

*Citation:*

H. Kamerlingh Onnes & Perrier, A., Magnetic researches. XII. The susceptibility of solid oxygen in two forms, in:

KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 894-901

as it appears after our modification, is shown in section and seen from above. The lower part remained unchanged <sup>1)</sup>.

The arrangement here described has some advantages over that with the electro-magnetic compensation. In the first place, a much greater force  $S$  can be measured by it, and moreover the method of working is simpler, as now only one current (that of the electro-magnet) has to be read, in the earlier arrangement three. On the other hand, while in the former arrangement the current through the electro-magnet was adjusted to certain fixed values, for which the corresponding strengths of field were accurately measured, in the modified arrangement it is best to place a certain weight upon the scale, and to regulate the current through the electro-magnet, until this weight is exactly compensated by the force exerted upon the experimental substance by the magnetic field. As the strength of field corresponding to this current must now be found by (graphic) interpolation, it can now only be as accurately known as by the method described in Comm. N<sup>o</sup>. 139<sup>a</sup>, if the field has been determined for a great number of current strengths. Naturally in the method of compensation by weights we could also work with a few accurately measured magnetic fields, if we had a sufficient number of small weights at our disposal inside the apparatus; but working in this way would greatly decrease the simplicity of the method. For this reason in these investigations by the method of compensation with weights, the field for the WEISS electro-magnet for different strengths of current, was very minutely studied.

**Physics.** — "*Magnetic researches. XII. The susceptibility of solid oxygen in two forms*". By ALBERT PERRIER and H. KAMERLINGH ONNES. Communication N<sup>o</sup> 139<sup>c</sup> from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of January 31, 1914.)

§ 1. *Introduction.* A former investigation <sup>2)</sup> had led us to the conclusion that the susceptibility of oxygen suddenly becomes considerably smaller when this substance changes into the solid state.

<sup>1)</sup> The sectional drawing of the upper portion of the apparatus is drawn on the same scale as the fig. in Comm. N<sup>o</sup>. 139<sup>a</sup>, and gives therefore, if placed upon that, the complete drawing of the apparatus as used in the researches of Comm. N<sup>o</sup>. 129<sup>b</sup>, 132<sup>e</sup> and 134<sup>d</sup>.

<sup>2)</sup> H. KAMERLINGH ONNES and ALBERT PERRIER, Leiden Comm. N<sup>o</sup>. 116 and 124<sup>a</sup>.

How great the jump might be, was uncertain, owing to the absence of a bath which would keep the temperature constant at which this change takes place. We were therefore obliged to draw our conclusions from what we observed during a gradual heating, at which the temperature can be only imperfectly estimated. A further investigation was therefore necessary. Moreover, in repeating our determinations, we encountered the difficulty, that we found a different value for the susceptibility of solid oxygen at the temperature of liquid hydrogen, than in our first experiments, which were conducted according to a different method. Although we thought we were justified (Comm. N°. 124) in considering that we had obtained reliable results only by the second method, and that in the meantime we need not attach any value to those obtained previously, it was still very desirable to confirm the more recent value for the jump by new measurements. Finally, in our experiments we came upon another problem that required to be solved. We had noticed (see Comm N°. 122a May 1911) as WAHL<sup>1)</sup> also observed later, that solid oxygen, besides appearing in the blue-grey opaque form that it usually presents, also occurs in a transparent vitreous form. This modification can optically be very clearly distinguished from the liquid state. We conjectured that the transition from the transparent condition to the other one might be accompanied by a second jump in the magnetic condition, following on that which took place on freezing. We wished to ascertain the truth of this also.

§ 2. *Arrangement of the experiments.* For the magnetic determinations, as in previous investigations, we made use of the method of measuring the attraction which the magnetic field exerts upon a rod of the experimental substance placed at right angles to the field in the interferrum of an electro-magnet, and held suspended there by a carrier with hydrometer-arrangement.

More specially the arrangement of the apparatus was in the main the same as that used for our investigations of the liquid mixtures of oxygen and nitrogen, of which we shall give a complete description in the next paper (Comm. N°. 139d). We do not give it here, because the investigation treated in this paper, is of a much more preliminary character than our investigation of mixtures, confining ourselves here in the main to that which is peculiar to our experiments on solid oxygen. At the outset it should be mentioned that the way in which the temporary connection was made between the carrier

<sup>1)</sup> Zeitschrift für physikal. Chemie. Bd. 84 (1913).

and the apparatus which introduced the oxygen from outside, was the same as in the experiments with mixtures of oxygen and nitrogen.

