**Chemistry.** — *Phase determination in direct Fourier-synthesis of crystal structures.* By J. M. BIJVOET.

A direct Fourier synthesis of the electrondensity in crystals is based on the fact that the amplitude of a density wave is proportional to that of the X-ray beam reflected by the corresponding netplane. The phases of the reflected waves being lost in ordinary X-ray methods [1]), the phase relations between the different density components remain unknown at this stage.

The method of isomorphous substitution $A_1R \to A_2R$ introduces, along familiar lines, known reference waves, viz. the density components of the A-configuration (for atomic scattering power $A_2 - A_1$; we suppose this configuration to be centrosymmetrical and its determination accomplished).

The reference waves being known, their superposition effect on the density waves of the $A_1R$ structure reveals their mutual phase differences, i.e. the unknown phases $\varphi_{hkl}$ of the density waves of the $A_1R$ structure relative to the centre of symmetry of the A-configuration:

$$F^2_{hkl\,A_2\,R} = F^2_{hkl\,A_1\,R} + F^2_{hkl\,A_2-A_1} + 2\,|F_{hkl}|_{A_1\,R}\,F_{hkl\,A_2-A_1}\,\cos\varphi_{hkl\,A_1\,R}\,.$$

Here $|F_{A_1R}|$ is derived from the diffraction-intensities of $A_1R$; $|F_{A_2R}|$ idem for crystal $A_2R$; $F_{A_2-A_1}$ is calculated for the A-configuration of atomic scattering power $A_2 - A_1$.

Now this procedure gives us $\varphi_{hkl}$ *except for its sign,* thus performing the phase (sign) determination only for the case of a centrosymmetrical $A_1R$ structure (projection). Otherwise a synthesis with both $\varphi_{hkl}$ and $-\varphi_{hkl}$ can be resorted to, resulting in a duplicated structure-model [2]).

Now we wish to call attention to the fact that in this non-symmetrical case there is, in principle, a general way of determining the sign of $\varphi_{hkl}$. We can use the abnormal scattering of an atom for a wavelength just beyond its K-absorption limit. This effect is made use of already in X-ray analysis to discriminate between atoms of scattering power nearly equal under normal conditions [3]). Even the abnormal phase shift has been used, as long ago as 1930, by COSTER in a manner similar to that proposed here [4]). Let the abnormal phase shift introduced at atom A be $\delta$. Then the

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[1]) C.f. those methods in which the scattered beam is made to interfere with the direct beam, i.a. H. OTT, Ann. Physik **31**, 264 (1938), D. GABOR, Nature **161**, 777 (1948).

[2]) C.f. C. BOKHOVEN, J. C. SCHOONE, J. M. BIJVOET, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, **52**, 120 (1949).

[3]) See R. W. JAMES, The Cryst. State II (1948) Chapter IV (1).

[4]) D. COSTER, K. S. KNOL and J. A. PRINS, Z. f. Physik, **63**, 345 (1930).

phase differences $\pm \varphi_{hkl}$ between the density waves concerned result in the phase differences $\varphi_{hkl} + \delta$ resp. $-\varphi_{hkl} + \delta$ for the scattered radiation, and so will become distinguishable. At present we are testing the applicability of his method in an actual analysis.

It will be clear that by the above method it also becomes possible to attribute the $d$ or $l$ structure to an optically active compound on actual grounds and not merely by basic convention as in organic chemistry.

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