Physics. — "*On the rings of connecting-electrons in* BRAGG's *model of the diamondcrystal.*" By D. COSTER. (Communicated by Prof. H. A. LORENTZ).

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The beautiful investigations of the two BRAGGS [1]) have given us a clear insight in the structure of the diamondcrystal. As is known according to these investigators the structure of this crystal may be represented by the following scheme: a set of cubes, where the *C*-atoms are situated in the corners and in the centres of the side-planes; in which another set of identical cubes, which may be obtained from the first by translating it parallel to itself in the direction of one of the cube-diagonals over a quarter of this diagonal (see fig. 1, where only those atoms are represented, which are situated within a fundamental cube). If we assume, that the valency of the atoms also have a principal meaning in the crystal, this system is of a perfect symmetry. Every *C*-atom namely has in its neighbourhood four other atoms at the same distance and symmetrically situated. (The lines which join each atom with its 4 neighbour-atoms form the diagonals of a cube). In this way the four valencies of the *C*-atoms are satisfied. Now we may assume, that the "bonds" between the atoms are formed by rings of electrons as it is the case in BOHR's model of the hydrogen-molecule. DEBYE and SCHERRER [2]) for instance suggest a model, where each carbon-atom should part with four electrons, one for each valency, for which consequently two electrons should be available. These should revolve about the connecting-axis of two nuclei in a plane perpendicular to this axis and half-way the distance between the nuclei. So the nucleus itself should still retain two electrons and behave at a distance as a four-fold charge. If once we have admitted, that the "bonds" are formed by rings of electrons, from the point of view of symmetry there is much to be said in favour of this model [3]).

DEBIJE and SCHERRER however arrive at the conclusion, that such a model is inconsistent with the experimental data of the two

[1]) Proc. Roy. Soc. Londen (1914) A 89, p. 277.
See also: BRAGG. X-rays and crystalstructure.

[2]) Phys. Z. S. (1918) XIX, p. 476.

[3]) Of course many difficulties yet remain, e.g.: how is the direction of rotation in the orbits. We can also say but little about form and magnitude of the orbit.

BRAGGS (and also with the data, they have obtained with their own method of crystal-photography). In my opinion however they neglect an important element in their reasoning and in this state of things nothing can be said about the existence or non-existence of such rings of electrons on account of data about scattering of Röntgen-rays. This I hope to prove in the following. To this purpose I intend to follow the clear method in which BRAGG has treated the subject.

We consider the octahedronplanes (the planes (111) in the usual notation), which contain the C-atoms, e.g. the plane A, B, C, F, G, H (see fig. 1), a second plane contains D, a third E. All these planes contain an equal number of atoms, their mutual distance is alternately $\frac{1}{4}\ d$ and $\frac{3}{4}\ d$, as represented by fig. 2. If we only regard the reflection by the planes a, according to the ordinary suppositions we shall have a maximum intensity in the reflected beam for

$$2d\ sin\ \varphi = n\lambda,$$

here n has the values 1, 2, 3 etc. Regarding also the planes a' we see that the spectrum of the 2nd order ($n = 2$) disappears, because the planes a' give half a wave-length phase-difference with the planes a. For the same reason the spectrum of the 6th order would disappear. The BRAGGS have observed with the use of *Rh.*-*K*-rays spectra as far as and including that of the 5th order; of the spectrum of the 2nd order nothing could be detected. This very result has given them one of their strongest arguments in favour of the crystalmodel they suggested. With the model of DEBIJE and SCHERRER it is another case. In the usual way they assume, that the scattering is only caused by the electrons and may be calculated in the classical manner. In their calculations they