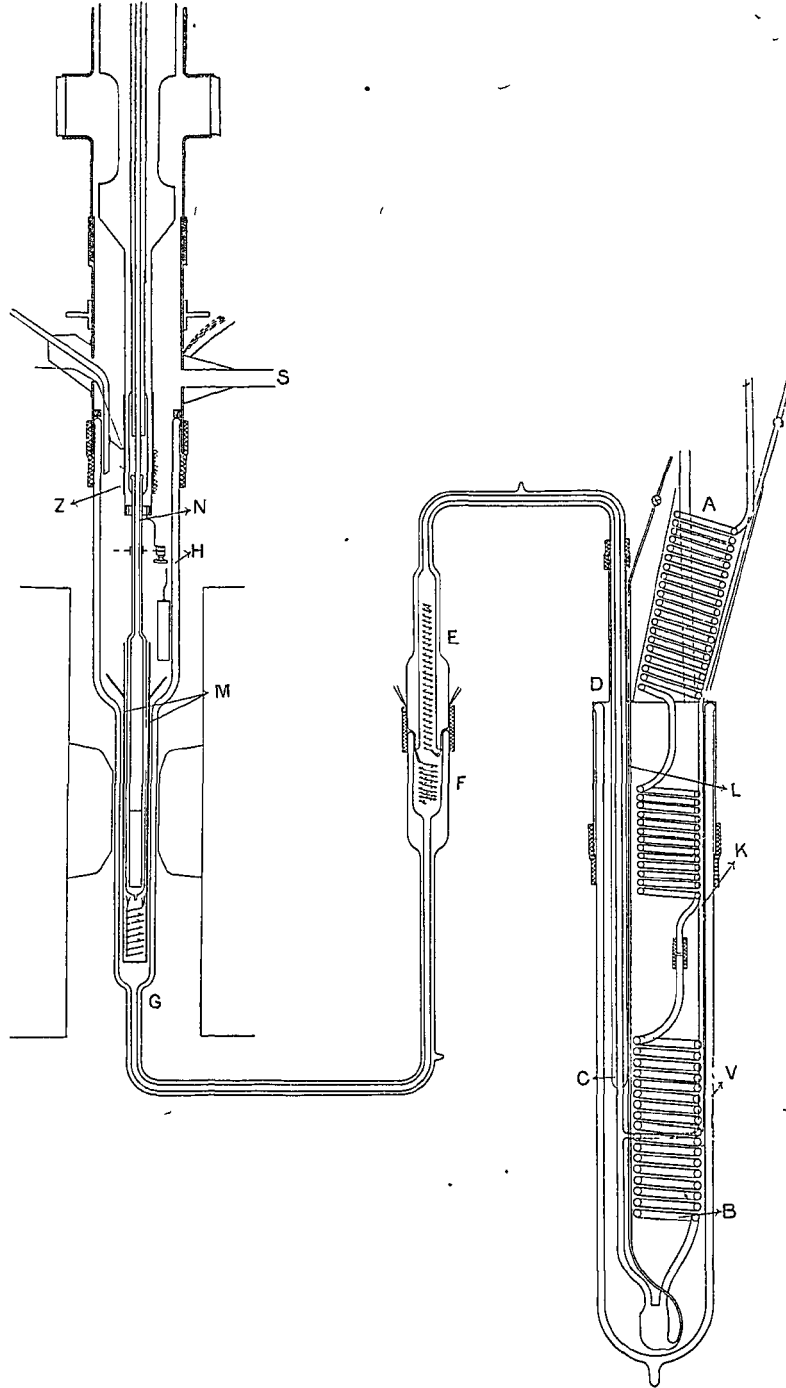


Fig. 1.

In the further description we shall assume that the drawing of the apparatus as it is given in this paper will be consulted as a modification together with that of the next paper (N°. 139*d*). The development of the apparatus there described, from our original apparatus and the modification due to OOSTERHUIS (Comm. N°. 139*b*) will be obvious on comparison with Comm. N°. 139*a*.

In the cryogenic part, we encountered in the first place a difficulty, which so far had not been provided for. Measurements had to be made at the temperatures between the melting-point of oxygen and the boiling-point of hydrogen, as well as at the temperatures of liquid and solid hydrogen. In order to be able to do this an arrangement was made which permitted us to work both in a bath of liquid hydrogen evaporating under various pressures, and in a bath of hydrogen gas, the temperature of which can be regulated.

