Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Physics. — *"Magnetic researches. IX. The deviations from Curie's law in connection with the zero-point energy"*. By E. Oosterhuis. Supplement N°. 31 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes).

(Communicated in the meeting of June 28, 1913).

§ 1. Curie [1]) found that for a number of paramagnetic substances the susceptibility is inversely proportional to the absolute temperature. Later measurements have shown, however, that with many substances considerable deviations from Curie's law occur. They were first disclosed about simultaneously by an investigation of Honda [2]) (afterwards continued by Owen [3])) who showed that the majority of paramagnetic elements does not obey Curie's law and by an investigation of liquid and solid oxygen by Kamerlingh Onnes and Perrier [4]), which proved that a substance which follows the law at higher temperatures, may begin to deviate from it at lower temperatures. Liquid oxygen showed an increasing deviation with falling temperature approximately in accordance with the relation $\chi = CT^{-\frac{1}{2}}$ (χ: susceptibility per gramme, T: absolute temperature); with solid oxygen at hydrogen temperatures the susceptibility deviated even more and seemed to approach a constant value. The investigation at low temperatures which promised to give an insight into the nature of paramagnetism [5]) was continued by Kamerlingh Onnes and Perrier [6]) with several other substances. By the results obtained they were led to the conception that for all paramagnetic substances or at least for one class of them the deviations from Curie's law are governed by a law of corresponding states, the corresponding temperature for each substance to be taken proportional to a certain temperature characteristic of that substance. The data obtained later on by Kamerlingh Onnes and the author [7]) may serve to confirm this view, as will be shown in § 7.

The majority of the substances investigated in the cryogenic laboratory at Leiden may be reduced to the following three types:

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[1]) P. Curie. Ann. chim. phys. (7). 5, p. 289; 1895.
[2]) K. Honda. Ann. d. Phys. 32. p. 1027. 1910.
[3]) M. Owen. Ann. d. Phys. 37. p. 657. 1912.
[4]) H. Kamerlingh Onnes and A. Perrier. Comm. N°. 116 (April 1910).
[5]) Comp. H. Kamerlingh Onnes, Comm. Suppl. N°. 21b.
[6]) H. Kamerlingh Onnes and A. Perrier. Comm. Nos 122a, 124a.
[7]) H. Kamerlingh Onnes and E. Oosterhuis. Comm. Nos. 129b, 132e, 134d.

a. For some substances (crystallized ferrous-sulphate, crystallized manganese sulphate etc.) the relation $\chi T =$ constant was found to hold as far down as the temperature of liquid nitrogen, but at hydrogen temperatures χT was always found smaller than would follow from Curie's law.

b. With other substances (e g. anhydrous manganese sulphate) the product χT began to diminish at once when the temperature was lowered below room-temperature ; in that case the relation $\chi(T+\Delta) =$ constant appeared to hold for the range between ordinary temperature and nitrogen-temperatures ; in liquid hydrogen, however, further deviations became apparent.

c. With platinum the susceptibility was found to change very little with temperature and in the range between liquid nitrogen and liquid hydrogen to be almost independent of the temperature, entirely in accordance with the results of Honda and Owen who found the product χT for platinum (and for many other elements) to diminish continually with falling temperature.

§ 2. Langevin[1]) in his kinetic theory of paramagnetism has given a theoretical deduction of Curie's law. He finds, that the susceptibility is inversely proportional to the kinetic energy of rotation of the molecules. When this energy is taken proportional to the absolute temperature, this gives χ proportional to $\dfrac{1}{T}$ or $\chi T =$ constant, i. e. Curie's law.

§ 3. It seems natural to try an explanation of the deviations from Curie's law by dropping the assumption that the rotational energy U^- of the molecules is proportional to the absolute temperature and adopting a different temperature relation for U[2]).

