verified within the limits of error.