

Chemistry. — “*The Scattering Power of Lithium and Oxygen, Determined from the Diffraction-Intensities of Powdered Lithiumoxide*”.
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1. Li_2O crystallizes in the Fluor-spar type. It is very fit for the determination of the scattering power F of the light oxygen particle as the structure contains no parameter crystallographically undetermined and the effect of the light atoms is not dominated here by heavy ones¹⁾. The fact that the scattering power of Lithium is found at the same time, has two more advantages.

First it enables us to test the intensity formula²⁾. When determining the scattering power a theoretical formula is used, which contains the reflecting power and some other factors changing according to the glancing-angle. In deducing the scattering power from the experimental intensities every error in the factors taken into account enters into the scattering power thus calculated³⁾. If an ionic-lattice were assumed, we can expect the scattering power of lithium to fall off only slightly with increasing glancing-angle, the distances of the electrons from the nucleus being small. In interpreting the intensities we found this dependence to agree with the theoretical estimation; this is considered a proof of the intensity formula used. There are but few substances adapted for the testing of the powder-formula. In the case of light atoms the dependence of the scattering power, in that of heavy atoms the absorption in the rod causes great uncertainty⁴⁾.

Secondly the simultaneous determination of F_{Li} has the advantage of giving a measure for the absolute value of the scattering power of oxygen

1) J. M. BIJVOET and A. KARSSSEN. Rec. Trav. Chim. **43**, 680 (1924).

2) (Note added September 1926). Lately this test was performed by comparing the powder intensities of NaCl with the well known measurements on the BRAGG-method. The powder intensities were measured ionometrically by R. J. HAVIGHURST (Proc. Nat. Acad. Sc. **12**, 375 1926), photographic measurements being made by L. HARRIS, S. J. BATES and D. A. MAC INNES (Phys. Rev. **28**, 235 1926). The powder-formula was found to hold good. Also c.f. A. H. COMPTON and N. L. FREEWAN, Nature **110**, 38 (1922).

3) J. M. BIJVOET, Werken van het Genootschap ter bev. van nat. genes- en heilkunde, XI, 512 (1926).

4) We are investigating whether in the case of a heavy powder the intensities of a rotating rod agree with the calculated intensities, assuming that the substance be homogeneously distributed over the surface. This is essential for the question to which degree quantitative measurements may be used in ordinary structure determinations.

(i. e. the ratio of the amplitude diffracted by the particle to that diffracted by a free electron). In general extrapolation of scattering powers as far as $\vartheta=0$ is very uncertain because of their strong angle-dependence; for the *Li*-ion this extrapolation was possible, the dependence being found to be much smaller in this case. Putting $F_{Li_{\vartheta=0}}^+ = 2$, F_O can be expressed in these units ¹⁾).

2. The intensity formula reads

$$I = \int I_{\vartheta} d\vartheta \cdot \frac{1 + \cos^2 \vartheta}{\sin^2 \frac{\vartheta}{2} \cos^2 \frac{\vartheta}{2}} \nu S^2 \quad 2)$$

Here I_{ϑ} is the intensity for diffraction-angle ϑ ; the integration extends over the small domain in which reflection takes place. ν is the plane-number-factor, S the structure factor.

$\int I_{\vartheta} d\vartheta$ was measured photographically.

In general a factor must be added, which gives the influence of absorption in the rod. In our case — thin celluloid cylinders filled with loose powder of Li_2O , diameter 0.4—0.8 mm — calculation shows this factor to be constant within a few percents ³⁾. This, together with the accuracy of our measurements, permits to neglect the absorption. For the present the influence of the heat-motion is taken up in the F 's.

The sample being very finely powdered the extinction may be neglected ⁴⁾. This important advantage over the one-crystal method causes the examination of the applicability of the powder-method to quantitative measurements.

3. *Photographic intensity-measurements.*

The powder films were made with the apparatus described *altero loco* ⁵⁾. $Cu_{K\alpha}$ radiation was used, sometimes the β -radiation was filtered out by a *Ni*-filter.

