reported for perfect and mosaic crystals. In particular it is shown, following Werner & Arrott (1965), that for mosaic crystals, contrary to that for perfect crystals, the condensation effect is compensated by a loss of reflectivity of the same factor.

In conclusion, this experiment, on one hand, constitutes a verification of some predictions of the dynamical theory of neutron diffraction, and, on the other hand, opens interesting perspectives to increase the neutron intensities in the diffractometry of small biological samples.

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A Structure Factor Equation for Structures Consisting of Point Scatterers with Known Minimum Distance

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For unitary, normalized and neutron structure factors the equation:

$$0=\sum_{\mathbf{m}} A(\mathbf{h},\mathbf{m})F(\mathbf{m})F(\mathbf{h}-\mathbf{m})$$

with

$$A(\mathbf{h},\mathbf{m})=F(\mathbf{m},\beta_{11})F(\mathbf{h}-\mathbf{m},\beta_{12})F(\mathbf{h},\beta_{21}\beta_{22})-F(\mathbf{m},\beta_{21})F(\mathbf{h}-\mathbf{m},\beta_{22})F(\mathbf{h},\beta_{11}\beta_{12})$$

is valid, where the $F(\mathbf{m},\beta_{\mu\nu})$ are the form factors of arbitrary artificial density functions $\beta_{\mu\nu}$, which are not more extensive than a sphere of diameter equal to the minimum atomic distance of the structure.

Since the early days of X-ray crystallography many attempts have been made to find procedures for the formulation of structure-factor relations, because these can be used as determinantal relations for the unknown phases and hence for structure analysis by direct methods.

A formalism to derive structure-factor equations, which are exactly valid for arbitrary crystals with known chemical content, was first developed by Woolfson (1958) by generalizing the equation of Sayre (1952). The multiple sums of these equations, which make practical application difficult, disappear if one replaces in Woolfson's theory the generating mappings, $\varrho^j(\mathbf{x})$, $j=1,2,\ldots$, of the scattering density, $\varrho(\mathbf{x})$, by linear combinations of $\mathrm{D}_{\nu1}\varrho\mathrm{D}_{\nu2}\varrho$, $\nu=1,2,\ldots$, where $\mathrm{D}_{\nu1}$ and $\mathrm{D}_{\nu2}$ are differential operators (Rothbauer, 1975, 1976).

In the following such a procedure is applied to a practical important degenerate case.

The equation

The electron density distribution, $\varrho_\mu(\mathbf{x})$, $\mu=1,2,\ldots$, of many kinds of atoms differs by a factor, which may be assumed to be constant for the purposes of structure analysis. There are therefore many crystal structures, whose scattering density function:

$$\varrho(\mathbf{x})=\sum_{\mu=1}^{p}\sum_{\nu=1}^{q(\mu)}\varrho_\mu(\mathbf{x}-\mathbf{x}_{\mu\nu}) \qquad (1a)$$

can be written approximately in the form:

$$\varrho(\mathbf{x})=\sum_{\mu=1}^{p}\sum_{\nu=1}^{q(\mu)}f_\mu\beta(\mathbf{x}-\mathbf{x}_{\mu\nu}), \qquad (1b)$$

where $\beta(\mathbf{x})$ is a function characteristic of the shape of the atoms of the structure, p equals the number of different kinds of atoms, f_μ and $q(\mu)$ describe the scattering density and the number of atoms of kind μ, respectively, and $\mathbf{x}_{\mu\nu}$ denotes the position of the νth atom of the μth kind.

If one introduces a distribution:

$$\tau(\mathbf{x})=\sum_{\mu=1}^{p}\sum_{\nu=1}^{q(\mu)}f_\mu\delta(\mathbf{x}-\mathbf{x}_{\mu\nu}) \qquad (2)$$

with a scattering density concentrated at the points $\mathbf{x}_{\mu\nu}$, one can express ϱ as the convolution of τ and β:

$$\varrho=\beta * \tau\,. \tag{3}$$

Hence, if we denote by $F(\mathbf{h},\varrho)$ and $F(\mathbf{h},\tau)$ the structure factors of ϱ and τ and by $F(\mathbf{h},\varrho_\mu)$ and $F(\mathbf{h},\beta)$ the form factors of ϱ_μ and β at lattice point $\mathbf{h}$, respectively, we have

$$F(\mathbf{h},\varrho)=F(\mathbf{h},\beta)F(\mathbf{h},\tau) \tag{4a}$$

$$F(\mathbf{h},\varrho_\mu)=f_\mu F(\mathbf{h},\beta)\,. \tag{4b}$$

This means that we can transform any structure-factor relation which is valid for a structure built up by non-penetrating scatterers with an electron density distribution $f_\mu\beta(\mathbf{x}-\mathbf{x}_\mu)$, $\mu=1,2,\dots p$, into a structure-factor relation valid for a structure consisting of point scatterers with a known minimum distance, and *vice versa*.

