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§ 7 above. In Fig. 15 are represented some separations observed in the laboratory *without* Nicol or other analyzer, 5', 6', 7' have been taken in non-uniform fields. 5' is the quartet of  $D_1$  observed across the field; 6' the sextet of  $D_2$  observed axially in a non-uniform, in the central part very strong, field; 7' also refers to  $D_2$  in a weaker field, the observation being made across the lines of force. The type 10' refers to the  $D_2$  line, when observed in a direction parallel to the field. The field is uniform. The separation gives an example of the superposition phenomenon mentioned in § 7.

The analogy of the type 10', Fig. 15 and the type of the "winged line" seems very remarkable. Of course observation of the state of polarization would be necessary in order to prove the analogy.

#### EXPLANATION OF PLATES I—III.

The figures 1—13 are about thirteenfold enlargements of the images given by the grating of the absorption lines  $D_1$  and  $D_2$  in a magnetic field.

The upmost and lowest of the three stripes' of these figures relate to (oppositely) polarized light; in the central part the phenomenon is represented as it is seen in natural light.

PLATE I. 1, 2, 3, 4, observations  $\perp$  lines of force with different vapour density.  
5, 6, observation // lines of force with different vapour density.

PLATE II. 7, 8, observation at  $\mathcal{S} = 60^\circ$  calcspat rhomb alone.  
9,  $\mathcal{S} = 60^\circ$ , calcspat combined with FRESNEL rhomb.  
10, 11,  $\mathcal{S} = 45^\circ$ .  
12,  $\mathcal{S} = 39^\circ$ .

PLATE III. 13,  $\mathcal{S} = 39^\circ$ .  
14, Types of sun-spot lines (adopted from MITCHELL).  
15, 5', 6' 7', separations in non-uniform laboratory fields. 10' superposition phenomenon § 7.

**Physics.** — "*The thermomagnetic properties of elements.*" By Prof. H. E. J. G. DU BOIS and Prof. KŌTARŪ HONDA. (Communication from the Bosscha-Laboratory).

(Communicated in the meeting of January 29, 1910.)

In 1895 CURIE<sup>1)</sup>, though he had investigated relatively few substances, believed that he could formulate his results in the following rules:

1. For paramagnetic substances the specific susceptibility is inversely proportional to the absolute temperature.

2. For diamagnetic substances, on the contrary, the susceptibility is almost independent of temperature.

3. For the latter class of substances, changes of physical state generally have hardly any influence.

<sup>1)</sup> P. CURIE, Ann de Chim. et de Phys. (7) 5 p. 289, 1895. — Oeuvres p. 232 Paris 1908.

4. The same holds for variations of chemical state (allotropy).

One of us in 1900 proposed to call the first of these thermomagnetic rules CURIE'S law and to introduce a *Curie's constant* such that:

$$\chi(\theta + 273) = C.$$

It was also expressly stated that very probably this was only a kind of "limit-law" in the sense of the analogous law for ideal gases. In addition it was very soon shown that the usual theory of directed magnecules leads to such a law, when generalised from a more magnetokinetic point of view; this was theoretically proved and experimentally confirmed in the LORENTZ- and BOSSCHA-volumes of the "Archives"<sup>1)</sup>. With all due regard for CURIE'S important researches and for his first rule, the second can and could have no general signification, for it at once contradicted the results of other observers, e. g. as in the special case of water.

With regard to the third and fourth rules even their author pointed out several exceptions. As the values of the susceptibilities of the diamagnetic substances tested proved much less than those of the paramagnetic bodies, CURIE came to the conclusion that these two opposite forms of magnetic induction were due to completely different causes.

Starting from these experimental conclusions, LANGEVIN<sup>2)</sup> in the year 1905 elaborated an electronic theory of magnetism; he also gave a kinetic representation of CURIE'S first law, completely analogous to the one mentioned above, without, however, mentioning it, and which is in addition perfectly independent of the introduction of electrons.

It appeared, therefore, desirable to investigate the thermomagnetic properties of more substances: in the first place those of elements, in order to judge whether CURIE'S conclusions admit of such an extensive generalisation. It may be at once remarked that such is not at all the case.

