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H. Kamerlingh Onnes & E. Oosterhuis, Magnetic researches. VII. On paramagnetism at low temperatures, in: KNAW, Proceedings, 15 II, 1912-1913, Amsterdam, 1913, pp. 965-971

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curve. (The observations for xenon, however, extend only to t = 0.7). The cause of this correspondence can well be explained on the assumption <sup>1</sup>) that the contracting influence of the simpler molecule and the diverging influence of the comparatively high critical temperature ( $+16^{\circ}.6$  C) have, at least in part, cancelled each other.

Physics. — Magnetic researches, VII. On paramagnetism at low temperatures (continued). By H. KAMERLINGH ONNES and E. OOSTERHUIS. Communication N<sup>o</sup>. 132e from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of December 28, 1912).

§ 9. Crystallized manganese sulphate. The salt was procured from MERCK as puriss. pro analysi. The results were <sup>2</sup>):

TABLE VII. Crystallized manganese sulphate MnSO <sub>4</sub> .4H <sub>2</sub> O. (I).					
T	106	z. T.10 <sup>6</sup>	Limits of H	Bath	
288°.7 K.	- 66.3	19140	10000-17000	Air.	
169.6	111.5	18910	8000 - 17000	Liquid ethylene.	
77.4	247	19120			
70.5	270	19030	6000—16000	Liquid nitrogen.	
64.9	- 292	18950	1		
		•			
20,1	914	18370			
17.8	1021	<sup>.</sup> 18170	4000	Liquid hydrogen.	
14.4	1233	17760	)		

Down to and at nitrogen temperatures, this substance follows pretty much the law of CURIE.

<sup>1</sup>) See N<sup>0</sup>, 34 of Enc. Math. Wiss. V. 10, Suppl. N<sup>0</sup>, 23.

<sup>2</sup>) Prof. WEISS has kindly informed us that in the determination of standards of susceptibility in Zürich, for this substance  $\chi = 66.77.10^{-6}$  at 14° 2 C. was found.

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§ 10. Anhydrous manganese sulphate. All the water was driven out of the salt by heating.

The results are given in Table VIII.

With anhydrous manganese sulphate another divergence from the law of CURIE over the whole field of low temperatures was found. Down to nitrogen temperatures, however, it is only a disturbance of the first kind. At hydrogen temperatures a further disturbance shows itself which is not unlike the disturbances with solid oxygen, and at any rate belongs to a kind of disturbances that we have notyet been able to reduce to a definite type. It is remarkable that just as with crystallized ferrous sulphate the presence of molecules of water of crystallization causes a diminution of the quantity  $\Delta'$  to a very small value in comparison with that of the anhydrous sub-

TABLE VIII. Anhydrous manganese sulphate $MnSO_4$ . (I). $\triangle' = 24^\circ$ .					
Ţ	×.10 <sup>6</sup>	$\chi(T+\Delta')10^6$	Limits of H	Bath	
293°.9 K.	87.8	27910	6—17 kilog.	Air.	
169.6	144.2	27920	5—17	Liquid ethylene.	
77.4	274.8	27870	1 - 10	Liquid nitrogen.	
64.9	314.5	27960	) 5-10		
20.1	603	26590	1		
17.8	627	26210	4—16	Liquid hydrogen.	
14.4	636	24420	1		

stance, here too  $\Delta'$  becomes less by the addition of molecules of water of crystallization, and to such a degree, that, if one does not go below nitrogen temperatures  $\Delta'$  appears to have become = 0, whereas with anhydrous salt  $\Delta' = 24^{\circ}$ .

If we calculate the number of magnetons for the crystallized salt with  $C = \chi T(\Delta'=0)$  and for the anhydrous with  $C' = \chi(T+\Delta')$  and with  $\Delta' = 24^{\circ}$ , we find the same number of magnetons in both cases, viz. 29. This is one less than is found in the solution <sup>1</sup>).

1) P. WEISS, Journal de physique, 1911, p. 976.

§ 11. Further observations upon ferrous sulphate and ferric sulphate. After the conclusion of the investigation treated in Comm. N<sup>o</sup>. 129b, we turned to the determination of the water contained in the preparations ferrous sulphate I and ferrous sulphate III.

Prof. VAN ITALLIE kindly investigated the preparations and found that they contained ferric as well as ferrous sulphate. They cannot therefore be taken as a reliable basis for calculations of the number of magnetons, and to make these possible the measurements will be repeated with purer preparations.

The quantitative result arrived at in Comm. Nº. 129b concerning the appearance of disturbances of the first kind in CURIE's law and the possibility of finding the constant of CURIE for these substances by means of a correction, still retains its value.

As regards the ferric sulphate, which the measurements in § 4 of Comm. N°. 129b referred to, the admixture of water may be put at about 1/7 in first approximation. The molecular susceptibility of ferrous sulphate is therefore 1/7 smaller than that of ferric sulphate, so that valency shows its influence in this iron salt also; all this in contradiction to what was observed in § 4.

