Physics. — *The susceptibilities of ceriumchloride and praseodymium sulphate at low temperatures.* By C. J. GORTER, W. J. DE HAAS and J. VAN DEN HANDEL. (Communication N⁰. 218c from the physical laboratory, Leiden.)

§ 1. *Introduction.* This investigation forms part of the series of investigations in the Leyden laboratory on the magnetic behaviour of compounds of rare earths at low temperatures [1]).

One of our previous investigations found its origin in the measurements of J. BECQUEREL and one of us on the paramagnetic rotation in crystals of tysonite [2]) and the theory, by BECQUEREL and KRAMERS [3]), which is based upon these measurements. We found the magneton number in CeF_3 at room temperature [4]) to correspond very well with that given by HUND [5]) for the free ion. At low temperatures however the effective magneton number decreases as was expected from the magnetic rotation. From this behaviour it is evident that in the CeF_3 no uncoupling of spin and orbit occurs, as was assumed by BECQUEREL and KRAMERS. It seemed to us worth while trying to find out, whether also other cerium salts show an analogous behaviour. The anhydrous $CeCl_3$ was the first salt we investigated.

With a view to the decomposition, which a degenerated energy term can undergo in an electric field it is of great importance to know whether the system contains an even or an odd number of electrons. This has recently been pointed out by KRAMERS [6]). In the first case it is possible, that non-degenerated terms occur, which evidently will have no magnetic moment. In the second case this is impossible, so that (in a system with one nucleus) we always have a magnetic moment.

As never as yet a compound of one of the rare earths with an

[1]) H. KAMERLINGH ONNES and E. OOSTERHUIS, Leiden Comm. 129b. H. R. WOLTJER, These Proc. **24**, 613, 1923, Leiden Comm. 167b. H. R. WOLTJER and H. KAMERLINGH ONNES, These Proc. **24**, 626, 1923, Leiden Comm. 167c. L. C. JACKSON and H. KAMERLINGH ONNES, C. R. **177**, 154, 1925, Leiden Comm. 168a. W. J. DE HAAS, E. C. WIERSMA and W. H. CAPEL, These Proc. **32**, 739, 1929, Leiden Comm. 201b. W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 949, 1930 and **34**, 1243, 1931, Leiden Comm. 210c and 218b.

[2]) JEAN BECQUEREL and W. J. DE HAAS, These Proc. **32**, 536, 1930, Leiden Comm. 193a.

[3]) JEAN BECQUEREL and H. A. KRAMERS, These Proc. **32**, 1176, 1930, Leiden Comm. Suppl. 68.

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

[5]) F. HUND, Zs. f. Phys. **33**, 855, 1925.

[6]) H. A. KRAMERS, These Proc. **33**, 959, 1930.

even number of electrons had been investigated magnetically at low temperatures, two of us measured the susceptibility of $Pr_2 (SO_4)_3 . 8H_2O$ [1]).

In the hydrogen region the susceptibility was found to become independent of T, which was to be expected, if the lowest level was a non-degenerated term.

Now it would be interesting to see, whether also other compounds of the rare earths with an even number of electrons show the same behaviour. For the moment however the only one of these metals with an even nuclear charge and of sufficient purity at our disposition was the Pr. So we only could vary the electric field and not the ion. For our investigations we chose the anhydrous $Pr_2 (SO_4)_3$.

§ 2. *Material and method.* Dr. GRONEVELD kindly prepared for us the $CeCl_3$, starting from the pure ceriumnitrate from the Auer-Co., from
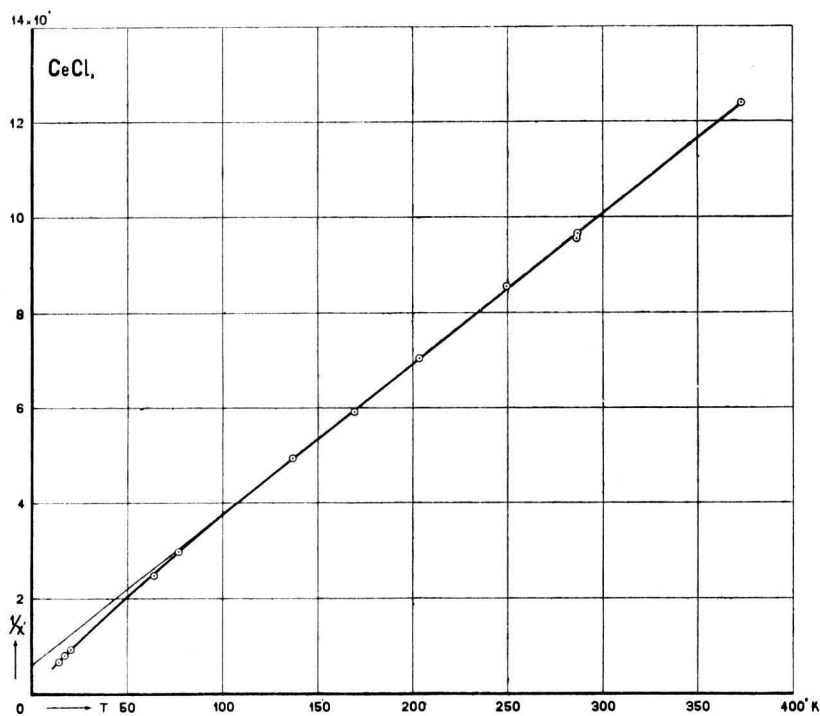