The blackening of the photographic plate by homogeneous *X* rays was found proportional to the incident radiation if the blackening is less than 0.6 ⁶⁾. The blackening was measured with the fotometer of MOLL.

¹⁾ We are investigating whether the powder method may give the absolute values of the scattering power from photograms of the substance in known mixture with a substance measured absolutely (e. g. NaCl).

²⁾ P. DEBYE and P. SCHERRER. Phys. Zs. **19**, 474 (1918).

J. M. BIJVOET. Rec. Trav. Chim. **42**, 886 and 898 (1924).

³⁾ A. CLAASSEN, Dissertation, Amsterdam 1926.

⁴⁾ C. G. DARWIN. Phil. Mag. **43**, 800 (1922).

W. L. BRAGG, C. G. DARWIN and R. JAMES, Phil. Mag. (7) **1**, 897 (1926).

⁵⁾ J. M. BIJVOET and A. KARSEN. l.c.

⁶⁾ P. P. KOCH. Ann. de Phys. **45**, 392 (1924).

R. GLOCKER and W. TRAUB. Phys. Zs. **22**, 345 (1921).

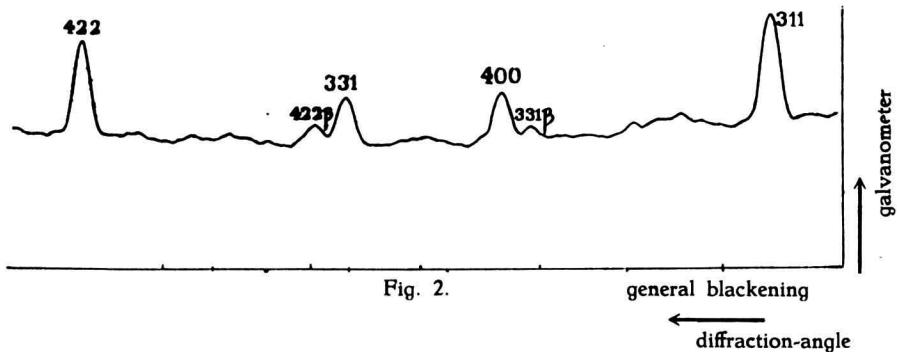
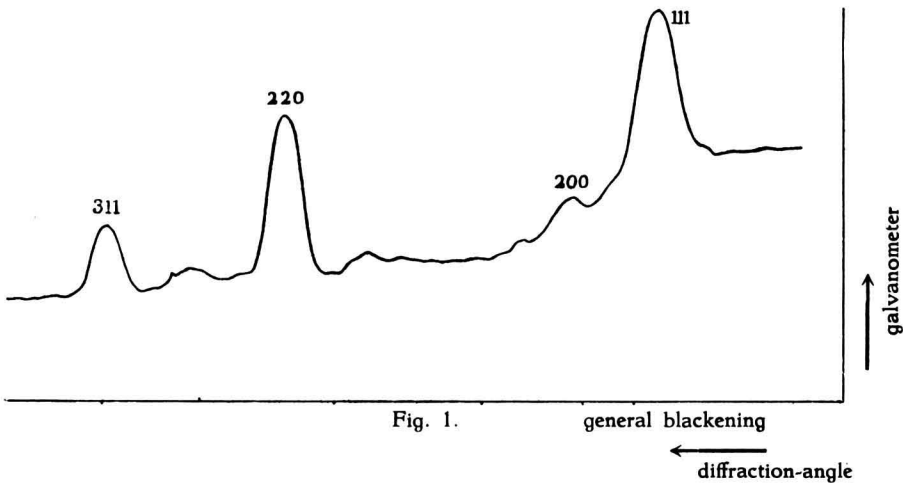
A. BROUWERS. Z. f. Phys. **14**, 374 (1923).

R. BLUNCK. Ann. d. Phys. **77**, 477 (1925).

The registered deviations of the galvanometer were transposed in terms of the blackening S , the quantity $\int S d\theta$ found by measuring the concerning area of the S -curve. In this way I of the intensity equation was found, S being proportional to I_g .

