Physics. — *Determination of the susceptibility of cupricsulphate-pentahydrate at low temperatures; the magneton numbers in the Iron group.* By W. J. DE HAAS and C. J. GORTER. (Communication N⁰. 210d from the Physical Laboratory Leiden).

§ 1. *Introduction.* In a preceding paper [1]) we mentioned our intention to measure at low temperatures the susceptibilities of a series of compounds the magnetism of which may be ascribed to one magnetic electron pro metallic ion.

Now the susceptibilities of the cupricsulphate-pentahydrate, the anhydroussulphate and chloride have been determined. The results of these measurements are less simple for the two anhydrous salts than for the $CuSO_4 . 5H_2O$, which was found to follow the law of CURIE-WEISS. They will be published within a short time.

Until now the only tests for the theories of paramagnetism were the magneton numbers. To determine these in the *Fe* group, measurements on salts of a great paramagnetic dilution over a wide range of temperature are important.

§ 2. *Method and material.* The material was the powdered $CuSO_4 . 5H_2O$ cryst. "Zur Analyse mit Garantieschein" of KAHLBAUM. Analysis showed that we really had to do with the pure pentahydrate.

The measuring method used was the same as has been described in earlier publications [2]).

§ 3. *Results.*

In the figure $1/\chi'$ has been plotted against the absolute temperature. The same corrections as in the earlier papers have been applied. χ' is the value of χ, corrected for the diamagnetism of the anion and of the crystal water. By the great paramagnetic dilution, the low magneton number of Cu^{++} and the small density of the substance measured the accuracy is not quite so

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[1]) W. J. DE HAAS and C. J. GORTER. These Proc. Vol. 33, N⁰. 9, 1930. Comm. Leiden N⁰. 210c.

[2]) W. J. DE HAAS and C. J. GORTER. These Proc. Vol. 33, N⁰. 7, 1930. Comm. Leiden, N⁰. 208c.

T	$\chi \cdot 10^6$	$\chi' \cdot 10^6$	$1/\chi' \cdot 10^{-4}$	$\chi' T \cdot 10^4$	$\chi'(T+0.70) \cdot 10^4$
290.0	5.95	6.35	15.75	18.42	18.46
249.4	6.92	7.32	13.66	18.26	18.30
203.1	8.56	8.96	11.16	18.20	18.26
169.4	10.35	10.75	9.30	18.21	18.29
138.0	12.65	13.05	7.66	18.01	18.10
77.47	22.87	23.27	4.29^7	18.03	18.19
64.10	27.63	28.03	3.56^8	17.97	18.16
20.32	86.7	87.1	1.148	17.70	18.31
17.20	102.2	102.6	0.975	17.65	18.37
14.29	121.6	122.0	0.820	17.43	18.29

good as in the earlier investigations. Within the limits of the accuracy of the measurements however the law of CURIE-WEISS is followed with $\theta = -0.70°$ and $\chi'T = 18.3°$, which gives the magneton number $p = 9.51$ W. M. At room temperature FEYTIS [1]), HONDA and ISHIWARA [2]) respectively found $5.9 \cdot 10^{-6}$ and $5.85 \cdot 10^{-6}$ ($T = 291.9$). BIRCH [3]) found, between 195° and 273°, $\theta = -24°$ and $p = 10.0$ W.M. At the lowest temperatures his curve nearly coincides with ours, at the highest temperature it deviates
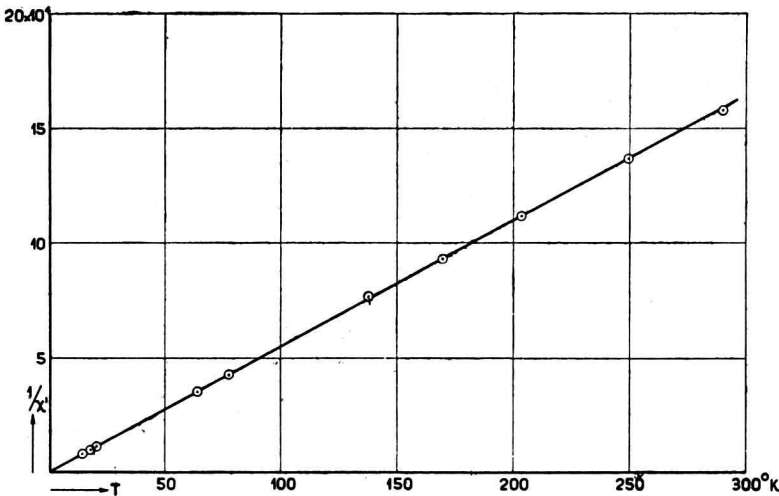

Fig. 1.

