$$v = (2/\sqrt{\pi}) \int_{\frac{|r-a|^1}{2\sqrt{\tau}}}^{\frac{r+a}{2\sqrt{\tau}}} (a/r)P_n \left[\frac{r^2 + a^2 - s^2\tau}{2ar} \right] e^{-s^2} ds \cdot Y_n(\theta \cdot \phi)$$

$$= \frac{a^2 Y_n(\theta, \phi)}{\sqrt{(\pi\tau)}} \int_0^\pi P_n(\cos \omega)\sin \omega . d\omega \frac{1}{\rho} e^{-(\rho^2/4\tau)}$$

(35)

where $\rho^2 = r^2 + a^2 - 2ar \cos \omega$. We have also the expressions

$$v = 2a^2(-)^n Y_n(\theta, \phi) \int_0^\infty e^{-k^2\tau} J_{n+1/2}(kr_1)J_{-n-1/2}(kr_2)dk/(ar)^{1/2}$$

$$r_1 = r, \; r_2 = a \text{ if } r < a$$
$$r_1 = a, \; r_2 = r \text{ if } r > a$$

and this, combined with (31) gives the relation

$$W_0(r_2)W_1(r_1) = (-)^n \int_0^\infty \frac{\lambda dk}{\lambda^2 + k^2} J_{n+1/2}(kr_1)J_{-n-1/2}(kr_2)/(r_1 r_2)^{1/2} \quad r_1 < r_2$$

which is closely related to an integral given by Sonine.[5]

[1] After P. A. M. Dirac, *Proc. Roy. Soc. Lond.*, 113 (1927), 621.

[2] Oeuvres, t. 1, p. 234.

[3] I. Fredholm, *Acta. Math.*, 23 (1900), 1; *Compt. Rend.*, 129 (1899), 32; *Rend. Palermo*, 25 (1908), 346. J. Le Roux, *Compt. Rend.*, 137 (1903), 1230. N. Zeilon, *Arkiv. Mat. Astr. och Fysik.*, 6 (1911), 9 (1914); *Nov. Act. Soc. Sc. Upsaliensis*, 4, (1919) 5, J. Hadamard, *Lectures on Cauchy's Problem,* New Haven, 1923, Ch. 3.

[4] *Ann. Math.*, 31 (1930), 158.

[5] N. Sonine, *Math. Ann.*, 16 (1880), 59. See also H. M. Macdonald, *Proc. Lond. Math. Soc.*, 1, 35 (1902), 428.

ON THE POSSIBLE INFLUENCE OF THE MOSAIC STRUCTURE OF CRYSTALS ON THE DETERMINATION OF AVOGADRO'S NUMBER

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(A) *The Experimental Situation.*—The experimental determination of Avogadro's number is very closely related to the determination of the charge of the electron on the one hand and to the absolute determination of the wave-length of x-rays on the other hand. Millikan, as is well known, measured the charge of the electron directly by the oil drop method, long before absolute measurements of the wave-lengths of x-rays were attempted. Values for these wave-lengths, therefore, were obtained from the charge e of the electron in the following indirect way. From e and Faraday's constant F, one derives immediately Avogadro's number,

equal to F/e. The next step is to calculate the lattice constant d of some suitable crystal, whose structure is known, calcite for instance. The spacing d is obtained from the density of the crystal and Avogadro's number. Observing then, the Bragg angle of reflection, Θ for a certain x-ray line one deduces λ from Bragg's relation $2d \sin \Theta = n\lambda$. Corrections for the refractive index of x-rays, etc., have, of course, to be introduced. (See R. T. Birge, *Phys. Review Suppl.*, No. 1, 1929.) For the K_α line of Cu, one obtains in this way $\lambda = 1.5386$ Å.

Recently, methods have been developed to measure the wave-length of x-rays directly by reflecting them on artificially ruled gratings of known spacing. The most accurate value for the above K_α of Cu has probably been obtained by Dr. J. A. Bearden[1] of the University of Chicago. His result is $\lambda = 1.5422$ Å, which is about 0.23% higher than the value of λ mentioned before.