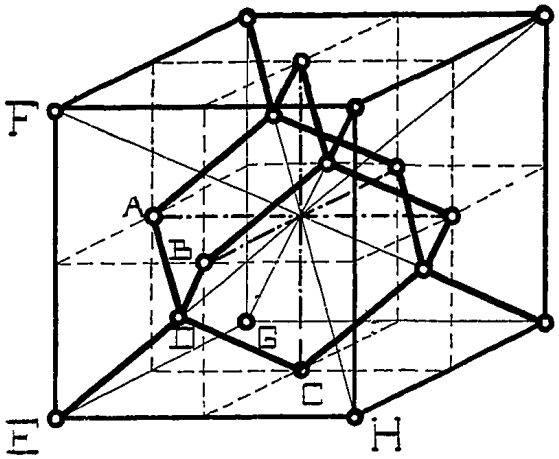
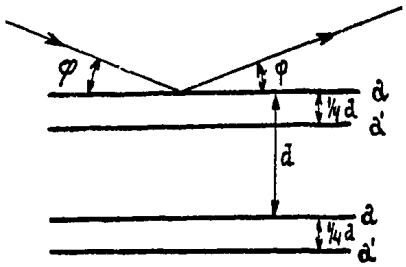


Fig. 1.



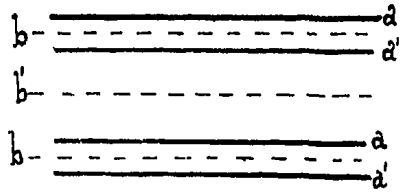


Fig. 2 and 3.

suppose, that the connecting-electrons may be placed in their common centre of gravity. The octahedron-planes are situated as represented by fig. 3. In b and b' we now have the connecting-electrons, in b three times as many as in b'. In this case the nucleus-electrons give also no contribution to the spectrum of 2nd order, the connecting-electrons however should give an intensive spectrum; whereas, as has been said before, the experiment does not give the slightest indication of it, therefore DEBIJE and SCHERRER reject this crystalmodel.

Regarding however a definite octahedron-plane (for instance that with *positive* indices 111), we see, that only $\frac{1}{4}$ of the orbits of the connecting-electrons coincide with those planes (i.e. those belonging to b fig. 3). The other orbits form angles of about 70° with these planes. From the following calculation it may be concluded that it is not admissible to assume, as in fact is done by DEBIJE and SCHERRER, that the electrons of these orbits always remain in the same octahedron-plane. For the sake of simplicity we assume the connecting-electrons moving uniformly in a circular orbit. Suppose $b\,b$ (fig. 4) to be the considered octahedron-plane, $c\,c$ the plane of the orbit, both perpendicular to the plane of the paper. The different phases of the beams reflected in the ordinary way by the electrons of the plane $b\,b$ are only determined by the distance h of the electron to $b\,b$.

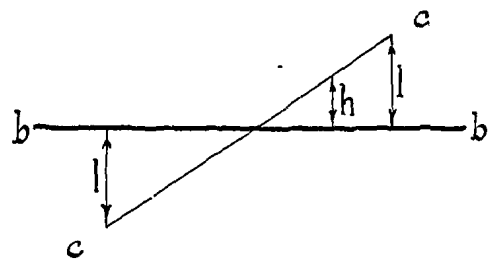


Fig. 4.

To calculate the total reflected beam we are to multiply the separate beam from each electron by the phasefactor $e^{-i\varkappa h}$, where $\varkappa = \frac{4\pi \sin\varphi}{\lambda}$ (φ is the complement of the angle of incidence). If we assume the electrons distributed at random in their orbits, then the probability that an electron is at a distance $h \to h + dh$, is

$$\frac{dh}{\pi\sqrt{l^2-h^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Therefore the total amplitude of the reflected beam is to be multiplied by

$$\int_{-l}^{+l} dh \frac{e^{-i\varkappa h}}{\pi\sqrt{l^2-h^2}} = -\int_{-\pi}^{0} \frac{1}{\pi} e^{-il\varkappa\cos\omega}\, d\omega = J_0(l\varkappa) \quad . \quad . \quad . \quad (2)$$

here J_0 is the BESSELIAN function of order zero.