4. Accuracy of the measurements.

The fainter lines were measured on long exposed films, the lines 111 and 220 on shorter exposed ones. The photograms reproduced — of half size, transmission X -ray film to photogram 1 : 10 — are examples of two of these film-parts; on a few films all the lines were well measurable.



The average intensities of column 5 of table I were deduced from the photograms of the right and left halves of some ten films. The extreme values in column 5 show the reproducibility of the measurements. This is better than we expected. For 111 the discrepancies are large; this might have been caused by the great general blackening round this line or perhaps

by its coincidence with the strongest diffraction line of $LiOH$. Li_2O being hygroscopic the hydroxide might have been formed in some small quantities in preparing the rod. The other diffraction lines of $LiOH$ being absent, only very small quantities of $LiOH$ must have been formed; no other $LiOH$ -lines coincide with Li_2O lines but 111.

TABLE I.

1	2	3	4	5		6
$h_1 h_2 h_3$	S	$\sin \vartheta/2$	A	I		S
				average	extreme values	
111	O	0.290	168	165	145—185	9.9
200	O — 2 Li	0.334	91	± 13		± 3.8
220	O + 2 Li	0.472	80	100		11.2
311	O	0.555	108	34	33— 35	5.6
400	O + 2 Li	0.669	18	14	13— 15	8.8
331	O	0.729	66	14	12— 15	4.6
422	O + 2 Li	0.819	70	30	29— 31	6.6
{ 333 511	O	0.870	109	16	16— 17	3.8

Of the reflections with structure factor $2Li-O$ the line 200 was the only one which could be measured on a few films.

For most reflections the accuracy in S may be estimated at a few percents, as a great number of films was measured and the relative error in S amounts to half that in I ($S = \sqrt{I}$).

§ 5. Calculation of the scattering powers.

In table I column 1 contains the indices of the reflecting planes, column 2 the structure factor, column 3 the values of $\sin \vartheta/2$, column 4 the values of $\nu \frac{1 + \cos^2 \vartheta}{\sin^2 \vartheta/2 \cos \vartheta/2} = A$, column 5 the intensities I measured photographically, column 6 values proportional to $\sqrt{I/A}$ or S . In fig. 3 the values of S are plotted against $\sin \vartheta/2_{Cu}$.

Then from the curves F_O and $2F_{Li} + F_O$ that for F_{Li} is deduced. The extrapolated part is dotted in the fig. 1).

In fig. 4 the curves for F_O and F_{Li} are reproduced once more, and here the value 2 is assigned to the ordinate of the intersection of latter curve with the axis.

¹⁾ This extrapolation assumes ions (see 6).

