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Electron Diffraction Investigations of Molecular Structures

I. Application of Fourier Analysis to the Rotating Sector Method

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In the present paper we shall deal with the theory of electron diffraction in gases and of a method for the determination of molecular structures from diagrams obtained by the sector method. In a subsequent paper [1] the results will be given for determinations of about 40 molecular structures which have been carried through by this method. The apparatus used was completed and the method of interpretation worked out at the beginning of the war. The method has now been used in our laboratory for some years and a series of minor modifications have been introduced. Parts of the theory and the results have been published previously in Norwegian periodicals. As these papers, however, are not easily accessible in other countries we shall give a survey both of the method and the results.

THE BASIC THEORY

In this summary we intend to follow chiefly a paper by Finbak.[2] Parts of the theory will be discussed more thoroughly elsewhere.[3]

The diffraction of an electron beam by a point charge of q elementary units may, according to Gordon,[4] be written

$$I_q = \frac{I_0}{R^2}\left[\frac{8\pi^2 m\varepsilon}{h^2}\right]^2 \frac{\lambda^4 q^2}{(4\pi \sin \frac{\vartheta}{2})^4} = K\,\frac{q^2}{s^4} \tag{1}$$

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Where

I_0 = intensity of the primary beam

R = distance between the diffraction point and the point of observation

m, ε = mass and charge of an electron

h = Planck's constant

$\lambda = \frac{h}{mv_0}$ = wavelength of the electrons in the beam

v_0 = the velocity of the electrons

$s = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}$ is used as variable instead of the scattering angle ϑ

The coherent scattering from a freely rotating system of point charges q_i, the mutual distances of which are given by r_{ij}, is then, according to Debye[5] and Ehrenfest.[6]

$$I(s) = \frac{K}{s^4} \Sigma\Sigma\, q_i q_j \frac{\sin sr_{ij}}{sr_{ij}} \tag{2}$$

If the two charges q_i and q_j are altering their mutual distance during the time of observation, the mean intensity is given by

$$I(s) = \frac{K}{s^4} \int_0^\infty \Sigma\Sigma\, q_i q_j\, p_{ij}(r) \frac{\sin sr}{sr}\, dr \tag{3}$$

The value of $p_{ij}(r)\, dr$ represents the probability of these two charges having a mutual distance in the interval from r to $r + dr$.

Eq. (3) may be written

$$I(s) = \frac{K}{s^4} \int_0^\infty \sigma(r) \frac{\sin sr}{sr}\, dr \tag{4}$$

where $\sigma(r)\, dr$ is twice the probability for *any* two charges in our system having a mutual distance between r and $r + dr$. For a neutral system we have

$$\int_0^\infty \sigma(r)\, dr = \Sigma\Sigma\, q_i q_j = (\Sigma q_i)^2 = 0 \tag{5}$$

The connection between the probability function $\sigma(r)$ and the density function $D(r)$[7] is given by the equation:

$$\sigma(r) = 4\,\pi\, r^2\, D(r) \tag{6}$$

Applying the function $\sigma(r)$ to actual systems we may assume that every volume element dv possesses a number of charges corresponding to $\varrho\, dv$ where ϱ is the charge density. We then have the following well known equation for the coherent scattering by a rigid system of spherical atoms

$$I_e(s) = \frac{K}{s^4}\left[\Sigma(Z_i - F_i)^2 + \Sigma\Sigma'\ (Z_i - F_i)\ (Z_j - F_j)\ \frac{\sin sR_{ij}}{sR_{ij}}\right] \tag{7}$$

Here the $F_i\ (s)$ is the atomic scattering functions for X-rays and R_{ij} is the distance between two nuclei. The sums must be taken over all the atoms in the system for which $i \neq j$.

For the coherent scattering by a single atom eq. (7) gives

$$I_i(s) = \frac{K}{s^4}\ (Z_i - F_i)^2 \tag{8}$$

Mott [8] has discussed the atomic scattering, employing wave mechanics, and finds that eq. (8) is valid when the energy of the incident electrons is greater than the binding energy of the K-electrons in the atom by which they are scattered. We then may assume that eqs. (4) and (7) also are valid under the same conditions.