[1]) Melle FEYTIS, C. R. **152**, 708.
[2]) K. HONDA and T. ISHIWARA, Toh. Imp. Univ. IV, 215, 1915.
[3]) F. BIRCH, J. de Phys, IV, IX, 136, 1928.

from ours about 2 % towards higher χ. Thus our value for room temperature lies between the values found by HONDA and ISHIWARA and the extrapolated values of BIRCH.

§ 4. *Discussion*. The theory of HUND [1]), which gives such good results for the rare earths, is known to be in disagreement with the magneton numbers found for the *Fe* group. Two theories have been developed to explain this disagreement e.a. the theory of LAPORTE and SOMMERFELD [2]) and the theory of BOSE-STONER. The first takes into consideration, that at room temperature not only the lowest level of the basic multiplet might be occupied. It provided only a slightly better agreement and since our measurements on the magneton number in chromic-alum it must be put aside. In the table below the experimental magneton numbers [3]) for the different ions of the *Fe* group have been given and besides the values deduced from the theories of HUND, LAPORTE-SOMMERFELD and BOSE-STONER [4]). (See table at following page.)

By far the best agreement is found with the theory of BOSE-STONER, in which it is assumed that the resulting spin vectors can be orientated by the magnetic field, the resulting orbital vectors however not. We should thus be obliged to suppose the connexion between the orbits and the spin to be broken either by inhomogeneous electric fields or by resonance action with the surrounding atoms. Then the decomposition of the energy caused by this uncoupling action would have to be large compared with the multiplet-decomposition of the free ion.

Because of the increasing effective nucleus charge this multiplet splitting is larger in the second half of the *Fe* group than in the first half. According to LAPORTE [5]) e.g. the doublet splitting for the free Ti^{+++} ion is about 385 cm—[1] and for the free Cu^{++} ion 2130 cm—[1].

For the first half of the *Fe* group the theory of BOSE and STONER proves to agree very well with the experiments. For the second half this agreement is less good.

It is therefore evident, that in the second half of the *Fe* group the energy splitting by the STARK effect or by resonance may not be considered as large compared with the multiplet decomposition, the latter amounting here to more than 1000 cm—[1]. This may imply [e.g. KRAMERS [6]) found this to

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[1]) F. HUND, Z.f. Phys. **33**, 855, 1925.

[2]) O. LAPORTE und A. SOMMERFELD, Z. f. Phys. **40**, 333, 1926.
   O. LAPORTE, Z. f. Phys. **47**, 761, 1928.

[3]) For the composition of the table of the magneton numbers we used measurements on salts and solutions, Those measurements have been omitted, for which the law of CURIE did not hold approximatively. In no case have been considered observations with $|\theta| > 20°$ nor (if possible) measurements in which θ has not been determined.

[4]) D. M. BOSE, Z. f. Phys. **43**, 864, 1927.
   E. C. STONER, Phil. Mag. **8**, 250, 1929.

[5]) O. LAPORTE, l.c.

[6]) H. A. KRAMERS, These Proc. **32**, 1176, 1929. Comm. Leiden, Suppl. 68*b*.

Ion	V····	V···	V··	Cr···	Cr··	Mn··	Fe···	Fe··	Co··	Ni··	Cu··
Hund	7.7	8.1	3.9	3.9	0	29.4	29.4	33.6	33.2	28.0	17.7
L—S	—	—	16.1	13.0	18.6	29.4	29.4	32.3	32.8	27.8	17.6
B—St	8.6	14.1	19.2	19.2	24.4	29.4	29.4	24.4	19.2	14.1	8.6
exp.	8.6[1]	14.1[2]	19.3[3]	19.0[4]	23.9[5]	29.0[6]	28.9[7]	25.5—27.4[8]	22.0—26.4[9]	15.5—16.0[10]	9.0—10.0

be the case for a doublet in a cylindrically-symmetrical field] that the lowest level does not give the exactly magneton number to be expected for perfect uncoupling. The deviation from this expected value will be determined by the degree of this uncoupling. When the latter differs for different

[1] S. FREED, Journ. Am. Chem. Soc. **49**, 2456, 1927.

