Physics. — *The anomalous magnetic properties of the anhydrous chloride of copper and of the anhydrous sulphate of copper at low temperatures; the field-dependency of paramagnetism.* By W. J. DE HAAS and C. J. GORTER. (Communication N°. 215*a* from the Physical Laboratory Leyden.)

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§ 1. *Introduction.* This investigation may be regarded as the completion of earlier experiments made in this laboratory on the magnetic properties of the anhydrous chlorides and sulphates of the *Fe* group at low temperatures [1]).

It also forms part of our series of measurements on ions with one magnetic electron [2]).

§ 2. *Material.* Dr. C. GROENEVELD kindly prepared for us the anhydrous chloride, starting from the crystallized cupricsulphate "zur Analyse" from KAHLBAUM, the magnetic properties of which have been investigated by us before [3]). The anhydrous chloride was obtained by double decomposition with $BaCl_2$ and heating of the $CuCl_2 \cdot 2\,H_2O$ so obtained to a constant weight, a voluminal analysis of this salt for copper was made afterwards.

The anhydrous sulphate was obtained by heating crystallized sulphate of copper for some hours at about 250° C. in vacuo. Measurements were made with three samples of the sulphate.

Sample I was made into a rod, like those used in earlier measurements, of about 8 cm length. Sample II had a length of about 7 mm only to make measurements at the maximum of $H\frac{dH}{dx}$ possible. These were prepared separately from crystallized sulphate of copper from KAHLBAUM "zur Analyse, mit Garantieschein". As a control a sample III was still made from the crystallized sulphate of copper "zur Analyse" from MERCK. This was also in the form of a rod of ca 8 cm long.

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1) H. KAMERLINGH ONNES and E. OOSTERHUIS, Comm. Leiden 129*b*, These Proc. **15**, 322, 1912.

L. C. JACKSON, Proc. Roy. Soc. Phil. Trans. A **224**, 1, 1923, Comm. Leiden 163.

H. R. WOLTJER, Comm. Leiden 173*b*.

H. R. WOLTJER and H. KAMERLINGH ONNES, Comm. Leiden 173*c*.

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

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

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

3) W. J. DE HAAS and C. J. GORTER, l.c.

The salts being very hygroscopic, the tubes were filled with the crystal powders in an atmosphere of dry carbon dioxide. Then, as usual, the tubes were evacuated; filled with dry helium and sealed off.

§ 3. *Method and results for* $CuCl_2$. At the room temperature and the lower temperatures the measurements with $CuCl_2$ were made in the way described already in a previous paper. The susceptibility was also measured at the boiling point of water, as the measurements at the higher temperatures had rendered it dubious whether here too, as generally, the law $\chi' (T-\theta) = C$ was valid.

For different reasons this could not well be done in the ordinary glass and so a simple apparatus was constructed, consisting of a copper tube. This tube was placed in a vessel just fitting between the pole pieces of the magnet and filled with water boiling under atmospheric pressure. The vessel was furnished with a condenser and absolutely separated from the cap of the cryostat; the vessel was heated electrically. In the copper tube the sample could freely move in the air.

The exchange of heat with the surrounding air was reduced with the aid of screens in the upper part (made of German silver), of the tube.

With a mercury thermometer suspended in the same way before and after the measurements as during the measurement with the sample, we found, that within the copper tube the temperature of the air was equal to that of the boiling water.

Without alterations this simple method might also be applicable for other temperatures e.g. with the aid of the higher boiling points of organic liquids.

We used the apparatus also for one measurement at room temperature. In fig. 1, where $1/\chi'$ has been plotted against T both measurements have been indicated with a small square.

χ' has been corrected for the diamagnetism of the anion. It is found indeed, that at the higher temperatures the change of the susceptibility cannot be represented by a linear law. If we draw a straight line approximately through the points for the highest temperatures, we find:

$\chi' (T + 93.0) = 37.3$, which would correspond to a magneton number of 9.97 W.M.