We should mention also some older absolute determinations of the wave-length of x-rays which yielded results less different from those obtained by Bragg's method. Wadlund,[2] in fact, obtained practically identical results for Cu K_α with the two methods. E. Baecklin,[3] on the other hand, found for the K_α line of Al the value $\lambda = 8.333$ Å $\pm$ 0.1%, whereas the value derived from reflections on a gypsum crystal is $\lambda' = 8.3229$ Å, the discrepancy being 0.12%. The values for the charge of the electron and for the Avogadro number as given by Millikan are therefore lower than those derived from the absolute determination of the wave-length of x-rays, the discrepancy being of the order of 0.4% (Baecklin) and 0.7% (Bearden).

(B) *On a Possible Explanation on the Basis of the Mosaic Structure of Crystals.*—The question arises, of course, immediately whether the above discrepancies are due to some sort of experimental errors or whether they are of a systematic nature. It seems to the author that a discrepancy between the results obtained by the two methods sketched in the above *necessarily must exist*. In the chain of reasoning which relates the electronic charge to the wave-length of x-rays, there is one doubtful step. Indeed one has to introduce the assumption that the atoms in the crystal are arranged in an absolutely uniform way, being located in the corners of an ideal crystallographic lattice. Now according to the conception of the *mosaic structure*[4] of crystals this assumption is not quite correct. The theory predicts that the mosaic pattern of rock salt, for instance, is represented by a cubic frame work of planes whose density is about 10% larger than the density of the perfect blocks in between them. As the latter cause the interference of the x-rays, their characteristic lattice constant d_0 must be introduced in Bragg's formula. d_0 is obviously larger than the distance d which is obtained in the usual way by assuming that the crystal is of perfectly uniform density throughout. It appears then,

that we really have to expect a too low value of λ, if the indirect determination is used without taking into account the mosaic structure of the crystals.

The theory is not yet advanced enough to allow us to treat accurately the effects due to the mosaic structure. It enables us, however, to estimate them within quite narrow limits. For rock salt, for instance, the planes which define the mosaic pattern contain 10% more atoms per unit area than the regular crystal planes. In order to abbreviate the expressions, I have proposed[4] to denote the mosaic planes with the letter Π in contradistinction to the regular p-planes. Suppose now, that we have in a regular cubic crystal, one Π plane of density $\rho' = \rho_0(1 + \Delta)$ for n p-planes parallel to it of the density ρ_0, then the average density of the crystal will be

$$\rho = \frac{(n - 2)\rho_0 + 3\rho'}{n + 1} = \rho_0 \left[1 + \frac{3\Delta}{n + 1}\right]. \tag{1}$$

For rock salt, we have $\Delta \cong 0.1$. For the distance D between the Π-planes the same argument can be given which I published in another place[5] for the mutual distance of the surface cracks yielding $D \cong 100$ Å. This means that among about 30 parallel p-planes, we will find on the average one Π-plane. This gives according to relation (1) a relative correction γ for the density equal to

$$\gamma = \frac{\rho - \rho_0}{\rho_0} \cong 0.01$$

which has to be considered as an upper limit as we have chosen the maximum possible value for Δ. The lattice constant d_0 entering Bragg's relation evidently must be deduced from ρ_0 rather than from the directly observed density ρ. The difference between the two according to the above is

$$d - d_0 \cong 0.01 \, d_0/3$$

and the same correction of 0.3% must be applied to the wave-length of x-rays as determined by Bragg's method. Our consideration, therefore, shows that a correction due to the mosaic structure may be of practical importance if the accuracy of the experiments is carried as far as it has been done recently.

(C) *On Some Possible Tests of the Theory.*—If the above considerations are correct, one should expect differences for the wave-lengths of x-rays if determined by Bragg's method on different crystals, rock salt and calcite for instance. For the commonly used heteropolar crystals such as NaCl, $CaCO_3$, $CaSO_4$, etc., the effects due to the mosaic pattern will probably be very nearly the same. Assuming that the difference to be expected is of the order of 10% in γ Bragg's method for the determination of the

wave-lengths of x-rays should yield results at variance by about 0.03% in λ if measurements on two different crystals, say calcite and rock salt are compared.   In order to check up on our consideration in this manner, it would be necessary to make all measurements accurate to within 10% of the above effects due to the mosaic structure.   The necessary operations obviously would be these:

(1) A determination of the density of different samples of two types of crystals, with an accuracy of about one part in 10,000.