*Experimental Arrangement.* The method, previously used by CURIE and other investigators, of the torsion-balance combined with a non-uniform field was applied, employing the semicircular electromagnet recently described in these Proceedings. The axes of the two cores formed an angle of 10° to 20°; the maximum gradient of the field then lies at a certain distance to one side of their point of intersection. The field

<sup>1)</sup> H. DU BOIS, Rapp. Congr. d. Phys. 2 p. 486, Paris 1900. — Arch. Néerl. (2) 5 p. 246, 1900, also 6. p. 581, 1901. — Verh. nat. en gen. Congr. 8 p. 60, Rotterdam 1901. *Notations:*

$a$ , Atomic weight.		$\theta$ , Temperature.
$C$ , CURIE'S constant.		$\chi$ , Specific susceptibility.

<sup>2)</sup> P. LANGEVIN, Ann. de Chim. et de Phys. (8) 5 p. 70, 1905. Journ. de Phys. (4) 4 p. 678, 1905.

itself at this particular point amounted to 25 kilogausses; it was measured from point to point by means of a small standardised spherical test-coil. The sensitiveness of the torsion-balance could be varied; it was determined in the usual way by means of applied additional moments of inertia.

The furnace consisted of a porcelain tube wound with platinum wire and insulated with kaolin powder and asbestos. With a consumption of 1.2 kilowatts a temperature of  $1250^{\circ}$  was attained, which was measured by means of a thermo-element, previously checked by observations on the melting-points of tin, tellurium, antimony, and gold.

*Test-samples.* The great difficulty with all experiments in this sphere of work is and always will be the prevalence of iron, with its overwhelming ferromagnetic properties, though it hardly ever seems to act quite freely. In the case of fifteen elements, their binary alloys with iron were examined in TAMMANN'S laboratory, not in the very diluted state, however, which generally corresponds to ferruginous impurities. Of 81 elements, 43 were tested; many of them were supplied as pure as possible by KAILBAUM; Prof. COHEN and Dr. HORTSMA of Utrecht kindly placed several elements at our disposal; as yet the 10 gaseous elements have not been tested; Li, Rb, Cs, Ca, Sr, Ba could not be obtained sufficiently free of iron; while Be, Sc, Ga, Ge, Y, Rd, and the rare metals could not be procured. Fe, Co, Ni, of course, form a class by themselves. Dr. M. HANDE kindly determined the percentage of iron colorimetrically by the Berlin blue-reaction.

*The experimental results*, moreover, furnish certain physical criteria of their own reliability, for in so far as the susceptibility proves independent of the field there can hardly be question of a ferromagnetic ingredient. With about one third of the samples this was not the case, for the susceptibility diminished (in the algebraic sense) with an increasing field according to a hyperbolic law. From this Mr. MORRIS OWEN calculated the value  $\chi_{\infty}$  which would hold asymptotically for an infinite field; and, in addition, the influence of the ferromagnetic ingredient, which at most amounted to only one sixth — and generally much less even — of what could be imputed to the iron in the free state. The thermo-magnetic properties also afford a test of purity up to a certain point; a few strongly ferruginous substances show a great diminution of susceptibility between  $500^{\circ}$  and  $600^{\circ}$ , whilst above  $700^{\circ}$  the influence of iron hardly need be feared. In no case is there reason to doubt that the value of the susceptibility of absolutely non-ferruginous elements would remain constant, at least within the usual

field-range. The full communication of the results obtained would require many tables and curves; we therefore draw attention to the principal points only.

*Specific susceptibility*<sup>1)</sup> at 18°. The values found lie between — 2 and + 5 (amorphous carbon and palladium respectively). It cannot be maintained that the positive paramagnetic values are on the whole larger than the negative diamagnetic ones. Oxygen alone forms an exception with a value of about 100: the value for manganese was approximately 10; this contained, however,  $\frac{1}{3}\%$  of iron.