In a different connection Einstein and Stern[3]) were led to the assumption that the rotational energy of a molecule with two degrees of freedom is equal to
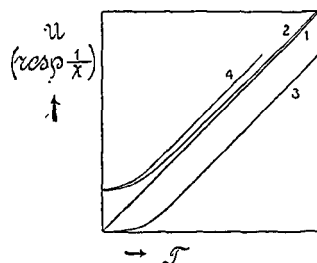
$$\frac{h\nu}{e^{\frac{h\nu}{kT}}-1} + \frac{1}{2}h\nu \quad \ldots \ldots \ldots \quad (1)$$

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[1]) P. Langevin, Ann. chim. phys. (8) 5, p. 70; 1905.

[2]) Kamerlingh Onnes and Perrier ascribed the deviations from the law to the electrons freezing to the atoms, in consequence of Planck's vibrators coming to rest. In that case, if the rotational velocities remain proportional to $\sqrt{T}$, the susceptibility approaches a constant value. In this paper a theory is developed in which the elementary magnets themselves remain unchanged.

[3]) A. Einstein and O. Stern, Ann. d. Phys. 40, p. 551; 1913.

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$(v =$ frequency of the rotational movement, h and k the const in PLANCK's radiation-formula). The connection between U and assuming v ~independent of the temp ture, is then approximately as indic by curve 2 in the figure. The stra line 1 gives the relation according to original assumption: $U = kT$.

The form (1) gives for $T = 0$ a v of U differing from 0, viz. $= \dfrac{1}{2} hv$

the zero-point energy is left out, the term $\dfrac{1}{2} hv$ in (1) disapp and the dependence of U on T is represented by curve 3.

If we may assume that the proportionality of the susceptibility $\dfrac{1}{U}$ holds (§ 2) and, therefore, that $\dfrac{1}{\chi}$ is proportional to U^1), $\dfrac{1}{\chi}$ show the same law of dependence on temperature as U, and it be possible by measurements of the susceptibility of paramagn substances at different temperatures to obtain an insight into changes of the rotational energy of the molecules for these substan

§ 4. Starting from this assumption it can be concluded at o from, the measurements of the susceptibility, that a curve as gi by 3 is unable to represent the changes in $\dfrac{1}{\chi}$ or U. In fact all observations at low temperatures which give deviations from CUR law always show that the product χT has smaller values at lo temperatures than at higher, whereas according to curve 3 the μ duct χT would continually increase towards lower temperature. ' assumption of a zero-point energy (curve 2 and also 4, see lo down) on the other hand leads to deviations from CURIE's law the same sense as found experimentally. According to a remark the paper by EINSTEIN and STERN quoted above WEISS had arri at a similar view and had inferred the existence of a zero-p(energy from CURIE's measurements of the susceptibility of gaseous oxyg

According to curves 2 and 4 $^1/_\chi$ and χ ought to approach a c stant finite value at low temperatures; this is actually the case

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1) In this case also U is the rotational energy for two degrees of freedom is, therefore, given by the expression (1), because the dependence of the susc bility on the temperature is determined solely by the rotation about axes at r angles to the magnetic axis of the molecule; for the sake of simplicity the mon of inertia — and therefore v — is taken equal for those axes.

platinum, and the other substances which have been investigated in liquid hydrogen show a similar tendency. There is therefore every reason for the assumption of the temperature-function (1) with the inclusion of a zero-point energy.

§ 5. It was further tried for a number of substances, whether the dependence of the susceptibility on the temperature is in quantitative agreement with the above hypothesis. In the calculations the frequency v which occurs in the formula for U was not taken independent of the temperature (v independent of T gives the curve 2 but following EINSTEIN and STERN it was assumed that

$$v^2 = 2v_0 \frac{U}{h} \quad \cdots \cdots \cdots \quad (2)$$

The change of $U \left(\text{ or } \dfrac{1}{\chi} \right)$ with T according to the relations (1) and (2) is represented by curve 4; v_0 is the value which v assumes at very low temperatures: it is related to the moment of inertia I of the molecule by the formula