Eq. (7) may now be written

$$I_c(s) = \frac{K}{s^4}\left[\Sigma(Z_i - F_i)^2 + \int_0^\infty \sigma_m\,(r)\ \frac{\sin sr}{sr}\ dr\right] \tag{9}$$

where $\sigma_m\,(r)\,dr$ is twice the probability of finding charges belonging to *different atoms* at a distance between $r + dr$ apart. Adding the incoherent scattering, the total intensity may be written

$$I_t(s) = \frac{K}{s^4}\left[\Sigma((Z_i - F_i)^2 + S_i) + \int_0^\infty \sigma_m\,(r)\ \frac{\sin sr}{sr}\ dr\right] = I_a(s) + I_m(s) \tag{10}$$

Using Fourier's integral theorem we have

$$\sigma_m\,(r) = \frac{2}{\pi}\, r \int_0^\infty \frac{I_m\,(s)}{K}\ s^5\ \sin sr\ ds \tag{11}$$

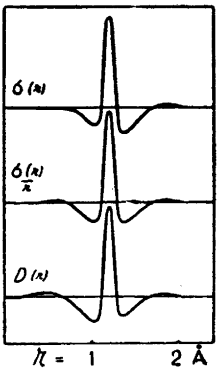

Fig. 1. Theoretical distribution curves without diffraction effects for a diatomic molecule.

The function $\sigma_m(r)$ may be written

$$\sigma_m(r) = \Sigma\Sigma' \sigma_{ij}(r)$$

where $\sigma_{ij}(r)$ depends solely on the charge distribution in two atoms i and j and the distance R_{ij} between their nuclei. Fig. 1 gives the function $\sigma_{ij}(r)$ for two oxygen atoms oscillating about the equilibrium distance 1.2 Å and the corresponding curves $D_{ij}(r) = \frac{\sigma_{ij}(r)}{4\pi r^2}$ and $\frac{\sigma_{ij}(r)}{r}$.

It may be proved that the function $\frac{\sigma_{ij}(r)}{r}$ is symmetrical with respect to the line $r = R_{ij}$, a property which is not shared by the function $\sigma_{ij}(r)$ or $D_{ij}(r)$. The function $\frac{\sigma_{ij}(r)}{r}$ should therefore be more suitable than the other two for the determinations of molecular structures (3). According to eq. (11), the function $\frac{\sigma_m(r)}{r}$ takes the form

$$\frac{\sigma_m(r)}{r} = \frac{2}{\pi}\int_0^\infty \frac{I_m(s)}{K} s^5 \sin sr \, ds \tag{12}$$

The function $\frac{I_m(s)}{K}$ must be determined experimentally, and this may be done by the rotating sector method described below.

THE EXPERIMENTAL TECHNIQUE

It is a well-known fact that a photometric record of an ordinary electron diffraction diagram gives only meagre information regarding the molecular scattering $I_m(s)$. This is due to the form of the intensity curve $I_t(s)$

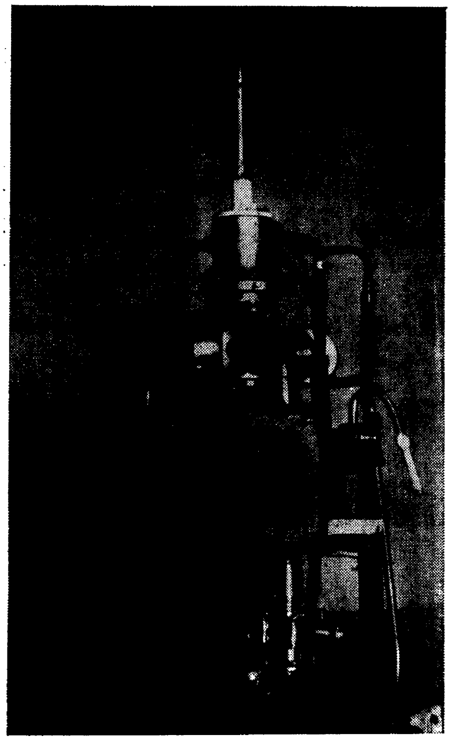

Fig. 2. Electron diffraction apparatus for gases.

which falls off very rapidly with increasing values of s. In order to obtain diagrams on which the blackening is more equally distributed over the whole range of the film, a sector of suitable form may be rotated in front of the photographic plate during the exposure. The sector must have a form such that its screening effect decreases with increasing values of s. The application of such a sector was first proposed by Finbak[9] and later by Debye.[10]

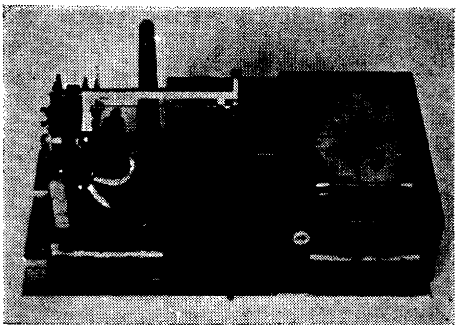

Fig. 3. The rotating sector in its place above the photographic plate.