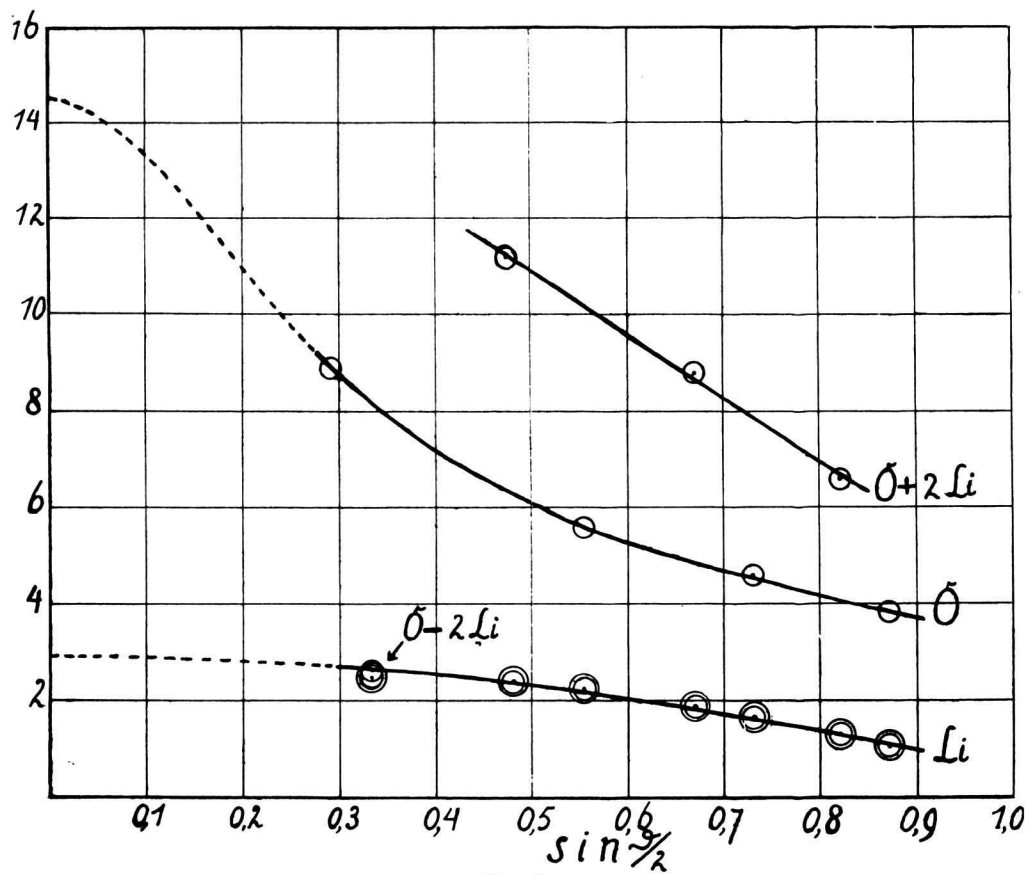


Fig. 3.

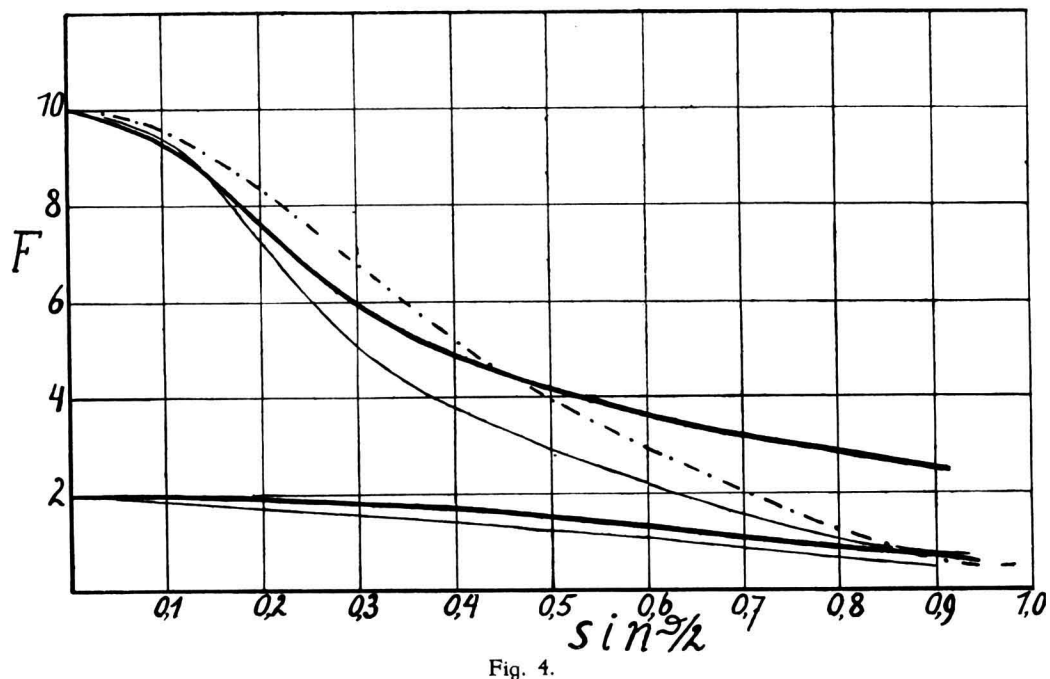


Fig. 4.

