Physics. — "*Further experiments with liquid helium. T. Magnetic researches.* XXIII. *On the magnetisation of gadolinium sulphate at temperatures obtainable with liquid helium.*" By H. R. WOLTJER and H. KAMERLINGH ONNES. (Communication N°. 167*c* from the Physical Laboratory at Leiden).

(Communicated at the meeting of September 29, 1923).

§ 1. *Introduction.* Previous[1]) preliminary researches and a detailed discussion[2]) of the results then obtained have shown the importance of a closer investigation of the magnetisation of gadolinium sulphate at very low temperatures: this substance is one of the comparatively few, that follow CURIE's law down to the region of temperatures obtainable with liquid hydrogen. Now in the light of LANGEVIN's theory the CURIE law holds only approximately, viz. as long as the susceptibility may be considered to be independent of the field strength: LANGEVIN gives for the ratio of the specific magnetisation, σ, to the specific saturation magnetisation, σ_∞,

$$\sigma : \sigma_\infty = cotgh\, a - \frac{1}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

$$a = \frac{\sigma_{m_\infty}}{R} \cdot \frac{H}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

(σ_{m_∞} being the saturation magnetisation of one gram molecule, R the gas constant per grm. mol., H the magnetic field applied and T the absolute temperature).

For small values of a

$$\sigma : \sigma_\infty = \frac{1}{3} a \quad \text{or} \quad \chi = \frac{\sigma}{H} = \frac{\sigma_\infty \cdot \sigma_{m_\infty}}{3R} \cdot \frac{1}{T} \quad . \quad . \quad . \quad . \quad (2)$$

If T is small and thus a large, χ is no longer independent of H, but the curve $\sigma : \sigma_\infty = f(a)$ deviates from the straight line $\sigma : \sigma_\infty = \frac{1}{3} a$, becomes concave towards the a-axis and approaches asymptotically to $\sigma : \sigma_\infty = 1$ (cf. fig.) The detailed discussion of the preliminary experiments has already made very problable the existence

[1]) H. KAMERLINGH ONNES, these Proceedings 17, p. 283; Leiden Comm. N°. 140d.

[2]) H. KAMERLINGH ONNES, Rapport Solvay 1921, p. 131; Leiden Comm. Suppl. N°. 44a. 1.

of deviations of this type. Yet it is not to be expected a priori that LANGEVIN's theory would be followed in this case, for this theory has been deduced for a gas with perfect rotational freedom of the molecules and starts from the assumption of the equipartition of energy in al degrees of freedom. Now the case of powdered gadolinium sulphate at low temperatures does not correspond to either of these assumptions. It is true that LANGEVIN's theory has been extended by WEISS [1]) to powdered crystals, but WEISS confines himself to small values of the parameter a; on the other hand EHRENFEST [2]) has developed a theory in which the relatition (2) is obtained for crystal powders on the assumption of the existence of quanta but then the saturation magnetisation is only half the value corresponding to perfect parallelism of all elementary magnets and in the preliminary experiments a higher value seemed to be reached.

Confirmation and extension of the preliminary results was thus very desirable; the same method has been followed as in the previous work: the specific magnetisation, σ, is calculated from the force F (in grammes) exerted on the mass m by an inhomogeneous magnetic field with aid of the formula $Fg = m\sigma \frac{\partial H}{\partial z}$. A detailed study of the apparatus, the corrections and the sources of error, a comprehensive account of which has been given in the preceding communication [3]), has made it possible to attain a much greater accuracy than in the previous work, at least as far as the magnetic measurements are concerned. The determination of the temperature from the vapour pressure of the bath is still a weak point, especially since the vapour pressure law is as yet not sufficiently well known [4]). The research relates to the same tubes, *Gd I* and *Gd II*, that have served for the research in liquid hydrogen and that have been mentioned in the preceding communication (§ 3*c*).

§ 2. *Observations.* The direct results of the observations may be given first: tables I and II (I being the number of ampères in the magnet coils; H_0 the field strength, in gauss, in the centre; F the force in grammes, on the total mass of substance).