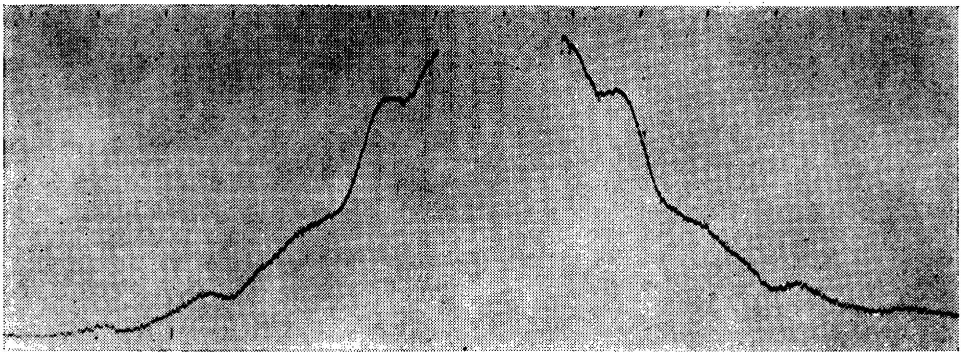

Fig. 4. Photometric record of a sector diagram (benzene)

The diffraction apparatus used in our laboratory, shown in fig. 2, has been described elsewhere.[11] A description of the apparatus will therefore not be given here, but some details concerning the rotating sector should be mentioned. This part of the apparatus is shown in fig. 3. The sector itself is rotated with the incident beam as an axis. Different forms of sectors have been tried, their screening effects being proportional to s^{-1}, s^{-2} and s^{-3}. Experience shows that the sector having the factor s^{-2} is most suitable and this sector has therefore been used almost exclusively in our laboratory. Fig. 4 gives photometric record of a sector diagram of benzene. The maxima and minima of the curve are very conspicuous and the curve is well suited as a basis for the determination of the structure.

The most strightforward way of determining the $I_m(s)$ function would appear to be the procedure used in the case of X-ray investigation of liquids,[12] but in the case of electron diffraction this method has not been successfull. We therefore adopted a different procedure originally proposed in a slightly modified form bv Finbak.[13]

The terms $I_t(s)$, $I_m(s)$ and $I_a(s)$, defined above, correspond to the intensities of the scattered beam before it strikes the rotating sector. Let $I_t'(s)$, $I_m'(s)$ and $I_a'(s)$ represent the same intensities after passing the sector and $P_t(s)$ the ordinate of the photometric record. In fig. 5 the curves $I_t'(s)$, $I_a'(s)$ and $P_t(s)$ are drawn with a common s-axis, the scale of which has been calibrated from gold-foil diagrams. In the same figure we have given the function $P_a(s)$, defined by the equation

$$\frac{I_t(s)}{I_a(s)} = \frac{I_t'(s)}{I_a'(s)} = \frac{P_t(s)}{P_a(s)} \tag{13}$$

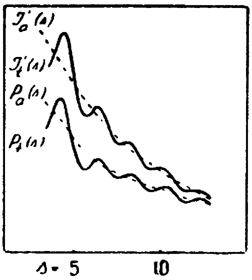

Fig. 5. The correction of the photometric record.

From eqs. (7), (10) and (13) follows that the function

$$\frac{I_m(s)}{I_a(s)} = \frac{P_t(s)}{P_a(s)} - 1 \tag{14}$$

consists of a sum of modified $\frac{\sin x}{x}$ functions. For a sufficiently great interval of s the mean value of this function is near to zero. Our experience indicates that it is possible to make a reliable determination of the curve $P_a(s)$ by applying these relations. A further control of the curve may be established by assuming that the curve $\frac{P_a(s)}{I_a'(s)}$ shall be of a smooth form. Lastly it may be mentioned that rather large modifications in the values of the function $P_a(s)$ have been found to produce very small alterations in the $\frac{\sigma_m(r)}{r}$ curve for $r > 1$ Å. For $r < 1$ Å, however, the form of the $\frac{\sigma_m(r)}{r}$ curve depends to some extent on the values of $P_a(s)$, but the part of the $\frac{\sigma_m(r)}{r}$ function between $r = o$ and $r = 1$ Å. is of practically no consequense to the structure determination.