The arrangement consists principally in a circulation of hydrogen. The hydrogen, after having been cooled to the boiling point, before it comes in contact with the experimental object, passes over a heating-spiral, in which JOULE heat is generated, and is thereby heated to the desired temperature. The whole hydrogen circulation is carefully shut off from the outside air. The gas streams from a supply-cylinder in which it is kept under pressure, through a copper spiral *AB*, the glass tube *CDL*, which from *CE* is double-walled, and silvered, and at *E* is widened, to the experimental space in the cryostat. It enters this through the twice bent double-walled tube *FG*, which forms the downward continuation of the vacuum-vessel of the cryostat. On the way down the gas is cooled by liquid air at *A* (copper spiral), and is further cooled first by hydrogen vapour and then by liquid hydrogen at *B* (glass spiral). At *E* the gas passes along a resistance thermometer; at *F* is the heating wire, at *G* in the lower part of the experimental space a resistance thermometer.

By means of regulating resistances the current through the heating wires is so regulated as to obtain the desired temperature in the experimental space. In the upper part of this there is a helium thermometer with a steel capillary, which forms part of our cryomagnetic apparatus in its usual form (Comm. N°. 139*a*). The gas then rises further in the vacuum-vessel, and escapes through *S* into the gasometer or the air-pump. The tubes *K* and *L* serve for leading off hydrogen.

Of the various auxiliary apparatus we must further mention the thick-walled copper tube *M*, which surrounds the experimental tube, and which serves to keep the temperature of the gas which sur-

rounds it even all over. Of course liquid hydrogen can be introduced into the cryostat in the ordinary way, to immerse the experimental tube in a bath of liquid hydrogen.

We had a good deal of difficulty in procuring a rod of solid oxygen of about 5 or 6 cm. length that was *completely homogeneous*. As in freezing the volume of the oxygen diminishes by about  $\frac{1}{6}$ , there is a great tendency to form hollows. A homogeneous rod can only be obtained by allowing the liquid in the cylindrical mould to gradually freeze *from the bottom upwards*. As soon as solid matter settles in the neck of the tube, hollows must arise in the experimental mass, as the entrance of liquid oxygen is cut off <sup>1)</sup>. The difficulty of procuring an homogeneous cylinder was increased by the fact that in our experiments the freezing had to take place inside a silvered vacuum glass, and could therefore not be followed by the eye.

In order to come a step nearer to the solution of this problem, which still presents difficulties, we made use of the possibility of regulating at pleasure the heat conducting power of a double-walled vacuum glass. The experimental tube in which the oxygen was frozen was made double-walled (not silvered); as much hydrogen was put in between the walls that the (small) pressure had exactly such a value, that according to preliminary experiments in a transparent bath the freezing took place under the most favourable circumstances. It appeared to be favourable to this that in the upper part of the tube latent heat was developed by the condensation of the gaseous oxygen which was admitted during the freezing. When a once formed stick partially melted, it was difficult to get it back into a dense condition. The double wall of the experimental tube is therefore also of use to eliminate temporary irregularities in the temperature of the surrounding bath (vapour or liquid). It was found that the temperature-range of the transparent modification did not extend more than 5 or 6 degrees below the melting point.

§ 3. *Results.* The figures in the following table are averages. To be able to express the results in absolute measure, the fields are measured in absolute measure, and the dimensions of the tubes carefully determined. The tubes were of the symmetrical type (see Comm. N°. 139a § 4), the lower part was evacuated, so that no

<sup>1)</sup> We shall return later to the freezing of oxygen and the change from the transparent to the opaque mass. When the access of gaseous oxygen is cut off, a long shaped hollow usually forms which as it increases assumes the shape of a worm fantastically coiled up in a confined space.

correction was needed for the magnetism of the bath or of the wall. The oxygen used contained not more than 0,001 foreign admixtures. The immediate result of the observations is the susceptibility  $K$  per unit of volume; to calculate the value of  $\chi$ , the specific susceptibility (or specific magnetisation coefficient), we must know the density  $\rho$ . We have taken 1.44 for this, on the ground of our determinations in 1910, and from a new one recently made, but neither determination can lay claim to great accuracy, so that the values of  $\chi$  (and also of  $K$  for the opaque modification if it should prove that in this innumerable little splits are present) will have to be recalculated when  $\rho$  is better known.

The four results refer to one freezing.

TABLE I.

Susceptibility of solid oxygen.			
bath	$T$	$K \cdot 10^6$	$\chi \cdot 10^6$ ( $\rho=1.44$ )
$H_2$			
vap.	43	166.1	115.3
	20.3	79.	54.9
$H_2$	17.3	77.3	53.7
liq.	13.9	76.7	53.3

A new freezing gave two values for  $K$  near  $165.5 \cdot 10^{-6}$  (before and after partial melting) at about the same temperature ( $-230^\circ \text{C.}$ ). This value is less to be relied upon than that in the Table. We had very little time at our disposal for our joint work, and this was even diminished by the apparatus being found somewhat deficient in some points. On this account we had not time to test a temperature lying between the melting point and the transition point from the transparent to the opaque modification. But we had already postponed the resumption of our researches after the departure of one of us from Leiden, for two years, and we shall not have an opportunity in the near future to continue our joint research. We therefore felt bound to publish what we had so far established.

