

**Physics.** — *On the Change of the Magnetic Moment of NO with Temperature.* By E. C. WIERSMA, W. J. DE HAAS and W. H. CAPEL. (Communication N<sup>o</sup>. 212b from the Physical Laboratory of Leiden.)

(Communicated at the meeting of December 20, 1930).

§ 1. VAN VLECK showed in a paper<sup>1)</sup> on Magnetism, that the magnetic moment of NO would probably change with the temperature and he calculated the values over the whole range of temperatures. Investigations to determine this dependence experimentally have been carried out by F. BITTER<sup>2)</sup> and by AHARONI and SCHERRER<sup>3)</sup>. As we had already begun our investigations at that time, we carried on with them, especially as it was possible for us to reach lower temperatures than those investigated by these authors<sup>4)</sup>.

§ 2. The method we used was as follows. A very thin walled glass bulb (F), (See fig. 1) was evacuated and fastened to a very fine wire (D) (less than 0.01 mm in diameter). The wire was fastened in its turn to the end of a brass rod (A) by means of a small copper disk and a copper wire. The rod could be moved horizontally, because it carried thread on its outside end. It was displaced by means of a nut, kept in its place by two brass plates. The part of the rod, which carried the thread had been made square, and the hole in the inner brass plate, which kept the nut in its place, was also square. In this way the rod was prevented from turning round.

By means of a packing box (E), the rod could be moved while the whole apparatus was kept airtight. The movable rod carried a mark (B) and on the fixed rod above it there was a fixed mark (C). The displacements, given to the upper end of the fine wire could be read as differences in the distances of the fixed and the movable mark. We read the marks by mean of a Zeiss measuring microscope. This microscope was fixed to the beams, which carried the apparatus. The whole displacement

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1) J. H. VAN VLECK, Phys. Rev. **31**, 1928, p. 585.

2) F. BITTER, Phys. Rev. **35**, 1930, p. 1572.

3) J. AHARONI and P. SCHERRER, Zeit. f. Ph. **58**, 1929, p. 749.

4) Professor W. PAULI communicated at the Solvay Congress in October 1930 new results by STOESEL, also at lower temperatures than formerly measured, which agree with the theory. As our measurements had just been finished by that time we communicate our results. A comparison as to the numbers is impossible as we have not yet received the publication.

apparatus was soldered to a brass tube (G), closed at the upper end. Inside the lower end of it we sealed a glass tube (H). To the excentrically drawn out lower part of this tube a narrow, clear glass tube had been joined.

The length of the fine wire had been chosen in such a way that the light

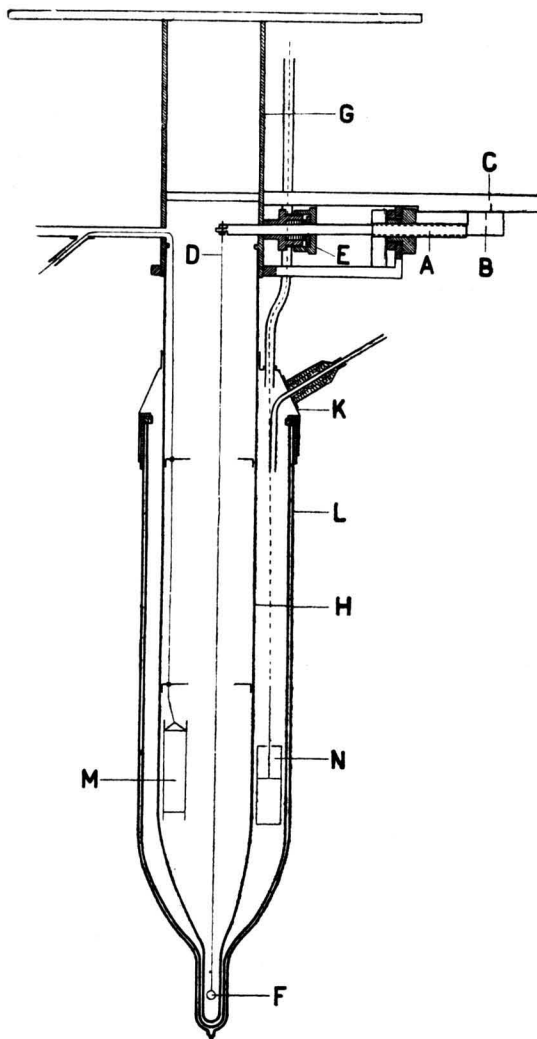


Fig. 1.