With *Gd II* between the points N°. 15 and N°. 28 points have been left out in which the observations have been taken at increas-

[1]) P. WEISS, Paris C. R. 156 (1913) p. 1674. According to O. STERN (Zs. f. Phys. 1 (1920) p. 147) WEISS' deduction is not sound.

[2]) P. EHRENFEST, these Proceedings 23, p. 989; Leiden Comm. Suppl. N°. 44b.

[3]) H. R. WOLTJER, these Proceedings p. 613; Leiden Comm. No. 167*b*.

[4]) l. c. § 3*e*.

TABLE I.

Gadolinium sulphate I						
Date	Vapour pressure	T	Nr.	I	H_0	F
March 1th, 1923	761 mm.[1])	4°.20 K.	1	30	17320	90.14
"	"	"	2	20	12940	55.26
"	"	"	3	10	6605	15.76
"	"	"	4	5	3295	3.89
"	"	"	5	5	3295	4.01
"	"	"	6	15	9875	33.83
"	"	"	7	30	17320	89.94
"	"	"	8	60	21600	114.76
"	"	"	9	70	22230	117.81
"	"	"	10	45	20235	109.54
"	"	"	11	30	17320	90.96
"	360 mm.	3°.53 "	12	70	22230	136.93
"	"	"	13	45	20235	123.42
"	"	"	14	30	17320	103.78
"	"	"	15	20	12940	65.61
"	"	"	16	10	6605	19.04
"	"	"	17	5	3295	4.76
"	"	"	18	5	3295	4.75
"	"	"	19	15	9875	40.26
"	"	"	20	30	17320	102.54
"	"	"	21	60	21600	129.12
"	"	"	[22	70	22230	130.68
"	100 mm.	2°.73 "	[23	70	22230	152.27]
"	"	"	24	45	20235	148.13
"	"	"	25	30	17320	121.71
"	"	"	26	20	12940	79.75
"	"	"	27	10	6605	24.36
"	"	"	[28	5	3295	6.12]
"	763 mm.	4°.20 "	29	30	17320	91.11
"	9.5 mm.	$1°.66_5$ "	30	70	22230	173.70
"	4 mm.	1°.48 "	[31	60	21600	173.41]

[1]) The difference between international and local m.m. mercury (these Proceedings 21 p. 658 note 2; Leiden Comm. No. 152*d* p 47, note 4)) is here of no importance.

TABLE II.

Gadolinium sulphate II						
Date	Vapour pressure	T	Nr.	I	H_0	F
April 13th, 1923	761 mm.	4°.20 K.	1	60	21600	108.27
"	"	"	2	30	17320	85.67
"	"	"	3	15	9875	32.44
"	"	"	4	5	3295	3.74
"	"	"	5	5	3295	3.77
"	"	"	6	10	6605	15.10
"	"	"	7	20	12940	53.00
"	"	"	8	30	17320	85.80
"	"	"	9	45	20235	102.76
"	"	"	10	60	21600	108.04
"	300 mm.	3°.40 "	11	30	17320	98.48
"	39 mm.	2°.30 "	12	30	17320	119.86
"	4 mm.	1°.48 "	13	30	17320	133.53
"	"	"	14	60	21600	152.29
"	"	"	15	30	17320	133.59
"	759 mm.	4°.20 "	28	30	17320	85.48
"	2.9 mm.	$1°.41_5$ "	29	70	22230	156.36
"	"	"	30	45	20235	152.69
"	"	"	31	30	17320	136.30
"	"	"	32	5	3295	10.20
"	"	"	33	4	2627	6.46
"	"	"	34	3	1960	3.68
"	1.7 mm.	1°.31 "	35	70	22230	157.74
"	"	"	36	60	21600	157.72

ing pressure in order to test whether temperature corresponded to pressure, the only stirring possible being made by the moving up and down of the carrier [1]). The magnetisations observed pointed to much lower temperatures than corresponded to the actual pressures and thus to a large temperature lag. Therefore these points have been left out of consideration.