With the values of $\frac{P_t(s)}{P_a(s)}$ obtained in this way we may calculate the values of

$$\frac{I_m(s)}{K}\, s^5 = \left[\frac{P_t(s)}{P_a(s)} - 1\right]\left[\Sigma\, ((Z_i - F_i)^2 + S_i)\right] s \tag{15}$$

if the functions F_i and S_i are known. These functions have been calculated by James and Brindly[14] and Bewilogua[15] for s values smaller than $s =$ ca 14.

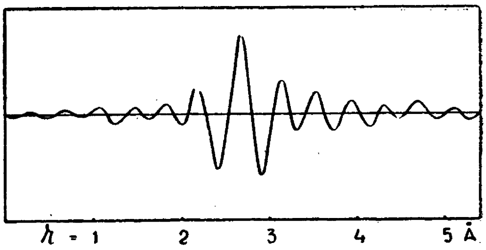

Fig. 6. Experimental σ_m (r) curve of a diatomic molecule.

For our purpose we have extended the calculations of the F_i and S_i functions to $s = 30$. These values will be published separately.

The experimental intensity curves may be obtained only for a limited interval of s between s_1 and s_2. This means that the function $\frac{\sigma_m(r)}{r}$ of eq. (12) has to be replaced by the function

$$\frac{\sigma_m(r)}{r} = \frac{2}{\pi} \int_{s_1}^{s_2} \frac{I_m(s)}{K} \; s^5 \sin sr \, ds \tag{16}$$

The computation of this function is carried out in our laboratory with the help of sin sr tables, the intervals of which are $\triangle s = 0.25$ and $\triangle r = 0.0698$ Å. The limits s_1 and s_2 depend on experimental conditions and are generally $s_1 = 3$ and $s_2 = 20$ or 22 when the field accelerating the electron beam is about 33 K. V.

THE INTERPRETATION OF THE EXPERIMENTAL CURVES

Fig. 6 shows the $\sigma_m(r)$ curve of a diatomic molecule (I_2) determined experimentally from eq. (16). The difference between this curve and the theoretical curve $\sigma_m(r)$ in fig. 1 is rather remarkable. As pointed out by Finbak[2] this difference is undoubtedly caused by the fact that the experimental curve gives the integral from $s_1 = 6$ to $s_2 = 16.5$ while the curve of fig. 1 corresponds with the integral from $s_1 = o$ to $s_2 = \infty$. The systematic errors thus introduced in the experimental $\sigma_m(r)$ curves may be called diffraction effects, as first proposed by Bragg and West[16] in the case of Fourier-analyses of X-ray diagrams from crystals. It should be pointed out, however, that in the case of electron diffraction this error is much more pronounced on account of the great influence of the nuclei on the scattering process.

The interpretation of the experimental $\sigma_m(r)$ curve may be based on the fact that every distance between two nuclei of the molecule gives a maximum

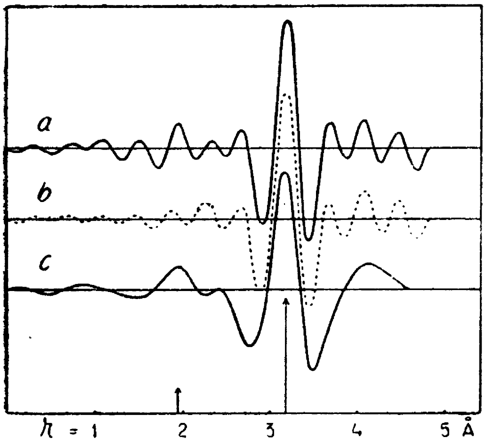

Fig. 7. (a) Experimental σ_m (r) curve of CBr_4. (b) Theoretical σ_m (r) curve with diffraction effects for the Br-Br distance. (c) Experimental σ (r) curve of CBr_4.

on the curve, the magnitude of which is approximately proportional to the product of the atomic number of the two nuclei. In addition to this maximum spurious undulations of period $\frac{2\pi}{s_2}$ are caused by the diffraction effects. Better results may be obtained by varying the limits s_1 and s_2 in the integral and thus altering the period of the diffraction error. In this way some molecular structures have been worked out on the basis of $\sigma_m\,(r)$ curves alone.