Table II gives some values of the scattering power of lithium and oxygen taken from fig. 4.

TABLE II.

$\text{Sin } \vartheta/2$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
F_{Li}	2	1.9 ⁵	1.9	1.8	1.7	1.5	1.3	1.1	0.9	0.7
F_{O}	10	9.3	7.6	6.0	4.9	4.2	3.7	3.2	2.9	2.6

6. Discussions of the scattering power of lithium and oxygen.

As stated above the slight angle-dependence we found in the case of F_{Li} confirms the intensity formula used.

The non-extrapolated part of the F curve of oxygen shows the following features:

1. The decline is so great as to make the assumption of constant scattering power in crystal analysis quite impermittable for light atoms ¹⁾.

2. The decline is much smaller than the one calculated for this domain by HARTREE, notwithstanding our F -values contain the temperature factor too. HARTREE's theoretical values, converted into Cu -radiation, give 3,3:0,9 for the ratio $F_{\text{O}_{311}}:F_{\text{O}_{333}}$; we found 3,9:2,7. On our basis of calculation the ratio $\frac{I_{311}}{I_{333}}$ should have been found some six times greater

to get HARTREE's decline. Even without quantitative measurements this must undoubtedly be rejected.

Extrapolation of the F -curve is possible without great inaccuracy in the case of lithium if ions be assumed. Then a decline as given in the figure is the only one possible. This corresponds with the calculated dependence if the distance of both electrons to the nucleus be about one half the radius of the one-quantum-orbit of hydrogen. This result seems to be plausible; more accurate calculation is not possible without surpassing the accuracy of the measurements, which also contain the effect of the heat motion. It appears fully possible that the F_{O} curve will end for $\vartheta=0$ at $F=10$.

In Fig. 4 the — — — line represents HARTREE's calculated values. As stated above, for $\text{sin } \vartheta/2 > 0,4$ our decline is much smaller than the one calculated.

Should an atomic lattice be assumed, than the X -ray data do not seem to be able to reject this assumption with certainty. ²⁾

¹⁾ N. H. KOLKMEYER, J. M. BIJVOET and A. KARSSSEN. Z. f. Phys. **20**, 82 (1923).

²⁾ In our case one can easily ascertain that this is true. In the well-known example of LiF (P. DEBIJE and P. SCHERRER. Phys. Zs. **19**, 474 (1918)) too the deduction of ions being present is by no means conclusive.

7. Comparison with other results.

F -values for lithium can be derived from the photometrical data of DEBIJE and SCHERRER on LiF . The data of their Table III l.c. give a decline about equal to ours; their values are represented in Fig. 4 by a thin line.

On oxygen one of us made absolute measurements with Fe_3O_4 (magnetite) in the laboratory of Prof. W. L. BRAGG ¹⁾. A decline was found still greater than that calculated by HARTREE. In Fig. 4 this decline is given by the thin line. The difference between both experimental curves seems to indicate that the scattering power of a particle is strongly dependent on its environment. For the oxygen ion with its relatively great number of outer electrons this is not astonishing.

8. We intend to continue our measurements with different wavelengths, at low temperature, on some analogous compounds and mixtures of known composition.

9. *Summary.* The scattering power F of lithium and oxygen is determined by photographic intensity measurements on Li_2O powder with $CuK\alpha$ rays.

F_{Li} was found to agree with the results of DEBIJE and SCHERRER on LiF . In the observed region F_o appeared to be much less dependent on the diffraction-angle as found by CLAASSEN in Fe_3O_4 ; the calculated values of HARTREE for a free oxygen-ion lie between both sets.

We wish to express our hearty thanks to our amanuensis Mr. A. KREUGER for his aid in the experimental part of this investigation.

We are much indebted to Prof. SMITS for his kind interest.

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Amsterdam, July 1926.

¹⁾ A. CLAASSEN. Proc. Phys. Soc. London August 1926.