§ 3. *Discussion.* For *Gd II* 0,02024 [2]) has been accepted as Curie-constant and with this value σ_∞ and $\sigma_{m\infty}$ have been calculated according to formula (2). Half the real molecular weight has been used in calculating $\sigma_{m\infty}$ from σ_∞, as the *atoms* of *Gd* are assumed to have rotational freedom. This is usually done for salts containing more than one metal atom in the molecule [3]); moreover, if the whole molecular weight had been taken, $\sigma_{m\infty}$ would have become $\sqrt{2}$ larger, σ_∞ $\sqrt{2}$ smaller and thus $\sigma : \sigma_\infty$ again $\sqrt{2}$ larger and one would have found values larger than 1, as for $\sigma : \sigma_\infty$ the value 0.84 has been attained (Cf. table IV).

We find:

$$\sigma_{m\infty} = 434{,}2 \times 10^2 \text{ (38.65 WEISS-magnetons).}$$
$$\sigma_\infty = 116{,}25.$$

For the Curie constant of *Gd I* we found [4])

$$C = 0{,}02149$$
$$\sigma_{m\infty} = 447{,}4 \cdot 10^2 \text{ (39.82 WEISS-magnetons)}$$
$$\sigma_\infty = 119{,}79.$$

From the tables I and II $\sigma : \sigma_\infty$ and a have been calculated for *Gd I* and *Gd II*, with its own particular Curie constant for each substance. The results have been collected in tables III and IV. The values placed in square brackets are a priori less reliable, mostly because during or immediately after the measurement the gadolinium sulphate appeared to be not sufficiently below the liquid helium level [5]). The differences between the observed values of $\sigma : \sigma_\infty$ and

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[1]) l.c. § 3*e*.

[2]) Cf. the preceding communication § 4, where on account of a later somewhat modified calculation 0,02030 has been given. The difference is of no importance.

[3]) P. WEISS, Arch. d. Sc. phys. et nat. (4) 31 (1911).
B. CABRERA, J. de Chim. Phys. 6 (1918) p. 442, especially p. 462.

[4]) Cf. the preceding communication § 4, where the difference between both results has been discussed.

[5]) At the points marked with an asterisk the helium level was certainly below the spring V_2 (cf. the preceding communication § 3*a*). Though a general tendency to higher values of $\sigma : \sigma_\infty$ (cf. the diagram) must be acknowledged to exist, there is no systematic difference between the points with and without asterisk.