In the case of complicated molecules, however, the interpretation of the experimental $\sigma_m\,(r)$ curves very often seemed to be somewhat arbitrary because of the diffraction effects. Following a suggestion by Finbak[17], we may then introduce a new function $\sigma\,(r)$ defined by*

$$\sigma\,(r) = \frac{2}{\pi}\,r \int_{s_1}^{s_2} \frac{I_m\,(s)}{K}\, e^{-ks^2}\, s^5 \sin sr\, ds \qquad (17)$$

The exponential factor e^{-ks^2} has the same influence on our curves as an increasing thermal agitation and thus makes the diffraction effects less conspicuous. With suitable values of the constant k, we may compute $\sigma\,(r)$ curves the interpretation of which is more straightforward than that of the original $\sigma_m\,(r)$ curves. This may be seen from the fully drawn curves of fig. 7. Here the constant k was chosen equal to 0.018, and the integration carried out for the interval $s_1 = 4.5$ to $s_2 = 17$. The two r-values which correspond to inter-

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* Originally this function was termed $\sigma_t\,(r)$ but for simplicity $\sigma\,(r)$ is now generally used.

atomic distances are indicated by arrows, the lengths of which are proportional to the theoretical heights of the maxima.

The influence of the diffraction effects on the $\sigma_m(r)$ curves may conveniently be studied by the use of so called »normal curves».[18] A combination of eqs. (7) and (16) gives

$$\frac{\sigma_m(r)}{r} = \Sigma\Sigma' \frac{2}{\pi R_{ij}} \int_{s_1}^{s_2} (Z_i - F_i)(Z_j - F_j) \sin sR_{ij} \sin sr \, ds \qquad (18)$$

which may be written

$$\frac{\sigma_m(r)}{r} = \Sigma\Sigma' \frac{1}{\pi R_{ij}} \left[\int_{s_1}^{s_2} (Z_i - F_i)(Z_j - F_j) \cos (R_{ij} - r) s \, ds \right.$$
$$\left. - \int_{s_1}^{s_2} (Z_i - F_i)(Z_j - F_j) \cos (R_{ij} + r) s \, ds \right] \qquad (19)$$

The first integral in this equation has its greatest maximum at $r = R_{ij}$ and is symmetrical with respect to the line $r = R_{ij}$. For $r > 0$ the second integral has the same form as the first with $r < 0$. The form of the »normal-function»

$$\int_{s_1}^{s_2} \left(1 - \frac{F_i}{Z_j}\right)\left(1 - \frac{F_j}{Z_j}\right) \cos \varrho s \, ds \qquad (20)$$

for given limits s_1 and s_2 depends only slightly on the atomic numbers and will be discussed more thoroughly elsewhere [3]. If we use the function $\sigma(r)$ defined in eq. (17) instead of the $\sigma_m(r)$-function, the normal curves are given by

$$\int_{s_1}^{s_2} \left(1 - \frac{F_i}{Z_i}\right)\left(1 - \frac{F_j}{Z_j}\right) e^{-ks^2} \cos \varrho s \, ds \qquad (21)$$

With the help of the functions (20) or (21) theoretical $D(r)$, $\sigma_m(r)$, $\sigma(r)$ or $\frac{\sigma(r)}{r}$ curves including diffraction effects may be easily computed for any atomic distance and it is fairly simple to build up such curves for a whole molecule or parts of it. These curves should show the same diffraction errors as the corresponding experimental ones and may directly be compared with them. The dotted curve of fig. 7 gives an example of such a $\sigma_m(r)$ curve for the Br-Br distance. Besides the true maxima at $r = 3.1$ Å, the spurious ones are found in close agreement with the experimental curve.

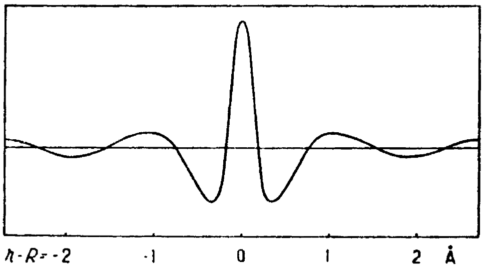

Fig. 8. Normal curve $\frac{\sigma(r)}{r}$ *with diffraction effects of a single interatomic distance.*

In our laboratory both the $\sigma_m(r)$ and the $\sigma(r)$-functions have been employed for the determination of molecular structures.[1] By the introduction of the exponential factor e^{-ks^2} the influence of the experimental errors has been reduced and in most cases a value of k equal to 0.01 was found to be suitable. Lately we have preferred to base our interpretation upon the $\frac{\sigma(r)}{r}$ curves alone, as this function has the most convenient form for the application of normal curves. Fig. 8 gives the normal curve of eq. (21) when the values of the constants are $k = 0.01$ $s_1 = 4$ and $s_2 = 20$. This curve corresponds closely with the $\frac{\sigma(r)}{r}$ curve of a single interatomic distance, and may be compared with the $\frac{\sigma(r)}{r}$ curves which have been worked out from the experimental data.