Fig. 1.

which the CeF_3 too had been prepared. The nitrate was treated with hydrochloric acid; the chloride thus obtained was dried by heating in a current of dry HCl.

We obtained the $Pr_2 (SO_4)_3$ by freeing the rest of the very pure $Pr_2 (SO_4)_3 . 8H_2O$ (kindly put at our disposition by Prof. URBAIN) of its crystal water.

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

As the substances were very hygroscopic the tubes were filled in an atmosphere of dry carbonic acid. The measuring methods were the same as those described in the former papers [1]). The two measurements made in the boiling-water-apparatus have been indicated with a little quadrangle.

§ 3. *Results.* The results for $CeCl_3$ were:

T	$\chi . 10^6$	$\chi' . 10^6$	$1/\chi' . 10^{-4}$	$\chi'.T . 10^4$	$\chi(T+20.0).10^4$
373.2	7.79	8.07	12.39²	30.12	31.73
286.5	10.17	10.45	9.57	29.94	32.03
287.0	10.08	10.36	9.55	29.73	31.81
249.5	11.43	11.71	7.87	29.22	31.56
203.3	13.92	14.20	7.04	28.87	31.71
169.5	16.60	16.88	5.92	28.61	31.99
137.2	19.97	20.25	4.94	27.78	31.83
77.52	33.2⁰	33.4⁸	2.98⁷	25.95	32.65
64.22	39.0⁴	39.3²	2.48⁰	25.85	33.96
20.42	106.6	106.9	8.935	21.83	43.91
17.25	124.7	125.0	0.800	21.56	46.56
14.35	149.0	149.3	0.670	21.42	51.28

Above the temperatures of liquid nitrogen the CURIE-WEISS law is seen to be followed with $\chi' (T + 20.0) = 31.81 . 10^{-4}$, which corresponds with $p = 12.46$.

At lower temperatures the line in the $1/\chi'$-T-diagram is curved toward the T-axis. The effective magneton number [2]) decreased from 12.13 at 273°.2 to 10.23 at 14°.25. These values are in good agreement with our measurements with CeF_3, which gave $p = 12.49$ and with the theory of HUND [3]), which gives $p = 12.5^6$.

The results for $Pr_2 (SO_4)_3$ have been given in the second table.

In fig. 2 $1/\chi'$ has again been plotted against T. The CURIE-WEISS-law is found to be valid from the nitrogen temperatures upward with: $\chi' (T + 45.0) = 57.43 . 10^{-4}$, which corresponds with $p = 18.00$. At lower temperatures the T-line is curved towards the T-axis.

The magneton number is in good agreement with the value found for

[1]) W. J. DE HAAS and C. J. GORTER, These Proc. **33**, 949, 1930 and **34**, 317, 1931 Leiden Comm. 208c and 215a.

[2]) See Comm. 210c.

[3]) F. HUND l.c.