We must also remark, that the sign and the order of magnitude of the corrections which would be necessary to deduce the number of magnetons for the pure materials from the measurements of the ferrous sulphate I of our Comm. N<sup>o</sup>. 129b and those of the crystallized ferrous sulphate of KAMERLINGH ONNES and PERRIER in Comm. N<sup>o</sup>. 122a, make it seem possible that there is a double analogy between ferrous sulphate and manganese sulphate. Just as in manganese sulphate the number of magnetons in the crystallized and in the anhydrous substance is equal, the same would be found for crystallized and anhydrous ferrous sulphate (viz. 26) (if for the anhydrous substance CURRE's constant is calculated with the help of the correction by  $\Delta' = 31^{\circ}$ ), and in further analogy with manganese sulphate, this number with ferrous sulphate is also one less than in the solution, if for the latter one may take the number, that has been found by WILLS <sup>1</sup>).

Should the disappearance of  $\Delta'$  with the introduction of water molecules be ascribable to the increase of distance between the iron atoms which is caused thereby, then it would be possible that with different contents of water of crystallization  $\Delta'$  decreases with the increase of the number of molecules of water of crystallization. We intend therefore, to examine a salt in this respect, that crystallizes ")

<sup>&</sup>lt;sup>1</sup>) P. WEISS. Journ. de physique 1911. p. 977.

<sup>&</sup>lt;sup>2</sup>) Compare the investigation of Mlle FEYTIS, C. R. 153, p. 668. 1911 on the

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with a series of different numbers of molecules of water of crystallization, and from that to deduce a possible dependence of  $\Delta'$  upon the density.

§ 12. *Platinum*. A small cylinder of pure platinum from HERAEUS was examined. The susceptibility changes very little with the temperature. On account of its small value it is difficult to determine  $\chi$  accurately. The results are contained in Table IX.

	TABLE IX. Platinum I.	
. <u>T</u>	х.10 <sup>6</sup>	Limit value of <i>H</i> in Kilogauss.
290 <sup>°</sup> .2 <i>K</i>	0.973	
77.4	1.061	11 17
20.1	1.080	
14.4	1.087	

The value at ordinary temperature lies about the middle of those of OWEN, 0.80 resp. 0.89, HONDA 1.097, KOENIGSBERGER 1.35, FINKE 1.06 (all at 18° C.). If one wished to go so far with the application of the rule  $C' = \chi (T + \Delta')$  that one applied it to platinum also, then it would follow from this that  $\Delta' = 2440^{\circ}$ , and for the number of magnetons *n* calculated from C' the value n = 10.

§ 13. Dysprosium oxide Referring to the data of § 7, we observe that, as will also appear from a further communication of KAMER-LINGH ONNES and PERRIER, all the values of  $\chi$  which occur there must be increased in the ratio of 1:1.065. By applying this correction also the difference from the value at ordinary temperature found by Mlle FETTIS which was stated upon in § 2 of Comm. N°. 122*a* and which was due to an error of calculation, is reduced to a divergence within the limits of accuracy; hence the dysprosium oxide appears to have been about in the same condition as the sample used by her. Our conclusions undergo no change by the correction.

influence of the successive molecules of water of crystallization upon  $\chi$ . This might be the consequence of a change in  $\Delta'$  with an unchanged number of magnetons.

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§ 14. Oxygen. The susceptibility of liquid oxygen has been determined by KAMERLINGH ONNES and PERRIER by two methods. It has now also been investigated by the attraction method in about the same way as the susceptibility of liquid hydrogen in Comm. N<sup>o</sup>. 122a. An evacuated cylindrical glass tube was hung in the magnetic field and then the repulsion measured that the tube underwent when the surrounding space was filled with liquid oxygen. The value found at  $T = 90^{\circ}$ . 1 K. agrees well with that in Comm. N<sup>o</sup>. 116; the small difference at the other temperatures is explained by the fact that the temperatures could not be very accurately ascertained.

In the following table the values found stand beside those of KAMERLINGH ONNES and PERRIER according to their formula  $\chi V T = 2.284.10^{-3}$ .

The question naturally arises whether the behaviour of liquid oxygen can also be represented by the formula  $C' = \chi(T + \Delta')$ . If we assume that  $\Delta' = 71^{\circ}$  this comes out pretty well, as appears from Table XI in which the values of  $\chi$  are taken from KAMERLINGH ONNES and PERRIER Comm. N° 116, Table III.