To these numbers which evidently represent the change of the susceptibility very roughly only, no value whatever may be ascribed.

ISHIWARA[1]) found for room temperature $\chi = 9{,}10 \cdot 10^{-6}$. At lower temperatures his curve differs from ours in this sense, that the susceptibilities as determined by us are the smaller ones. As the susceptibilities are so small, small quantities of strongly paramagnetic impurities may have great influence already at lower temperatures.

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[1]) T. ISHIWARA, Tok. Imp. Univ. III, 303, 1914.

Results:

T	$\chi \cdot 10^6$	$\chi' \cdot 10^6$	$1/\chi' \cdot 10^{-4}$	$\chi' T \cdot 10^4$	$\chi' (T + 93.0)\, 10^4$
373.3	7.67	7.97	12.55	29.75	37.16
287.0	9.59	9.89	10.11	28.38	37.58
289.0	9.51	9.81	10.19	28.35	37.47
249.8	10.59	10.89	9.18	27.20	37.33
246.4	10.70	11.00	9.09	27.10	37.33
203.3	12.24	12.54	7.97	25.49	37.16
170.0	13.49	13.79	7.252	23.44	36.27
136.3	15.07	15.37	6.506	20.95	35.24
77.52	17.33	17.63	5.672	13.67	30.06
69.25	17.61	17.91	5.583	12.40	29.06
64.19	17.48	17.78	5.642	11.41	27.95
20.43	13.63	13.93	7.179	2.846	15.80
17.21	13.20	13.51	7.402	2.325	14.89
14.42	13.07	13.37	7.479	1.928	14.36

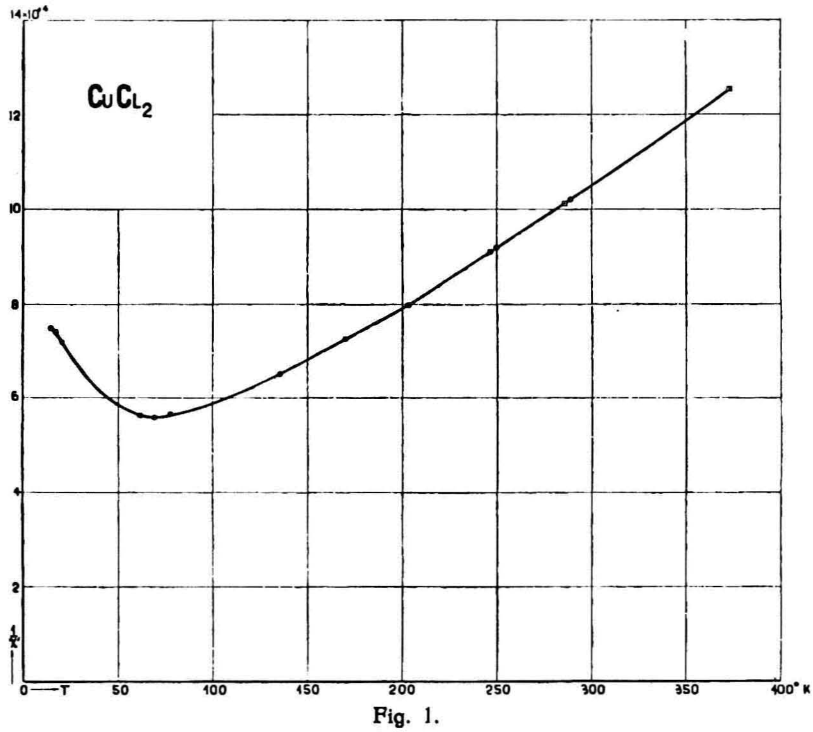

Fig. 1.