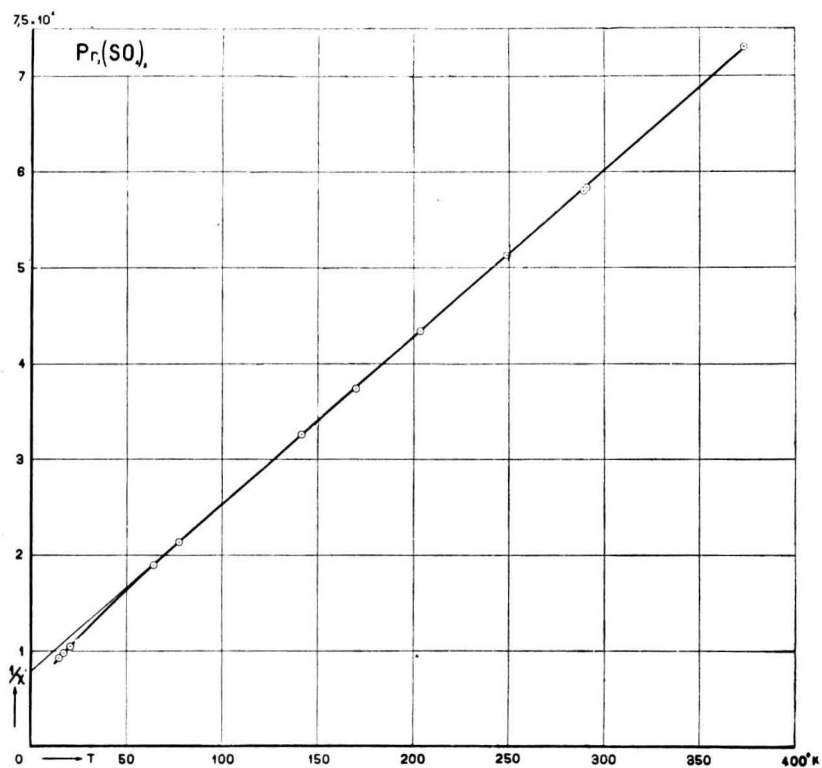| T	$\chi \cdot 10^6$	$\chi' \cdot 10^6$	$1/\chi' \cdot 10^{-4}$	$\chi' \cdot T \cdot 10^4$	$\chi'(T+45.0) \cdot 10^4$
373.6	13.50	13.68	7.31	51.11	57.26
291.0	16.95	17 13	5.84	49.05	57.56
289.5	17.06	17.24	5.80	49.90	57.67
249.0	19.32	19.50	5.13	48.56	57 33
203.6	22.89	23.07	4.34	46.97	57.35
169.7	26.61	26.79	3.73³	45.45	57.52
141.5	30.55	30.73	3.25⁴	43.48	57.31
77.44	46.7	46.9	2.13²	36.32	57.42
64.17	52.8	53.0	1.88⁷	34.01	57.86
20.44	95.5	95.7	1.045	19.56	62.63
17.20	101.6	101.8	0.982	17.51	63.32
14.67	107.5	107.7	0.929	13.80	64.26

Fig. 2.

$Pr_2 (SO_4)_3 . 8H_2O$ ($p = 17.90$ WM) and with the value predicted by HUND ($p = 17.71$) especially when we consider the small temperature independent paramagnetism that must exist in Pr''' [1]).

CABRERA, who has measured with the same material (from AUER VON WELSBACH) gives between 293° K and 673° K the formula: $(M\chi - 160) \times (T + 41.2) = C$ [2]) where C corresponds with $p = 18.05$ WM. This gives again for $T = 373°.6$ and $289°.5$ resp. $\chi' = 14.48$ and $\chi' = 18.12$.

We don't know the cause of this difference between CABRERA's measurements and ours. As however a temperature independent magnetism as large, as has been found by CABRERA, is not to be expected from the theory [3]), we may remark, that our results are somewhat better in agreement with recent theoretical conceptions.

§ 4. *Discussion of the results.* $CeCl_3$ shows a behaviour quite analogous to that of CeF_3, with a lower value only of $|\theta|$. This might be due to the greater electric forces which are exerted on the Ce^{+++}ion by the F-ion because of its small radius.

An analogous phenomenon is found for the praseodymium salts. The $|\theta|$ for $Pr_2 (SO_4)_3$ is higher than for the octahydrate (where probably the water molecules round the metal ion will be the cause of weak fields.

Further it is evident that in the H_2 region the susceptibility of $Pr_2(SO_4)_3$ does not become dependent on the temperature. On the contrary the $1/\chi'$-T-curve becomes there steeper. We therefore have no reason to assume here that the lowest term is not doubly degenerated [4]). As might have been expected, an even number of electrons is a necessary but not a sufficient condition for the occurrence of a temperature independent paramagnetism : the decisive factor is the nature of the electric fields.

§ 5. *Summary.* The susceptibilities of $CeCl_3$ and $Pr_2 (SO_4)_3$ were measured between 373° and 14° K. The behaviour of $CeCl_3$ is quite analogous to that of CeF_3. At higher temperatures the law of CURIE-WEISS is followed with $\chi (T - 21.0) = 31.81 . 10^{-4}$, which gives $p = 12.46$ WM. At lower temperatures the $1/\chi'$-T-line is curved towards the T-axis.

$Pr_2 (SO_4)_3$ too follows the law of CURIE-WEISS with $\chi (T - 45.0) = 57.43 . 10^{-14}$, which gives $p = 18.00$ WM. Though the number of electrons is even, so that according to KRAMERS non-degenerated terms may occur, this character of the lowest term could not be proved.

The magneton numbers obtained are in good agreement with the predictions of HUND.

[1]) J. H. v. VLECK and A. FRANK, Phys. Rev. **34**, 1494, 1929.

[2]) B. CABRERA, J. de Phys. VI, **6**, 273, 1925. B. CABRERA and A. DUPERRIER, C. R. **188**, 1640, 1929.

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

[4]) It may be, that this is still the case, but that the decompositions are so small, that they could only be detected at still lower temperatures.