Some modifications of the interpretation technique which have been used in our laboratory should also be mentioned. When the $\sigma(r)$ function was introduced[18] it was pointed out that this function for a given system may be split into two or more different parts. Each of these parts gives information concerning smaller parts of the scattering system. According to eq. (19) the functions $\frac{\sigma_m(r)}{r}$ or $\frac{\sigma(r)}{r}$ may be written as a sum of functions each belonging to a single interatomic distance. Upon these facts various types of differential methods have been based.

If one or more interatomic distances are common to two molecules, the experimental $\sigma_m(r)$, $\frac{\sigma_m(r)}{r}$, $\sigma(r)$ or $\frac{\sigma(r)}{r}$ curves may be determined for both substances. The difference between the two sets of experimental curves may then give more information about other distances which are not common to these molecules. Sometimes the difference may be taken between the experimental curve and a theoretical curve including diffraction effects for a certain number of distances in the molecule.[13] In both cases the difference curve will be less influenced by the diffraction effects and therefore yields more accurate information about the structure. In many cases the differential methods have made possible the determination of rather fine details in the molecular structures as will be seen from examples given in the following paper.

It must be emphasized that the methods described here demand intensity measurements of high accuracy. These may be obtained by the sector method described. Our experience is that these methods can give better results than any of those based on visually estimated intensities. The best justification of our methods seems to be satisfactory agreement between the experimental curves and the theoretical curves for which diffraction effects have been taken into consideration.

SUMMARY

The determination of molecular structures by use of the sector method is discussed and the different forms of distribution functions introduced by Fourier analysis are compared to each other. Because of the diffraction effects, the interpretation of the experimental distribution curves for complicated molecules seems to be somewhat arbitrary. By the use of normal curves, theoretical curves including the diffraction effects may be obtained for any atomic distance. These curves may then be compared directly with the experimental ones when the structures are to be determined. For the determination of fine details in the structure different types of differential method are introduced. The structures of about 40 molecules obtained by the sector method are given in a subsequent paper.[1]

REFERENCES

1. Hassel, O., and Viervoll, H., *Acta Chem. Scand.* **1** (1947) 149.
2. Finbak, Chr., *Avhandl. Norske Videnskaps-Akad. Oslo I Mat.-Naturv. klasse* (1941) no. 7.
3. Viervoll, H., (in publication).
4. Gordon, W., *Z. Physik* **48** (1928) 180.
5. Debye, P., *Ann. Physik* **46** (1915) 809.
6. Ehrenfest, P., *Amsterdam Acad.* **23** (1915) 1132.
7. Pauling, L., and Brockway, L. O., *J. Am. Chem. Soc.* **57** (1933) 2684.
8. Mott, N. F., *Proc. Roy. Soc.* **127** (1930) 658.
9. Finbak, Chr., *Avhandl. Norske Videnskaps-Akad. Oslo I Mat.-Naturv. klasse* (1937) no. 13.
10. Debye, P. P., *Physik Z.* **40** (1939) 66.

11. Finbak, Chr., Hassel, O., and Ottar, B., *Arch. Math. Naturvidenskab* **XLIV** (1941) no. 13.
12. Finbak, Chr., and Viervoll, H., *Tids. Kjemi, Bergvesen, Metallurgi* 3 (1943) 36.
13. Finbak, Chr., *Tids. Kjemi, Bergvesen, Metallurgi* **1** (1941) 33.
14. James, R. W., and Bundley, G. W., *Phil. Mag.* **12** (1931) 81.
15. Bewilogna, L., *Physik Z.* **32** (1931) 740.
16. Bragg, W. L., and West, J., *Phil. Mag.* **10** (1930) 823.
17. Finbak, Chr., *Tids. Kjemi, Bergvesen, Metallurgi* **2** (1942) 53.
18. Viervoll, H., *Avhandl. Norske Videnskaps-Akad. Oslo I Mat.-Naturv. klasse* (1944) no. **5**.
19. Finbak, Chr., *Tids. Kjemi, Bergvesen, Metallurgi* **1** (1941) 33.

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