$$v_0 = \frac{h}{4\pi^2 I}. \quad \cdots \cdots \cdots \quad (3)^{1)}$$

In the first place it may now be observed that for temperatures, which are not too. low, the relation between U and T expressed by (1) and (2) leads to the empirical relation $\chi(T + \Delta) = \text{const.}$, which was deduced from the observations (comp. § 1). This is seen by developing (1) in a series and neglecting the terms beyond the third which is certainly allowed for high values of T; this gives

$$U = hv \left(\frac{1}{\dfrac{hv}{kT}} - \frac{1}{2} + \frac{1}{12} \frac{hv}{kT} \right) + \frac{1}{2} hv$$

$$U = kT + \frac{1}{12} \frac{h^2 v^2}{kT}$$

When we substitute: $v^2 = 2v_0 \dfrac{U}{h}$ in this, we find

$$U = kT + \frac{1}{6} \frac{hv_0}{kT} U$$

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[1] The relations (2) and (3) are at once arrived at when it is remembered that $U = \dfrac{1}{2} I(2\pi v)^2$. For $T = 0$ this gives: $\dfrac{1}{2} hv_0 = \dfrac{1}{2} I(2\pi v_0)^2$ or $v_0 = \dfrac{h}{4\pi^2 I}$. When this is introduced into $U = \dfrac{1}{2} I(2\pi\cdot)^2$ the result is (2).

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$$U = \frac{kT}{1 - \frac{1}{6}\frac{hv_0}{kT}} = kT\left(1 + \frac{1}{6}\frac{hv_0}{kT}\right) = k\left(T + \frac{1}{6}\frac{hv_0}{k}\right) = k(T + \Delta),$$

As further by hypothesis $\frac{1}{\chi}$ is proportional to U, the following relation is obtained

$$\frac{1}{\chi} = C(T+\Delta) \quad \text{or} \quad \chi(T+\Delta) = C,$$ which is the relation found empirically e.g. for anhydrous manganese sulphate above nitrogen temperatures. That for other substances, like crystallized manganese sulphate above nitrogen temperatures, CURIE's law was found approximately fulfilled, is obviously due to a small value of Δ, or of $\frac{hv_0}{k}$.

By means of formulae (1) and (2) the value of $\frac{U}{kT}$ was calculated for a series of values of $\frac{kT}{hv_0}$; if the underlying suppositions are correct, $\frac{1}{\chi T}$ must have the same relationship to T for a paramagnetic substance as $\frac{U}{kT}$ to $\frac{kT}{hv_0}$. The comparison of the two functions is made by means of logarithmic diagrams [1]); in the one diagram the abscissae were $log\frac{kT}{hv_0}$ and the ordinates $log\frac{U}{kT}$, in the other $log\,T$ and $log\frac{1}{\chi T}$ respectively. For nearly all the substances examined the curves could be made to coincide with sufficient approximation. The shift along the axis of abscissae required to produce coincidence gives the value of $\frac{hv_0}{k}$ for the substance under consideration.

Subjoined in the two tables are the results obtained for two of the substances. At the head of the table is found the value of $\frac{hv_0}{k}$ which has to be assumed for the particular substance to bring about the closest coincidence of the two curves. The first column gives the absolute temperature T, the second the observed values of χ. Starting from any one of the observed values, the values for the other temperatures may be calculated by means of (1) and (2). The fourth

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[1]) Comp. H. KAMERLINGH ONNES and W. H KEESOM. Math. Enz. V 10, Leiden Comm Suppl N⁰. 23, § 33.

column gives the calculated values of χ, the fifth the percentual differences between the values observed and calculated. Finally in the third column are given the values of the product χT in order to show the magnitude of the deviations from Curie's law.

TABLE I.