CURIE had already pointed out the influence of allotropy in the case of phosphorus and antimony, and also that there is no such influence with sulphur, though it is so well-known for its polymorphous properties. A difference was shown to exist between diamond (— 0,49) and amorphous carbon (— 2,02); silicon crystalline (0,12) and amorphous (— 0,14); and especially between common tetragonal tin (+ 0,03) and grey tin (— 0,29). In the case of tin, the first — the tetragonal — was KAHLBAUM's very pure electrolytic material; it was afterwards inoculated with a small quantity of grey tinpest, kindly sent by Prof. COHEN from the stores of the VAN 'T HOFF Laboratory.

For weak fields indium seemed to be paramagnetic; in a field of 7 Kgs. the value of the susceptibility passed through zero and became negative, doubtless in consequence of 0,013% iron: this phenomenon is of no consequence because it is also discovered in complicated substances such as certain kinds of porcelain, glass, etc.

Notwithstanding many omissions, it was still possible to follow the general course of the curve  $\chi = \text{funct. } (a)$ ; the curve appears to be rather intricate, but still shows a distinct relation to the periodic system. According to the arrangement of MENDELJEFF-BRAUNER's table, the rows (1, 2, 3, 4), (5, 6, 7, 8), and (9, 10, 11, 12) each form a division I, II, III in which the shape of the curve repeats itself in a peculiar way. At the junction of I and II Cr, Mn, Fe, Co, Ni lie on a positive maximum; between II and III, in the same way, the "rare" metals: within I, II and III the diamagnetic negative peaks are occupied by the similar pentavalent elements P, Sb and Bi of the fifth group (3<sup>d</sup>, 7<sup>th</sup>, 11<sup>th</sup> row). In more than one respect further magnetic analogies of secondary importance exist, which, however, must be left unmentioned in this communication.

*Susceptibility at high temperatures.* As a rule the path of the curve  $\chi = \text{funct. } (\theta)$  for any substance proved to be the same when the temperature was increased or afterwards decreased; certain deviations probably depend on a change of condition of the iron present after

<sup>1)</sup> Everywhere below expressed in millionths

( 600 )

<i>C</i>	<i>I</i>	<i>D</i>	<i>C</i>	<i>I</i>	<i>D</i>
Na (0°—97°)	Ti	[O]	B, cryst (400°—1200°)	B cryst (0°—400°)	C, amorphous
Al (657°—1100°) <sup>2</sup>	V (500°—1200°)	Mg (0°—657°)	Si, crystalline	Diamond	Cu
K (0°—150°)	Cr (500°—1100°)	[Fe] (800°—1350°)	P, white	Ag <sup>r</sup>	Zn (300°—700°)
V (0°—500°)	Mn	Co (1150°—?) ?	S, rhombic	I (9°—114°)	Zr (500°—1200°)
Cr (0°—500°)	Mo	[Ni] (350°—800°)	Zn (0°—300°)		Cd (300°—700°)
Nb (0°—400°)	Ru (550°—1200°)	Pd	As, Sublim.		In (0°—150°)
W	Rh	Rare metals?	Se, Metallic		Sb (0°—631°)
Os	Ir	Ta	Zr, cryst (0°—500°)		Te
	Th (0°—400°)	Pt	Cd (0°—300°)		I (114°—200°)
		U	Au		Tl
			Hg (0°—350°)		Pb (0°—327°)
			Pb (327°—600°)		Bi (0°—268°)

heating. Mg and Ru shewed the above mentioned diminution in a marked manner between 500' and 600°. The results are collected in the table p. 600. The elements in square brackets have previously been examined by others; the atomic weights in each column increase from top to bottom; the elements under column *C* show a constant susceptibility, under *I* a numeric increase on heating and under *D* a numeric decrease. The fewest number (4) of elements appears in the fifth column, in the case of which the susceptibility increases on heating, the increase being, however, very small in each instance.