glass bulb came to about half the height of the narrow glass tube. In this way an entirely closed gas space has been made, joined to the NO and N<sub>2</sub> containers by means of a tube.

To the wide glass tube we sealed the cap of a cryostat by means of Dekhotinsky cement. This cap was excentric in such a way that the vacuumglass, when put on was centered with the narrow part of the

inner glass tube. Inside the vacuumglass we put a small stirrer (N), to keep the temperature homogeneous throughout the liquid. Inside the inner glass tube we fixed a platinum thermometer (M). In this way the temperature was measured inside the gas itself.

Two screens with slits were also placed in the wide tube, to avoid convection.

§ 3. To make the measurements the bulb was brought into the field of a Weiss electromagnet. It was put in the horizontal plane of symmetry in the place where  $H \frac{\partial H}{\partial x}$  is maximum. It is blown out of the field or drawn into it with a horizontal force, proportional to the difference of the volume susceptibility of the gas in which the bulb is placed and the mean volume susceptibility of the bulb itself. The measurements were then made in the following way. The whole gas space and the apparatus in which NO was prepared were well evacuated. Then NO was prepared out of a 10 % solution of chemically pure  $\text{NaNO}_2$  and  $\text{H}_2\text{SO}_4$  of 10 %. It was passed thrice through very strongly concentrated  $\text{H}_2\text{SO}_4$  and then through  $\text{P}_2\text{O}_5$ . We liquified the gas, let part of it boil off and then distilled it twice. Then we filled the gas space with the so prepared NO. In the mean time the cryostat had been filled and the temperature adjusted. The pressure of the NO used was always about one atmosphere excepted at the lowest temperature, which is beneath the boiling point; there pressures of 9 and 13 centimeters were used.

By means of a microscope with micrometer eyepiece and a total reflecting prism the zero position of the bulb was determined through the narrow part of the vacuumglass and the inner tube. Then we measured the distance of the fixed and the movable index.

We put the magnetic field on slowly, keeping the bulb as well as possible in its zero position by turning the nut. The horizontal component of the stress in the wire compensated the force exerted by the magnet. When the right field had been reached the bulb was brought back accurately in its zero position and the new distance of the movable and the fixed mark was read.

This difference of distance, from that formerly measured, divided by the length of the wire gives the ratio between the force exerted by the magnet and the weight of the bulb in the gas.

In order to be able to apply correction for the mean volume susceptibility of the bulb, we then evacuated the gasspace and filled it with nitrogen. This nitrogen did not contain  $\text{O}_2$  as far as we were able to determine by means of a gasanalysis carried out by means of copper, cleaned with  $(\text{NH}_4)_2\text{CO}_3$  with ammonia; certainly it is less than 0.1 %.

We then repeated the measurements in  $\text{N}_2$ . In both of the gases we made two determinations in each of three different fields.

The pressure of the gases was measured.

§ 4. For a certain fieldstrength the difference of the measurement in NO and N<sub>2</sub> gives the difference of the volume susceptibility of the two gases at that given temperature. The susceptibility of the bulb drops out, but one has to make the measurement in N<sub>2</sub> at each temperature. The values were then corrected for the diamagnetism of N<sub>2</sub>, which we supposed not to depend on temperature.

This is right in any case, as the correction for the diamagnetism is small. Then we divided the values by the densities at the measurement and made the ratio of the thus found susceptibility to the susceptibility in the same field at 238.40° K. We thought it better not to take the values at room temperature as that is the only temperature where there is no liquid in the vacuumglass and one is therefore less sure of the temperature equilibrium throughout the gas.