Taking into consideration, that $\varkappa = \frac{4\pi \sin\varphi}{\lambda}$, we find, if BRAGG's relation

$$2d \sin\varphi = n\lambda$$

is satisfied,

$$\varkappa = \frac{2\pi n}{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As is known the function J_0 is real for real values of the argument and oscillates between decreasing positive and negative limits and so behaves like a "damped" sinefunction. Here this means, that the phase-difference between the resultant beam and a beam reflected by the plane bb is zero or 180°. The absolute value of (2) is always less than 1 except for the argument 0; the motion of the electrons therefore implies a decreasing of the intensity of the reflected Röntgenbeam. The experiment requires, that the spectrum of the second order by reflection from b and b' disappears. This happens strictly if

$$3 J_0(l\varkappa) + 1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since the plane b contains thrice as many electrons as b'.

The smallest value of l, which satisfies (4) and (3) for $n = 2$ is 0,258 d. If we assume according to BRAGG $d = 0{,}203.10^{-8}$ c.m., then $l = 0{,}524.10^{-8}$ c.m., which should give for the radius of the orbit of the electron $r = 0{,}56.10^{-8}$ c.m., which value cannot be excluded for being impossible [1]). Here it is of importance that the relation (4) holds independently of the wave-length of the Röntgenrays. Now I do not intend to attach high value to this calculation of the radius of the orbit. Firstly because my supposition (uniform circular motion of the electrons) is too schematic, secondly it is not probable, that DEBYE and SCHERRER should have been able to ascertain an intensity which should remain for instance below a 100th of that of the spectrum of the first order. This gives in the above case for r all values between about 0,52 and $0{,}62.10^{-8}$ and also between 0,70 and $0{,}81.10^{-8}$ c.m. Greater values of r are a priori improbable.

Now the question arises if the existence or non-existence of the rings of connecting-electrons yet may be proved in the manner suggested by DEBYE and SCHERRER. The spectra of higher order obtained by reflection from the octahedron-plane are not adapted for the purpose. Thus the spectrum of the 6th order should give a difference between the model with the connecting-electrons and that without.

[1]) If we only take account of the change of the two nuclei concerned (as a fourfold charge) and neglect all the disturbances, then according to BOHR an orbit of one quantum and two electrons has a radius of about 0,75 10^{-8} c.m.

First however the intensity decreases in general with the order of the spectrum [1]); secondly the intensity which we should expect according to (2) is very small, because $J_0(lx)$ is again negative for $n = 6$ for the considered value of r (about $0{,}55.10^{-8}$ c.m.).

Now it is interesting to consider the reflection by the other crystal-planes. Here we shall follow the method also used by DEBYE and SCHERRER. When we have a regular crystal, then the intensity of a beam reflected according to the relation of BRAGG is proportional to the square of the so-called structure-factor [2]) S, which is given by

$$S = n \sum A_n e^{i 2\pi (p_n h_1 + q_n h_2 + r_n h_3)} \quad . \quad . \quad . \quad . \quad (5)$$

Here A_n is proportional to the amplitude of the beam radiated by the n^{th} centre of the fundamental cube, $p_n\, q_n\, r_n$ are the ordinates of this centre in the cube, whose edge is 1; $h_1\, h_2\, h_3$ are the indices of the considered crystalplane. These may have a common divisor. If they are for instance 024, then the spectrum of the 2nd order of the plane 012 in the ordinary notation is meant.

For BRAGG's crystalmodel this factor is:

$$S_B = 6\left(1 + e^{i\frac{\pi}{2}(h_1+h_2+h_3)}\right)\left\{1 + e^{i\pi(h_1+h_2)} + e^{i\pi(h_2+h_3)} + e^{i\pi(h_3+h_1)}\right\} \quad . \quad . \quad (6)$$

DEBYE and SCHERRER assume that the connecting-ring scatters in the same way as the nucleus-electrons. Also for their model we may put all A_n's $= 1$.