This is, besides the numerical values of our table within the limits of accuracy given for it, that the transition from the transparent

modification of oxygen to the opaque, which takes place at about  $-225^{\circ}\text{C}$ ., *is not accompanied by any conspicuous magnetic modification*, so that it probably does not involve any important change in molecular structure. Further, that in the whole range from the freezing point of oxygen down to about  $-240^{\circ}\text{C}$ . the susceptibility is markedly less than in the liquid state. In this region it changes little with the temperature, in fact increases slightly on cooling. This does not seem to agree with the much smaller value which the table gives for  $-253^{\circ}\text{C}$ . but here a phenomenon intervenes which has not been observed before, viz. that at about  $-240^{\circ}\text{C}$ . *the susceptibility suddenly falls to about half its value*. The exact value of the temperature must still be more accurately determined; it is also not settled whether the transition is actually discontinuous or is completed in a very small range of temperature (1 or 2 degrees). The susceptibility falls in this transition to about the values that are found in liquid hydrogen.

It will be seen that these last values agree with the values of 1911, within the limits of accuracy of the latter. The results of 1910 are thereby, as we expected, condemned, and the cause to which we attributed the discrepancy between these results and those of 1910, gains in probability at the same time.

As regards the change in the susceptibility below  $-252^{\circ}\text{C}$ . with the temperature, although it is slight, yet it allows no doubt that it is a decrease. The observations permit the comparison of the susceptibility at different temperatures at constant density without the intervention of any correction. We have here, therefore, a new example of a substance that follows CURIE'S law at a higher temperature, and on approaching the absolute zero completely deviates from it. As the ratio of the susceptibilities observed above and below the transformation point is

$$\lambda_1 = \frac{115.3}{54.2} = 2.10,$$

it becomes probable that the exact value of the jump is precisely 2. For above  $20^{\circ}\text{K}$ , the magnetisation must still increase distinctly.

For the ratio of the susceptibility of liquid oxygen and solid oxygen at  $-230^{\circ}\text{C}$ . we find

$$\lambda_2 = \frac{313.3}{115.3} = 2.72.$$

This value is less certain than that of  $\lambda_1$ , for it contains the uncertainty concerning the density of solid oxygen and that of the change of susceptibility between  $-220^{\circ}\text{C}$ . and  $-230^{\circ}\text{C}$ .

From our previous investigations we had inferred a sudden change



in the susceptibility to a fifth or sixth part of its value between the liquid state and the solid state at hydrogen temperatures. It now appears that a sudden change of this amount really exists, but takes place in two parts, namely, once to  $\frac{1}{3}$  at freezing, and subsequently,

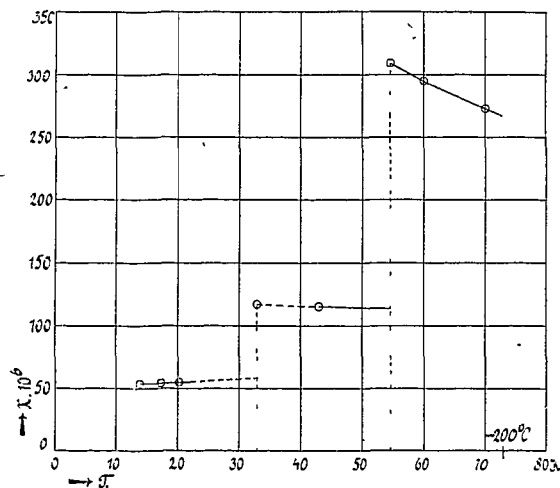


Fig. 2.

after the susceptibility has again increased a second time to  $\frac{1}{2}$  at the transformation point — 240° C., after which the susceptibility further decreases. In the accompanying figure our results are put together.

**Physics.** — “*Magnetic researches XIII. The susceptibility of liquid mixtures of oxygen and nitrogen, and the influence of the mutual distance of the molecules upon paramagnetism.*”

By ALBERT PERRIER and H. KAMERLINGH ONNES, Communication N°. 139d from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of January 31, 1914).

§ 1. *Introduction.* In 1910 and 1911 we published experiments upon the susceptibility of oxygen at very low temperatures, by which it was demonstrated that the specific susceptibility of this substance, which, in the gaseous form above 0° C. follows CURIE-LANGEVIN'S law, deviates considerably from this law in the liquid state at low temperatures, and even more so in the solid state.

Subsequently we have observed similar phenomena in other substances (paramagnetic salts). The (solid) substances referred to follow CURIE'S law at ordinary temperature, and also at temperatures that do not lie too far below it; but when the temperature falls to the