§ 4. *Discussion of the results for $CuCl_2$.* It is evident, that the magnetic behaviour of $CuCl_2$ is quite different from that of most other anhydrous chlorides of the *Fe*-group: $CrCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$ [1]) ($MnCl_2$ was not measured in a *purely* anhydrous state [2]), but seems to follow the law of CURIE—WEISS with $\theta = 1.9^\circ$), which showed a positive θ and a dependence on the field in the hydrogen region.

The susceptibility has a maximum in the nitrogen region and shows a tendency to become independent of the temperature in the hydrogen region. A similar phenomenon had been observed already for $FeSO_4$ and also for $NiSO_4$, the maximum of χ lying here between the nitrogen and hydrogen temperature.

§ 5. *Method and results for $CuSO_4$.* Sample I, prepared from the crystallized $CuSO_4$, was simply measured by the rod method. Results:

T	$\chi \cdot 10^6$	$\chi' \cdot 10^6$	$1/\chi' \cdot 10^{-4}$	$\chi' T \cdot 10^4$	$\chi' (T + 77.5) \cdot 10^4$
289.0	8.29	8.50	11.76	24.57	31.15
249.3	9.25	9.46	10.57	23.58	30.92
227.6	9.98	10.19	9.81	23.19	31.09
203.2	10.81	11.02	9.07	22.39	30.93
169.8	12.40	12.61	7.930	21.41	31.18
136.3	14.32	14.53	6.882	19.80	31.07
77.53	19.81	20.02	4.995	15.52	31.04
64.48	21.59	21.80	4.587	14.06	30.95

Evidently down to the N_2 region the law of CURIE—WEISS is valid: $\chi' (T + 77.5) = 31.05$.

This gives for the magneton number $p = 9.91$ W.M.

In fig. II $1/\chi'$ has been plotted against the absolute temperature. For $T = 294^\circ.2$ ISHIWARA [3]) found $\chi' = 8{,}26 \cdot 10^{-6}$, which is in very good agreement with our value.

At lower temperatures his results are somewhat different from ours in this sense, that our measurements give lower susceptibilities. Mlle FEYTIS [4]) found $\chi = 8{,}6 \cdot 10^{-6}$ at room temperature. In the H_2 region a dependence

1) H. R. WOLTJER, l.c.
H. R. WOLTJER and E. C. WIERSMA, l.c.

2) H. KAMERLINGH ONNES and E. OOSTERHUIS, Comm. Leiden 129*b*, These Proc. **15**, 322, 1912.

3) T. ISHIWARA, l.c.

4) Mlle FEYTIS, C. R., 152, 708.

on the field was observed, so that here the susceptibility could not be determined by the rod method.

Therefore we used the small sample II, which was placed at the maximum of $H\frac{dH}{dx}$, where as usual we determined the force acting on it. The small WEISS magnet used was calibrated topographically with great care by the aid of a little solenoid, originally used for the calibration of one of the large magnets in this laboratory.

The results were :

$H \cdot 10^{-3}$	$T = 20.40$ $\chi' \cdot 10^{-6}$	$T = 18.04$ $\chi' \cdot 10^{-6}$	$T = 16.65$ $\chi' \cdot 10^{-6}$	$T = 14.20$ $\chi' \cdot 10^{-6}$
10.00	41.6^9	41.9^9	42.1^4	42.6^7
9.12	42.0^9	42.4^7	42.6^2	43.1^4
7.85	42.2^6	42.6^8	42.8^1	43.3^4
6.04	42.4^4	43.0^1	43.1^0	43.5^8
4.06	43.1^6	43.8^1	43.8^1	44.8^7
2.43	44.1	46.0	45.0	44.9

In column I we have given the mean intensity of the field in the small region occupied by the sample. We have used here $\chi' \cdot 10^{-6}$ that is the measured value corrected for the diamagnetism of the anion. As here the forces are much weaker than in the case of the rod method, the measurements are accurate to no more than about 1 %. The accuracy for the lowest field intensity does not exceed 2 %, so that we are not sure about the occurrence of the maximum of χ' as a function of the temperature, at that field strength.