Crystallised manganese sulphate. [1]

	Mn SO_4 . 4 H_2O			$\dfrac{h\nu_0}{k} = 6.6$
T	$\chi_{obs.} \cdot 10^6$	$\chi_{obs.} \cdot T \cdot 10^6$	$\chi_{calc.} \cdot 10^6$	$100 \dfrac{\chi_{obs.} - \chi_{calc.}}{\chi_{obs.}}$
288.7 K.	66.3	19140	66.3	—
169.6	111.5	18910	112.6	— 0.9
77.4	247	19120	245	+ 0.8
70.5	270	19030	268	+ 0.7
64.9	292	18950	291	+ 0.4
20.1	914	18370	904	+ 1.1
17.8	1021	18170	1015	+ 0.6
14.4	1233	17760	1231	+ 0.2

TABLE II.

Anhydrous manganese sulphate. [2]

	Mn SO_4			$\dfrac{h\nu_0}{k} = 83$
T	$\chi_{obs.} \cdot 10^6$	$\chi_{obs} \cdot T \cdot 10^6$	$\chi_{calc} \cdot 10^6$	$100 \dfrac{\chi_{obs.} - \chi_{calc}}{\chi_{obs.}}$
293.9 K.	87.8	25800	86.3	+ 1.7
169.6	144.2	24460	145.4	— 0.8
77.4	274.8	21270	284.0	— 3.3
64.9	314.5	20410	325.7	— 3.5
20.1	603	12120	603	—
17.8	627	11160	619	+ 1.3
14.4	636	9158	628	+ 1.3

[1] Comm. No. 132e. [2] Comm. N⁰. 132e.

Crystallized manganese sulphate does not show distinct deviations from CURIE's law till hydrogen temperatures are reached and therefore belongs to class a of § 1, the anhydrous salt on the other hand shows deviations over the whole range (class b). For both substances the agreement between observed and calculated values appears satisfactory, although the differences seem somewhat larger than the experimental errors. In the same manner we found:

for crystallized ferrous sulphate: $\dfrac{h\nu_0}{k} = 10$

for crystallized manganese chloride: $\dfrac{h\nu_0}{k} = 13$.

For a substance like platinum the deviations from CURIE's law are enormous and the value of $\dfrac{h\nu_0}{k}$ must be correspondingly large. The measurements with platinum made at Leiden (Comm. N°. 132e) give $\dfrac{h\nu_0}{k}$ about equal to 1500, those by HONDA (above normal temperature) give a still higher value.

§ 6. The above shows that substances which deviate strongly from CURIE's law give large values of $\dfrac{h\nu_0}{k}$. This result is in itself evident, considering that substances with a high value of $\dfrac{h\nu_0}{k}$ must also have a large zero-point energy ($\frac{1}{2}h\nu_0$), so that $U\left(\text{or } \dfrac{1}{\chi}\right)$ will be far from proportional to T at low temperatures.

According to (3) ν_0 is inversely proportional to the moment of inertia of the molecule. It may therefore be expected that substances with large moment of inertia (i.e. small ν_0) will show small deviations from CURIE's law and vice-versâ. This is in general well confirmed by the results. A substance like gadolinium-sulphate $Gd_2(SO_4)_3 . 8 H_2O$ (comp. Comm. N°. 122a) with very heavy molecules, each moreover loaded with 8 molecules of water of crystallization, shows hardly any deviation from CURIE's law even in liquid hydrogen. Anhydrous manganese sulphate deviates strongly even at the ordinary temperature; with the crystallized salt, each molecule of which carries 4 water molecules and must therefore have a large moment of inertia, distinct deviations from the law only appear at hydrogen temperatures. Platinum which deviates very strongly would have molecules with very small moment of inertia.

The possibility of the water of crystallization acting through the increase of the moment of inertia which it produces was previously expressed by KAMERLINGH ONNES and PERRIER. They worked on the view that the deviations were due to the PLANCK-vibrators coming to rest and that their frequency would be smaller for the molecule of crystallized gadolinium-sulphate than for the unloaded molecule.