For the temperature of 238.40 we assumed the value given by the curve of VAN VLECK to be right and calculated from that the other susceptibilities. We then took the mean of the values for the three different fields and calculated from the so found susceptibility the value of the magnetic moment of a molecule of NO in ratio to the BOHR magneton.

§ 5. Though the general way of the calculation has been indicated there were some other corrections applied. First we applied a correction for the fact, that the ratio between the force exerted by the magnet and the weight of the bulb is not given by the sine of the angle between the vertical and the direction of the fine wire but by the tangent thereof. The bulb changes in volume with temperature; as it is made out of Jena 16-III glass the expansion coefficient is known and the exact volume was calculated. We determined the weight of the bulb in the gas by calculating the buoyant force, and made a correction for the difference of this force in NO and N<sub>2</sub>.

As we have no ideal gases it is necessary to apply corrections for the  $B$  values in the formula  $pv_a = (A_A)_0 (1 + \alpha t) + Bd + \dots$

Now these values are known for N<sub>2</sub> but we found difficulties in determining them for NO. As a matter of fact isotherms of this gas have been measured by E. BRINER, H. BIEDERMAN and A. ROTHER<sup>1)</sup>. From these we tried to determine the values of  $B$ . However the results depended strongly on the points chosen to calculate the coefficients in  $pv = A + pB + p^2C$ , so strongly, that we could not make use of them. In order to have some ground for our calculations of the densities we calculated values of  $B$  for NO from the reduced values of  $B$  of N<sub>2</sub> and O<sub>2</sub>, which fall closely together<sup>2)</sup>.

This seems allowable as the critical points do not differ very much; however the fact of the NO molecule having an electric moment, though a small one, may interfere with the accuracy of the calculation of the

1) E. BRINER, H. BIEDERMAN and A. ROTHER, *Helvetica Chimica Acta*, 1925, p. 926.

2) G. P. NIJHOFF, *Academisch proefschrift*, Leiden 1928. p. 36 and 48.

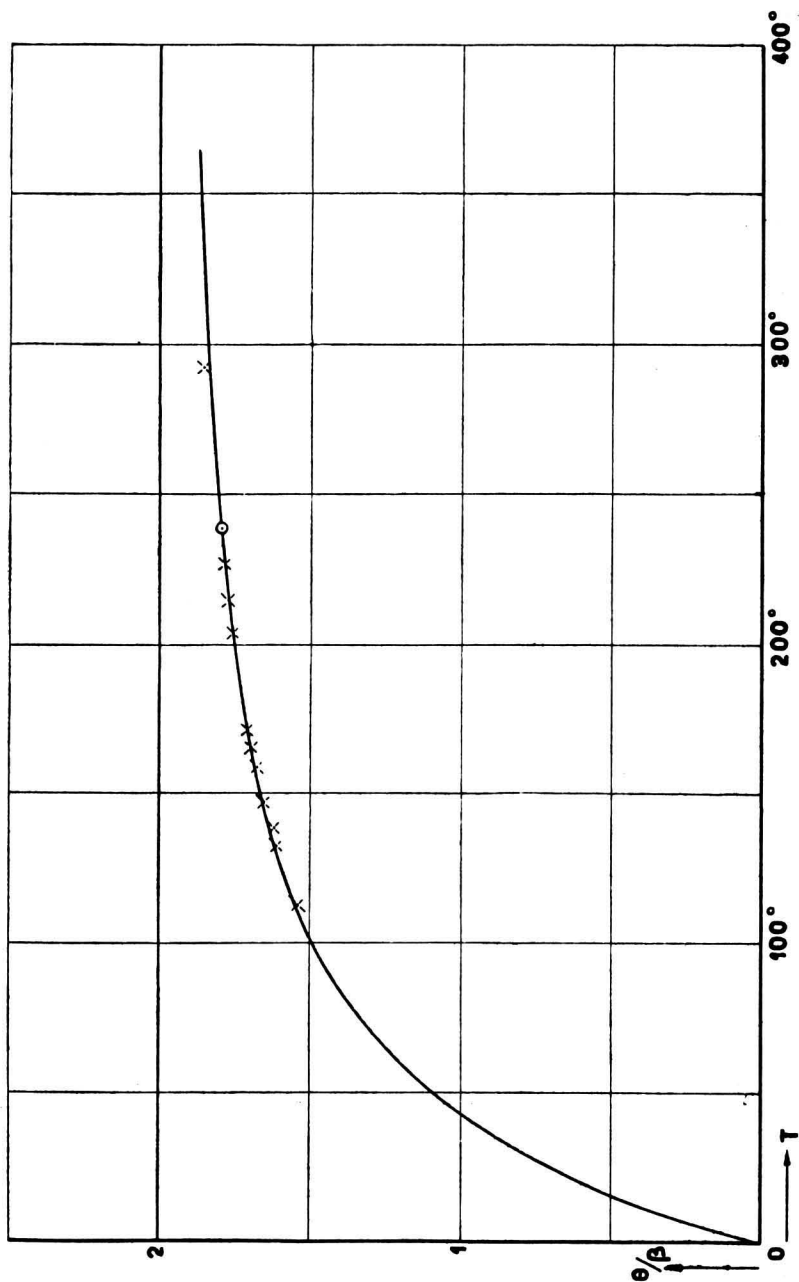
densities in this way. For the lowest temperatures it has been necessary to extrapolate the reduced values of  $B$  of  $N_2$  and  $O_2$ , as the determinations of the values of  $B$  for these gases have not been carried out at the low reduced temperatures, we used. A slight inaccuracy may have been introduced in our calculations by these facts, which could only be corrected if isothermes of  $NO$  were measured. It is very difficult to estimate, whether the slight systematic differences we find at the very low temperatures can be entirely due to the fact that the densities are not absolutely known.