In fig. 2 the two points for $H = 10.00$ KG and $H = 4.06$ KG at hydrogen temperatures have been indicated.

In order to find out, whether the dependence on the field may perhaps be due to small quantities of impurities in the KAHLBAUM-salt and to see whether a dependence on the field could be observed, already at nitrogen temperatures we made measurements with sample III from MERCK.

The results were in good agreement with those found for sample I ; only the dependence on the temperature in the H_2 region was a little greater. It is not impossible that the small dependence on the temperature may be due to traces of impurities and that here the χ' for the pure $CuSO_4$ may be quite independent of the temperature.

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[1]) W. J. DE HAAS, E. C. WIERSMA and W. H. CAPEL, Comm. Leiden 201*b*, These Proc. **32**, 739, 1929.

In the N_2 region χ' was quite independent of the field.

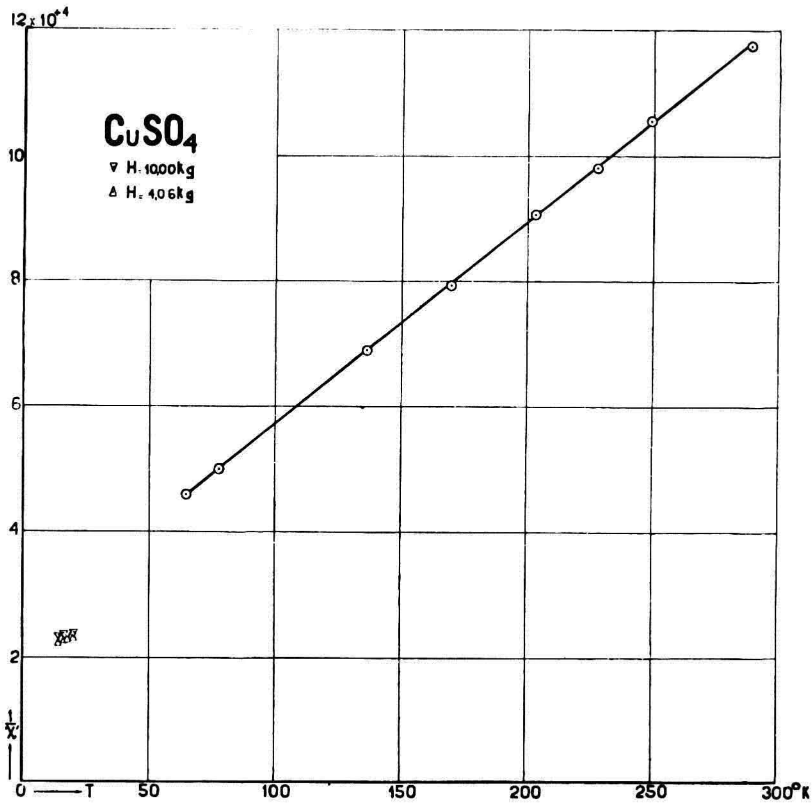

Fig. 2.

§ 6. *Discussion of the results for $CuSO_4$; the dependence on the field of paramagnetism.* The phenomenon, that for some paramagnetic substances at low temperatures the susceptibility depends on the temperature, was discovered in this laboratory by H. R. WOLTJER for $CoCl_2$, $NiCl_2$ and $CrCl_3$ [1]). At higher temperatures all these substances followed the low of CURIE—WEISS : $\chi = \frac{C}{T-\theta}$ with positive θ's and, according to the ideas of WEISS on ferromagnetism, we might expect ferromagnetic properties below this apparent "CURIE point".

In fact χ was found to become dependent on the field, but in the case of $CrCl_3$ only the susceptibility proved to decrease for higher field intensities namely to show signs of saturation.