(2) A chemical analysis of the same samples with an accuracy of 1 in 10,000.

(3) A determination of the wave-length of a given x-ray line on the two crystals applying Bragg's generalized relation, the accuracy required being 0.003%.

Individual investigations of the above kind have already been carried out with sufficient accuracy in the past.   As regards (1), I mention, for instance, the work of O. K. de Foe and A. H. Compton[6] on the density of calcite and of rock salt with an accuracy of 0.1 to 0.2 mg. per cm.[3] Chemical analyses of crystals with the accuracy required under (2) have also been carried out.   It is known, for instance, that Iceland spar of the purest kind contains only 0.03% Fe_2O_3 and no other chemically measurable contaminations.   As to the third point, it may be mentioned that the precision measurements carried out in Siegbahn's laboratories are of adequate accuracy.   It seems to me, however, that all these investigations are too disconnected for our purpose and do not allow us to draw any definite conclusions.   A systematic combined investigation of the three points mentioned under (1), (2) and (3), therefore would be very desirable.

(D)   *On Other Tests of the Mosaic Structure.*—It may seem more hopeful to determine directly the mosaic structure of the crystals used for the reflection of x-rays and to derive the corrections which have to be applied to the observed wave-lengths afterwards.   Investigations with this purpose in mind are now in progress at this Institute, but no definite results have as yet been obtained.   The mosaic pattern, although it is of absolute geometrical regularity, at least in good crystals, nevertheless makes a very inefficient grating because of the small difference in reflective power between the II-planes and the p-planes.   We have succeeded in showing, for instance, that the mutual distances of the II-planes in perfect metal single crystals are constant within a few per cent, but have not yet been able to observe the diffraction pattern for light reflected from the cross gratings which are formed by the intersection of the mosaic structure with the cleavage faces.   The low efficiency of these gratings is probably responsible for the fact that no ghosts of the x-ray lines reflected from crystals have been resolved, though they should theoretically exist.

(E)   *Effects Due to Internal Cracks.*—In an earlier paper,[5] I have pre-

sented some theoretical reasons for the existence of surface cracks on heteropolar crystals. Both theoretical and experimental evidence can be adduced showing that cracks of the same kind also exist in the interior of these crystals. Different authors[7] have discussed the possibility of clearing up the discrepancy mentioned at the beginning of this paper on these grounds. Most of them came to the conclusion that the existence of internal cracks would make it necessary to introduce corrections which would make the stated discrepancy still worse. It appears to me, however, that no effect is to be expected at all, at least, not if the cracks are of the nature which I have proposed in my paper. The opening of the cracks and the resulting decrease of the average density of the crystal is, indeed, exactly compensated for by the contraction of one or more surface planes bounded by the cracks. The interior structure of the blocks which are formed in this manner, is hardly affected, and it is these blocks, which constitute the major part of the crystal. Their structure, therefore, determines the interference pattern of the reflected x-rays and this will be the same as that given by an ideal crystal except for the intensity and the width of the reflected lines.

[1] J. A. Bearden, *Proc. Nat. Acad. Sci.*, **15**, 528–533 (1929).
[2] A. P. R. Wadlund, *Phys. Review*, **32**, 841 (1928).
[3] E. Baecklin, *Upsala Dissertation*, 1928.
[4] F. Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 816 (1929).
[5] F. Zwicky, *Ibid.*, **15**, 253 (1929).
[6] O. K. de Foe and A. H. Compton, *Phys. Review*, **25**, 618 (1925).
[7] See for instance, A. H. Compton, *J. Frank. Inst.*, **208**, 605 (1929).

THE PROBLEM OF PREPARING OPTICALLY ACTIVE FREE RADICALS

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In carrying out certain investigations on the Beckmann rearrangement Jones and Wallis[1] studied the nature of the products formed by the rearrangement of certain optically active acid azides, and optically active hydroxamic acids. d-Benzylmethylacetazide, $C_7H_7(CH_3)HCCON_3$, was found to give on rearrangement an optically active isocyanate, $C_7H_7(CH_3)HCNCO$, which could be converted into an optically active amine hydrochloride, and by treatment with aniline into an optically active monosubstituted urea. These experiments together with certain other facts taken from a survey of the properties of optically active compounds