From a thermomagnetic point of view a certain relation also exists in connection with the periodic curve  $\chi = \text{funct. } (\alpha)$ : the paramagnetic elements under *D* all lie at the principal maxima or at the secondary peaks; on the contrary, those under *I* lie on the ascending branches of the curve. Therefore the sharpness of the bends would be flattened more and more at higher temperatures; probably at lower temperatures they would become more accentuated, and it may be that only then do they attain their most characteristic shape; of course the temperature of  $+18^\circ$  is quite arbitrary. Concerning CURIE'S rules the following statements may be made:

1. Only palladium foil from KAHLBAUM, with 0,70% of iron and  $\chi = +6,12$ , on heating followed, more or less, CURIE'S law, but on cooling it shewed complications. With much purer palladium from Dr. HERAEUS, with 0,03% iron and  $\chi = +5,79$ , the susceptibility fell less rapidly than would follow from CURIE'S rule; temperature-hysteresis was not observed on cooling<sup>1)</sup>.

2. There are only 6 diamagnetic elements which do not vary within the whole temperature-range. Of these P, S and Se had already been experimented upon by CURIE.

3. On melting or solidifying, sometimes — not always — a discontinuity appears, which can be classified under one or other of the two following divisions: I, a large or small leap in the curve of  $\chi$  itself, as with P (44°), Ag (961°), Sn (233°), Sb (631°), Te (450°), Au (1064°), Tl (290°), Pb (327°), Bi (268°); II, a rather sudden change of  $d\chi/d\theta$  as with Mg (633°), Cu (1065°), Cd (322°), I (114°); with regard to sulphur, the curve at the melting-point departs slightly from its otherwise absolutely rectilinear character, which variation was probably overseen by CURIE.

<sup>1)</sup> By chance palladium is the only paramagnetic element examined by CURIE; perhaps it was not pure enough. The important results for oxygen, for ferromagnetic metals at very high temperatures and also for their salts crystallised or in solution, of course continue to hold.

4. As regards the thermomagnetic examination of polymorphous transformations, a discontinuous diminution of 15% of the specific susceptibility was found at the transition-point of  $\alpha$ -thallium and  $\beta$ -thallium at 234°. But the most remarkable properties are shewn by tin: If diamagnetic grey tin is slowly heated, at 32° the specific susceptibility ( $-0,29$ ) changes almost suddenly (like the density) and at 35° passes through zero. Possibly this change would wholly take place at the point of transformation (18°) but then at a much slower rate. Further heating continuously increased the susceptibility so that at about 50° the value ( $+0,03$ ) for paramagnetic tetragonal tin was reached, which afterwards remained practically constant; according to DEGENS the point of transformation tetragonal  $\rightleftharpoons$  rhombic tin lies at 161° at which temperature nothing particular was noticed; at the melting point (233°) a discontinuity from  $\chi = +0,03$  to  $\chi = -0,04$  once more appeared; the diamagnetic liquid metal remained nearly unchanged.

An extension of these thermomagnetic investigations towards low temperatures is in preparation

From the above, especially from the conclusions arrived at under 1 to 4, it seems to follow that CURIE's four corresponding rules are certainly devoid of the general meaning, which has rather rashly been ascribed to them. At the same time the experimental starting-points of LANGEVIN's theory are evidently undermined; more solid and broad foundations for future theories can only be laid with the aid of more extensive research.

**Chemistry.** — “*Studies on Tellurium: 1. The mutual behaviour of the elements sulphur and tellurium*”. By Prof. F. M. JAEGER. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of January 29, 1910)

§ 1. Whilst we are in the main thoroughly informed as to the relation of selenium and sulphur, the views as to the mutual behaviour of the elements tellurium and sulphur still differ somewhat. KLAPROTH<sup>1)</sup> has already investigated this subject. He states that on melting together tellurium and sulphur leaden coloured masses are formed crystallising in rays, which, on heating, give off sulphur and yield a porous metallic looking mass, which he takes to be telluriumsulphide. BERZELIUS<sup>2)</sup>, thirty years later again broached the subject; he found that no compounds were formed on melting, but thought that the

<sup>1)</sup> KLAPROTH, Crelle's Ann. (1798). 191.

<sup>2)</sup> BERZELIUS, Gilb.-Pogg. Ann. 8. (1826). 413.