For $NiCl_2$ and $CoCl_2$ however the susceptibility increased with the field. And from measurements with $FeCl_2$ [3]), in which not the susceptib-

[1]) H. R. WOLTJER, l.c.

[2]) P. WEISS et G. FOEX, Le magnetisme, p. 66.
H. KAMERLINGH ONNES, Congres Solvay 1921, Comm. Leiden 44a.

[3]) H. R. WOLTJER and E. C. WIERSMA, l.c.

ility but only the force exerted on a long rod of the substance was measured, we may conclude, that the susceptibility first increases and afterwards decreases again with increasing field intensity.

Evidently we have here to do with a combination of two phenomena; one of which is observed for $CrCl_2$ and $NiCl_3$ while the other is manifest for $CrCl_3$. The maximum of χ as a function of H was also found to vary with the temperature. Hysteresis could never be detected.

The paramagnetism dependent on the field proved to be always practically independent of the temperature. For $CoCl_2$ and $NiCl_2$ a weak variation inversely with the temperature was found, so that for constant field intensity χ must somewhere have a maximum.

We get the impression, that the weak temperature dependence is only a secondary phenomenon, sometimes perhaps due to impurities, and that the independence of the temperature is intimately connected with the dependence on the field.

The principal interest of our recent results lies especially in the fact, that the field dependence is not restricted to salts with positive θ's.

Thus the simple analogy between the θ's of paramagnetism and ferromagnetism, as required by the law of WEISS, is still further disturbed.

It is in the line of modern theory of magnetism to assume, that the independence of χ from the temperature found for several salts (sometimes associated with a dependency on the field) is caused by the total removal of the double degeneration of the lowest terms of the ions in question. A non-degenerated term cannot be split up in an external magnetic field; it can only undergo a shift, in first approximation proportional with the square of the field intensity (quadratic ZEEMAN-effect). This will give rise to a paramagnetism, which will be independent of the temperature, in contrast with the ordinary paramagnetism, which is due to a BOLTZMANN distribution over the different levels produced by a ZEEMAN decomposition. Probably the cause of the removal of the degeneration is the homopolar reciprocal action between the ions and their neighbours [1]).

According to our previous considerations the high positive or negative θ's which until now are always associated with the temperature-independent paramagnetism, may, perhaps, be indications of great decompositions of the fundamental terms [2]).

The phenomenon of the dependence on the field shown by some anhydrous salts or, in our way of reasoning, the non-quadratic character of the secondary ZEEMAN-effect might be ascribed either to other terms at a distance small compared with kT of the fundamental term, which might give rise to phenomena analogous with the PASCHEN—BACK-effect, or to

[1]) H. A. KRAMERS (These Proc. 33 959, 1930), has proved that electric fields can only then cancel the double degeneration of the energy terms of a system of nuclei and electrons, when the number of the electrons is even.

[2]) W. J. DE HAAS and C. J. GORTER, Comm. Leyden 208c, These Proc. 33, 676, 1930.

the reciprocal actions between the magnetic vectors of the different ions which would point to an analogy with ferromagnetism.

§ 7. *Summary.* The susceptibility of $CuCl_2$ was measured between 373°.3 K and 14°.42 K. At higher temperatures this salt does not follow the law of CURIE—WEISS. At lower temperatures we found a maximum of the susceptibility as a function of the temperature.

The susceptibility of $CuSO_4$ was measured between 289.° K and 14.°20. Down to the N_2 region the susceptibility was independent of the field and followed the law of CURIE—WEISS with $\theta = -77.5$ and $p = 8.91$ W.M.

In the H_2 region we observed a dependence on the field in the sense of saturation together with a very weak dependence on the temperature.

So evidently a dependence of the field can also exist for substances with negative θ, in contradiction with what we might expect according to the theory of WEISS.

The possible cause of these phenomena was discussed and we expressed the supposition, that we have always to do with non-degenerated fundamental terms, when at low temperatures χ is independent of the temperature.