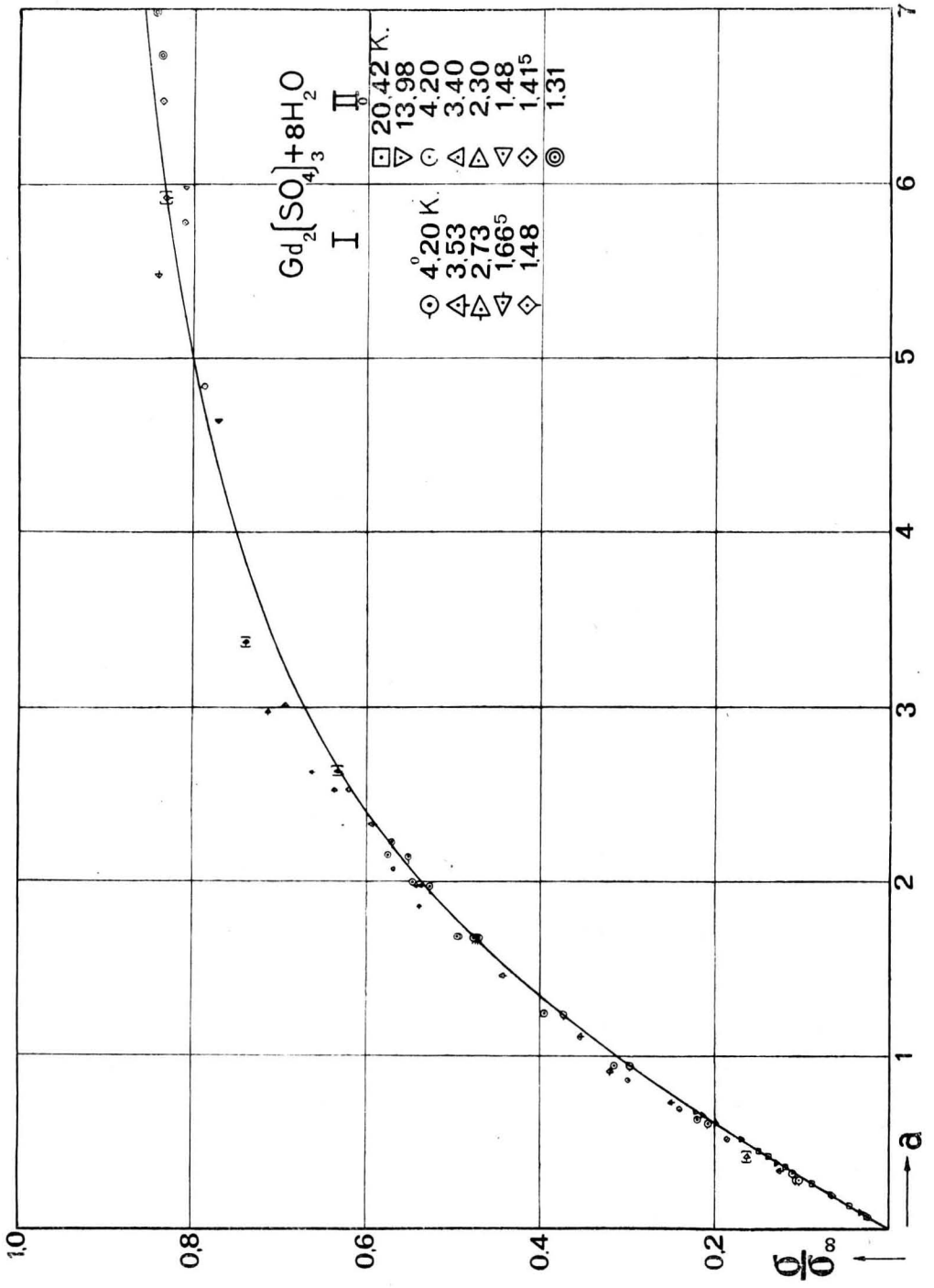
TABLE III. Gadolinium sulphate I.

I	4°.20 K.				3°.53 K.				2°.73 K.				1°.66$_5$ K.				1°.48 K.			
	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100 . \frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100 . \frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100 . \frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100 . \frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100 . \frac{O-C}{O}$
5	4	0.2888	0 1036	+ 7.6	17*	0.3384	0.1268	+11 7	[28*	0.4267	0.1630	+13.8]								
"	5	0.2882	0.1068	+10.5	18*	0 3384	0.1266	+11.6												
10	3	0.6174	0.2075	+ 3.2	16*	0.7246	0.2508	+ 6.9	27*	0.9162	0.3208	+ 9.8								
15	6	0.9408	0.2977	+ 0.4	19*	1.106	0.3544	+ 3.6												
20	2	1.239	0.3732	− 0.8	15*	1.458	0 4430	+ 3.2	26	1.857	0 5384	+ 5.0								
30	1	1.675	0.4710	− 1.0	14*	1.976	0.5425	+ 1.7	25	2.528	0.6362	+ 3.0								
"	7	1.675	0.4700	− 1.2	20*	1.977	0.5360	+ 0.5												
"	11	1.673	0.4753	0.0																
"	29*	1.673	0.4763	+ 0.2																
45	10	1 970	0.5269	− 1.0	13	2.328	0.5936	+ 0.7	24	2.975	0.7124	+ 6 1					[31*	5.917	0.8339	+ 0.3]
60	8	2.140	0.5516	− 1.7	21*	2 529	0.6209	+ 0 6												
70	9	2 223	0.5702	− 0.6	12	2.624	0.6627	+ 5.0	[23	3.371	0 7369	+ 4.2]	30*	5.475	0.8406	+ 2.8				
"					[22*	2.631	0.6324	+ 0.3]												