[2] S. FREED, l.c.

[3] S. FREED, l.c.

[4] K. HONDA and T. ISHIWARA, l.c.
  W. J. DE HAAS and C. J. GORTER, l.c.
  B. CABRERA and MARQUINA. An. Soc. Esp. Fis. y. Quim. **15**, 199, 1917.

[5] B. CABRERA and S. PIÑA, An. Soc. Esp. Fis. y Quim. **17**, 149, 1919.

[6] PH. THEODORIDES. J. de Phys. VI, III, 1, 1922.
  G. FOEX, Ann. de Phys. **16**, 174, 1921.
  H. KAMERLINGH ONNES and E. OOSTERHUIS, These Proc. Vol. **21**, p. 322, 1912, Comm. Leiden 129*b*.
  L. C. JACKSON and H. KAMERLINGH ONNES, Proc. Roy. Soc. A **104**, 671, 1923. Comm. Leiden 168*b*.
  The measurements of B. CABRERA and A. DUPERIER (J. de Phys. VI, VI 121, 1925) of solutions give θ's of about $+25°$ and have been omitted like those of FOEX and BRUNET (C. R. **184**, 443, 1927 which lead to $p = 30.0$ and $\theta = -23°$.

[7] H. KAMERLINGH ONNES and E. OOSTERHUIS, These Proc. Vol. **21**. p. 322, 1912. Comm. Leiden, 129*b*.
  K. HONDA and T. ISHIWARA, l.c.
  B. CABRERA and MOLES. An. Soc. Esp. Fis. y Quim. **10**, 216, 394, 1912. These investigators found that for great dilutions p rapidly decreases. θ however was not determined.

[8] K. HONDA en T. ISHIWARA, l.c.
  H. KAMERLINGH ONNES and E. OOSTERHUIS. l.c.
  L. C. JACKSON, l.c.
  G. FOEX, Ann. de Phys. **16**, 174, 1921.
  P. WEISS and C. A. FRANKAMP, These Proc. **18**, 254, 1915.
  B. CABRERA, MOLES and MARQUINA, An. Soc. Esp. Fys. y Quim. **13**, 256, 1915.

[9] Many measurements. See the summary of CHATILLON, Ann. de Phys. Bd. IX, 187, 1928.

[10] L. C. JACKSON, l.c.
  P. WEISS and E. D. BRUINS, These Proc. **18**, 246, 1915.

[11] PICCARD et CHARBULIEZ, Arch. Sc. Phys. et Nat. **42**, 324, 1916.
  B. CABRERA and MOLES, Arch. Sc. Phys. et Nat. **40**, 284, 1915.
  K. HONDA and T. ISHIWARA l.c.
  F. BIRCH, J. de Phys. VI, IX, 136, 1928.

compounds of the same ion, the magneton number too will vary. In fact the known variability of the magneton number is found just there (for Fe^{+++}, Co^{++}, Ni^{++} and Cu^{++}) where deviation from the BOSE-STONER values occur.

Our recent experiments show that at low temperatures the anomal magneton number is also found for Cu^{++} in high paramagnetic dilution and a certain symmetry of the electric fields caused by the crystal water, that probably surrounds the Cu^{++} ion.

This was also found for Fe^{++} [1]).

The measurements of JACKSON [1]) on $NiSO_4 . 7H_2O$ and on $NiSO_4$ $(NH_4)_2 . SO_4 . 6H_2O$ seem to indicate a different behavior of the Ni-ion in the two salts. For all hydrates of Co^{++} [2]) the curve in the $1/\chi'$, T plane shows a curvature in such a sense that the "effective magneton number" becomes lower.

In this last case the degeneration proves thus to be reduced further than for Cu^{++} and Fe^{++}. A more detailed theoretical discussion is however desirable.

§ 5. *Summary*. The susceptibility of $CuSO_4 . 5H_2O$ was measured from 290° K to 14°.29 K. This substance follows the law of CURIE-WEISS with $\theta = -0.70°$ en $p = 9.51$ W. M.

In connection with this result the theory of BOSE and STONER was developed more in detail, so that the deviations in the second part of the Fe group, and the variable magneton numbers here, can be understood.

Finally we express our thanks to Mr. J. V. D. HANDEL for his valuable help during the measurements.

[1]) L. C. JACKSON, I. c.

[2]) L. C. JACKSON, I. c.

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