TABLE X. Liquid oxygen.				
7.10 <sup>6</sup> K.O. and O.	x.10 <sup>6</sup> (K.O. and P.)			
241.1	240.6			
258.1	256.8			
270.7	272.6			
	TABLE X. Liquid oxyger <u>x.10<sup>6</sup></u> <i>K.O.</i> and <i>O.</i> 241.1 258.1 270.7			

When the atoms are assumed to be free in the molecule C' gives for the number of magnetons 11 per atom (calculated 11.04),

TABLE XI.Representation of the susceptibility ofliquid oxygen by the formula $\chi(T + \Delta') = C', \Delta' = 71^{\circ}.$				
Т.	x.10 <sup>6</sup>	$\chi(T+71)$ 106.		
90°.1 K.	240.6	38760		
71.35	269.9	38420		
64.9	284.2	38620		

and on the hypothesis that in the liquid two gas molecules are rigidly connected it gives 11 per mclecule of two atoms.

From  $\chi$   $(T + \Delta') = 38600$  (the mean of the numbers in the table) with  $\Delta' = 71^{\circ}$  one finds for  $T = 293^{\circ}$  K

$$\chi_{293^{\circ}}$$
 K = 106.0  $\times$  10<sup>-6</sup>.

This is very close to the value for gaseous oxygen at  $20^{\circ}$  C found by WEISS and PICCARD<sup>1</sup>), from which follows 7 magnetons for each<sup>-</sup> of the oxygen atom assumed to be rigidly connected.

Seeing that above 20° C gaseous oxygen follows CURIE's law <sup>2</sup>) it seems to be by some chance that our formula with  $\Delta' = 71^{\circ}$  gives that figure.

The graphic representation of  $1/\chi$  as a function of T, if our formula actually remained true up to 20° C. would consist of two intersecting lines that have their point of intersection just at the temperature at which the value quoted is determined, which certainly would be a curious coincidence.

Another possibility which Prof. WEISS suggested, in a kind private communication, is that there might be discontinuity in the region between 0° C. and  $-183^{\circ}$  C. which has not been investigated, by which it remains accidental that the continuation of the line for liquid oxygen cuts that for gaseous oxygen just at 20° C. There is much to be said for this explanation. It is quite possible that the change of density between liquid oxygen and gaseous oxygen makes  $\Delta'$  into 0. This would be in accordance with what was deduced in § 10 for the influence of the water molecules upon the value of  $\Delta'$  for manganese sulphate, and moreover quite in accordance with WEISS's idea that the molecular field essentially depends upon the density.

We can further observe, that the change of density, which takes place discontinuously with evaporation, can take place continuously by an indirect transition. In the above line of thought, if we assume that the divergence for liquid oxygen from CURIE's law may be defined by a  $\Delta'$  and pay attention to the change of the number of magnetons which must be assumed in that case, the graph which represents 1/2 for oxygen of a given density as a function of the temperature would be as in magnetite a succession of straight lines perhaps connected by rounded off pieces. The magnetic equation of state which expresses the susceptibility as a function of density and

<sup>&</sup>lt;sup>1</sup>) P. Wriss et A. Piccard. C. R. 155, p. 1234, 1912.

<sup>&</sup>lt;sup>2</sup>) Prof. WEISS who has particularly investigated this question, kindly tells us that the experimental results of CURIE agree so well with CURIE's law within the limits of observation errors that  $\Delta'$  could not be more than  $\pm 8^{\circ}$  or  $\pm 8^{\circ}$ .

temperature (with a view to determining which the experiments of KAMERLINGH ONNES and PERRIER were undertaken (see Comm. N<sup> $\circ$ </sup>. 116 § 1) would be given by a series of similar lines, differing for the different densities.

We must not forget that it is by no means established that in the case of oxygen the divergence from CURE's law is determined by a  $\Delta'$  which changes with the density, and that it obviously may be due to an association of molecules into complexes with a diminution of the number of magnetons.

However this may be, our attention is again drawn to the important question whether the divergences from CURIE's law depend upon a peculiarity of the atom within the single molecule or from the approach of the molecules up to a very small distance.

In § 3 of Comm. N°. 122*a* by KAMERLINGH ONNES and PERRIER, it is said that preliminary experiments with mixtures of liquid oxygen and nitrogen, which will soon be replaced by better final ones and which were based on the above mentioned association hypothesis, seemed to indicate that bringing the molecules to a greater distance by dilution in the liquid state has no influence of importance upon the divergences from CURIE's law. Here the question is raised in this form: whether  $\Delta'$  is a quantity which as peculiar to the atom in the single molecule can also be found in the gaseous state or whether it can only be developed by bringing the molecules into immediate vicinity of each other. Further experiments ') with oxygen, already planned, must decide this.

(To be continued).

## **Physics**. — "The law of corresponding states for different substances." "By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of December 28, 1912).

In the following pages I shall give an account of the result of the researches which I have made of late about the properties of the equations of state for different substances. And I shall communicate in them the simple conclusion at which I have arrived for all the substances for which a chemical combination does not take place, and the molecules continue to move separately, either really isolated, or perhaps joined to groups, if this aggregation (quasi association) behaves in the same way.

<sup>1</sup>) As this communication is going to press, these experiments have advanced so far, that we may accept with great probability as the result of them, that gaseous oxygen of 90 times the normal density obeys CURRE's law down to -130° C.