Therefore they obtain:

$$\left.\begin{aligned} S_D = 2\Big[\Big(1 + e^{i\frac{\pi}{2}(h_1+h_2+h_3)} + e^{i\frac{\pi}{2}(h_1+h_2+h_3)}\Big(1 + e^{i\frac{\pi}{2}(h_1+h_2)} + \\ + e^{i\frac{\pi}{2}(h_2+h_3)} + e^{i\frac{\pi}{2}(h_3+h_1)}\Big)\Big] \\ \Big\{1 + e^{i\pi(h_1+h_2)} + e^{i\pi(h_2+h_3)} + e^{i\pi(h_3+h_1)}\Big\} \end{aligned}\right\} \quad . \quad . \quad (7)$$

Taking into consideration the position of the orbits of the ring-electrons in the above-given way, we get for the structure factor:

$$\left.\begin{aligned} S = 2\Big[1 + e^{i\frac{\pi}{2}(h_1+h_2+h_3)} + e^{i\frac{\pi}{2}(h_1+h_2+h_3)}\Big(J_0(l_1 x) + \\ + J_0(l_2 x)e^{i\frac{\pi}{2}(h_1+h_2)} + J_0(l_3 x)e^{i\frac{\pi}{2}(h_2+h_3)} + J_0(l_4 x)e^{i\frac{\pi}{2}(h_1+h_3)}\Big)\Big] \\ \Big\{1 + e^{i\pi(h_1+h_2)} + e^{i\pi(h_2+h_3)} + e^{i\pi(h_3+h_1)}\Big\} \end{aligned}\right\} \quad . \quad . \quad (8)$$

Here l and x have the same signification as in (2) and (3); the indices at the different magnitudes l refer to the four different angles

[1]) See e.g. BRAGG. Proc. Roy. Soc. A. 89, p. 279, fig. 2.

[2]) See D. and SCH. Phys. Z. S. (1916), p. 279.
For the meaning of this factor see: MARX. Handb. d. Rad. Bd. V. p 581.

which the orbits of the electrons can make with the crystallografic plane under discussion.

The annexed table gives $\frac{|S^2|}{64}$ calculated [1]) for the three cases; in the last case once for a value $r = 0{,}56.10^{-8}$ and once for $r = 0{,}81.10^{-8}$ c.m. Here the ratio between the numbers standing in the same column is only of importance. We have to remark that the spectra (002) and (024) disappear independently of the assumed value of r. Only to make also the spectrum (222) disappear we are bound to certain limits in the choice of r.

Indices.	Br.	D. and Sch.	$r = 0.56.10^{-8}$	$r = 0.81.10^{-8}$
(111)	18	11.6	2.9	5.8
(002)	0	0	0	0
(022)	36	4	0.61	7.8
(113)	18	0.34	1.64	3.55
(222)	0	16	0	0.038
(004)	36	4	11.1	9.0
(133)	18	2	2.1	2.42
(024)	0	0	0	0

In calculating this table no account has been taken of the different factors [2]) that strongly affect the intensity of the expected spectra (mostly those of higher order). Because as yet all is quite uncertain and the foregoing speculations are very schematic, I thought it unnecessary to involve them in the calculations. The table however shows that especially the numbers of the fourth column do not more contradict the experimental data than those of the first [3]). From which we may conclude that for the present it will not be possible to draw a conclusion from the experimental data concerning the existence or non-existence of the connecting-rings. Perhaps here the study of the crystals of homologous elements (*Si*, *Ge*) [4]) may bring a decision.

[1]) The first two columns are taken from D. and SCH.

[2]) e.g. LORENTZ- and DEBIJE factor, see MARX Handbuch V, p. 581 a.f.

[3]) See BRAGG l.c. and DEBIJE and SCHERRER l.c.

[4]) *Si* seems to behave completely as diamond, cf. DEBIJE and SCH. Phys. Z. S. (1916) p. 282.

With *Ge* the number of connecting-electrons is already small compared with that of the nucleus-electrons.