TABLE IV. Gadolinium sulphate II

	4°.20 K.				3°.40 K.				2°.30 K.				1°.48 K.				1°.41$_5$ K.				1°.31 K.			
I	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100.\frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100.\frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100.\frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{osb.}$	$100.\frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100.\frac{O-C}{O}$	Nr.	*a.*	$\left(\frac{\sigma}{\sigma_\infty}\right)_{obs.}$	$100.\frac{O-C}{O}$
3																	34*	0.5260	0.1854	+ 7.1				
4																	33	0.6952	0.2403	+ 6.5				
5	4	0.3238	0.1102	+ 2.7													32	0.8587	0.3005	+ 9.1				
"	5	0.3238	0.1111	+ 3 5																				
10	6	0 6315	0.2199	+ 6.7																				
15	3	0 9433	0.3157	+ 5.9																				
20	7	1.243	0.3956	+ 4.7																				
30	2	1.682	0.4951	+ 3.6	11	2.063	0.5691	+ 3.7	12	3.009	0.6928	+ 2.9	13	4.634	0.7716	— 1.7	31	4.839	0.7878	— 0.7				
"	8	1.682	0.4959	+ 3.8									15*	4 634	0.7721	— 1.6								
"	28*	1.684	0.4941	+ 3.3																				
45	9	1.995	0.5464	+ 1.8													30	5.777	0.8119	— 1.8				
60	1	2.150	0.5756	+ 2.3									14*	5.978	0.8096	— 2.9					36*	6.738	0.8385	— 1.6
"	10	2.150	0.5744	+ 2.1																				
70																	29	6.467	0.8365	— 1.1	35*	6 982	0.8439	— 1.5

the values calculated according to LANGEVIN's formula, expressed in percents of the observed value, are given in the columns headed $100.\frac{O-C}{O}$.



It cannot be denied that while on the one hand, one gets the strong impression that LANGEVIN's formula is followed (cf. the figure, in which the LANGEVIN curve and the observed points have been drawn), on the other hand the deviations are larger than was anticipated. However they may be explained from the sources of error. Besides all that has been said in the preceding communication as to the accuracy, it must be pointed out that the larger deviations occur especially at the lower field strength values, where the topographical corrections are rather uncertain and also the measurements of the field strength less reliable. Further, the magnetic moment acting at the very low temperatures is so large that the assumption of a rigid distribution of the magnetism on the pole faces (and on this assumption the field measurements and the determination of the topographical corrections are more or less based) certainly holds no longer.

Moreover it must be observed, that errors in σ_∞ and in H, exert on the abscissae an influence opposite in direction to that on the ordinates and thus appear greater in the diagram. Taking all these circumstances into account, especially also the uncertainty of the demagnetisation, it may be concluded, that powdered gadolinium sulphate follows LANGEVIN's formula down to about 1°.3 K; thus it seems possible to use the magnetic susceptibility of gadolinium sulphate in thermometry.

§ 4. *Results.* The specific magnetisation of powdered hydrated gadolinium sulphate has been investigated for the temperatures of liquid hydrogen and liquid helium. It appears that though the fundamental assumptions to LANGEVIN's theory do not apply, yet LANGEVIN's formula is followed. For the parameter a of LANGEVIN's theory the value 7 has nearly been reached. The highest magnetisations obtained are about 84 % of the magnetisation corresponding to perfect parallelism of all elementary magnets. This result is independent of the uncertainties in the temperature and the value of the demagnetising field. So it appears that Prof. EHRENFEST's theory is here not applicable without further extension, since this theory (which is based on quanta assumptions and holds, contrary, to LANGEVIN's theory, directly for crystal powders) gives for the saturation magnetisation only 50 % of the value mentioned.