§ 6. The results are given in the table and in fig. 2. On the figure the full drawn curve gives the curve as predicted by VAN VLECK.

$T$ °K.	$\chi \cdot 10^6$	$C = \chi T \times 10^3$	$C$ mol.	$\theta/\beta$	$\theta/\beta$ Value after v. VLECK	Differences in promilles
292.1	49.07	14.336	0.4302	1.852	1.838	+ 7
238.40	56.42	13.450	0.4036	1.794	1.794	—
226.27	58.87	13.320	0.3997	1.785	1.783	+ 1
214.45	61.21	13.126	0.3939	1.772	1.770	+ 1
203.8	63.16	12.873	0.3863	1.755	1.756	— 1
170.84	71.45	12.207	0.3663	1.709	1.708	+ 1
165.41	72.26	11.953	0.3587	1.691	1.694	— 2
158.75	73.59	11.683	0.3506	1.672	1.682	— 6
146.90	77.45	11.377	0.3414	1.650	1.655	— 3
138.29	79.11	10.940	0.3283	1.618	1.630	— 8
132.51	81.45	10.794	0.3239	1.607	1.616	— 6
112.77	87.32	9.847	0.2955	1.535	1.547	— 8

The circle indicates the point at  $238.40^\circ$ , that has been used to compare the values of the other points with. The crosses indicate our points, with temperature ( $T$ ) and value of the magnetic moment in BOHR magnetons ( $\theta/\beta$ ) as coordinates. It is seen, that the measurements are in very good general agreement with the theoretical curve. At the very low temperatures slight systematic differences exist, reaching 8 promille at the utmost. Those seem to be outside the errors of the magnetic measurements, as the difference between the results for the susceptibilities in three different fields never exceeded 7 ‰. This would give an accuracy of at least 3.5 ‰ for the moments as these are calculated from the square roots of the values of  $\chi T$ . As the differences we find are somewhat bigger, there may be a very slight deviation from the theoretical curve, though the

differences may perhaps be due to inaccuracy in the calculated densities.



### SUMMARY.

The magnetic moment of NO molecules has been measured at different temperatures. The apparatus for these measurements is described. The results show generally a very good agreement with the values predicted by VAN VLECK.