By comparing anhydrous and crystallized manganese sulphate an estimate may be formed of the distance between the centra of the water-molecules and of the sulphate molecule. The moments of inertia of $Mn\,SO_4$ and of $Mn\,SO_4 . 4\,H_2O$ are found equal to 8.7×10^{-41}, and 109.7×10^{-41}. On the supposition that two of the water-molecules are placed along a line at right angles to the axis of rotation and the other two on the axis, the difference of the two above numbers gives for the distance in question the value $4,4 \times 10^{-9}$. This distance is of the order of the molecular dimensions, but smaller than the adopted value for the radius of a hydrogen molecule (1×10^{-8}): our result would thus seem to indicate that the water-molecules partly penetrate into the molecule to which they are attached.

§ 7. At the suggestion of Dr. KEESOM — to whom I am indebted for several useful hints — I have also compared the observations with a different formula which takes into account the possibility of more than one frequency of rotation, whereas EINSTEIN and STERN assumed that at a definite temperature all the molecules rotate with the same velocity. On Dr. KEESOM's theory the molecular rotational motions in the body under consideration are analysed into a number of stationary waves, which may be supposed to be governed by similar partial differential equations as, say, sound waves in a gas with corresponding conditions at the boundary (crests may take the place of nodes). Along these lines he was led to the hypothesis, that equation (4) of Suppl. N°. 30a (May 1913) with the additional assumption $v_m \sim U^{\frac{1}{3}}$ (as in equations (5) and (7) l. c.) might also hold for the rotational motions. I have found that the correspondence between observation and calculation by the new formula is not appreciably better than by the method followed above and I have therefore in this paper confined myself to the calculation according to the EINSTEIN-STERN view i. e. assuming one value of v at each temperature.

§ 8. *Summary.* The existence of a zero-point energy has recently been made probable by various investigations.

1. The change of the specific heat of hydrogen at low temperatures

has been explained by EINSTEIN and STERN in a satisfactory manner by the assumption of a zero-point energy.

2. The assumption of a zero-point energy for the translational motion of gas-molecules appears to be also required [1]).

3. KEESOM [2]) has shown that the quanta-theory with the additional assumption of a zero-point energy is of great importance in the theory of free electrons in metals and removes a number of difficulties inherent in the equipartition-theory.

4. In conclusion it is shown in this paper, that the assumption of a zero-point energy for the rotations finds a strong support in the observations on the susceptibility of paramagnetic substances; it appears that by means of it the majority of the deviations from CURIE's law observed at low temperatures [3]), which seem to be reducible to three seemingly largely different types may be correlated [4]) and quantitatively explained in a satisfactory manner.

Physics. — "*The vapour pressures of hydrogen from the boiling point down to near the triple-point.*" By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N°. 137d (*On the measurement of very low temperatures.* XXIII) from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 28, 1913).

§ 1. The vapour pressures of hydrogen between the boiling point and the triple-point have been determined by DEWAR [5]) and by TRAVERS and JAQUEROD [6]). The value, which was obtained at

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[1]) Communication to the Wolfskehl-Congress at Göttingen by H. KAMERLINGH. ONNES and W. H. KEESOM. Comp. also W. H. KEESOM. Comm. Suppl. N°. 30a.

[2]) W. H. KEESOM. Comm. Suppl. N°. 30b.

[3]) The abnormal behaviour of anhydrous ferrous sulphate which has a maximum in its susceptibility is here left out of account.

[4]) The theory given in this paper confirms the supposition by KAMERLINGH ONNES and PERRIER mentioned in § 1, that as regards paramagnetism corresponding temperatures exist, which must be taken proportional to a definite temperature, characteristic of each substance; on the above theory the temperature of maximum-susceptibility chosen by the authors for the purpose is to be replaced by the "internal" temperature $\frac{1}{2}\frac{h\nu_0}{k}$, which may be calculated from the zero-point energy.

[5]) J DEWAR. Proc Roy. Soc London, A. 76 (1905), p. 336.

[6]) M W. TRAVERS and A JAQUEROD. Phil. Trans. (A) 200 (1902), p. 155.