We will now apply the formalism to derive structure-factor equations of convolution type for the specified case.

The generating, locally defined mappings $\Gamma_v(\varrho)$ to derive the equations are linear combinations of the kind $\mathrm{D}_{v1}\varrho\mathrm{D}_{v2}\varrho$, $v=1,2,\dots$, where D_{v1} and D_{v2} are differential operators (Rothbauer, 1975). We will here restrict ourselves to the case

$$\Gamma_v(\varrho)=\mathrm{D}_{v1}\varrho\mathrm{D}_{v2}\varrho\,. \tag{5a}$$

The direction derivative of

$$\varrho(\mathbf{x})=1/V\sum_{\mathbf{m}}F(\mathbf{m},\varrho)\exp(-2\pi i\mathbf{m}\mathbf{x})$$

along $\mathbf{v}$ is

$$\mathrm{d}\varrho(\mathbf{x})/\mathrm{d}\mathbf{v}=1/V\sum_{\mathbf{m}}(-2\pi i\mathbf{m}\mathbf{v})F(\mathbf{m},\varrho)\exp(-2\pi i\mathbf{m}\mathbf{x})\,.$$

Taking into account higher and mixed derivatives along different vectors $\mathbf{v}_j$, $j=1,2,\dots$, we see that the Fourier sum of $\mathrm{D}_v\varrho$ must be of the kind

$$\mathrm{D}_v\varrho(\mathbf{x})=1/V\sum_{\mathbf{m}}G(\mathbf{m})F(\mathbf{m},\varrho)\exp(-2\pi i\mathbf{m}\mathbf{x})\,,$$

where $G(\mathbf{m})$ is a polynomial in $mv_1,mv_2,\dots$. The structure factor of $\Gamma_v(\varrho)$ is then given by:

$$F[\mathbf{h},\Gamma_v(\varrho)] \\ =1/V\sum_{\mathbf{m}}G_{v1}(\mathbf{m})G_{v2}(\mathbf{h}-\mathbf{m})F(\mathbf{m},\varrho)F(\mathbf{h}-\mathbf{m},\varrho)\,. \tag{5b}$$

The essential property of $G(\mathbf{m})$ we will make use of is that the basis (German: *Träger*) of the Fourier transform of $G(\mathbf{m})F(\mathbf{m},\beta)$ is not more extensive than the basis of β.

From (4*b*) we obtain:

$$F[\mathbf{h},\Gamma_v(\varrho_\mu)]=f_\mu^2F[\mathbf{h},\Gamma_v(\beta)]\,. \tag{6}$$

The system of equations:

$$F(\mathbf{h},\varrho_\mu)=\sum_v a_vF[\mathbf{h},\Gamma_v(\varrho_\mu)] \\ =\sum_v a_vf_\mu^2F[\mathbf{h},\Gamma_v(\beta)]\,,\ \mu=1,,2,\dots,p\,,$$

does not allow for a solution for the coefficients a_v introduced by Woolfson (1958), since for any two mappings Γ_1 and Γ_2 with the required properties (5)

$$F[\mathbf{h},\Gamma_1(\varrho_\mu)]F[\mathbf{h},\Gamma_2(\beta)]=F[\mathbf{h},\Gamma_2(\varrho_\mu)]F[\mathbf{h},\Gamma_1(\beta)]\,, \tag{7}$$

as follows from (6). This means, that an equation of type:

$$F(\mathbf{h})=\sum_{\mathbf{m}}A(\mathbf{h},\mathbf{m})F(\mathbf{m})F(\mathbf{h}-\mathbf{m})$$

(Rothbauer, 1976), cannot be deduced in this case. But we can obtain another type of structure-factor equation. The parts, $f_\mu\beta(\mathbf{x}-\mathbf{x}_{\mu v})$, of the scattering density function, $\varrho(\mathbf{x})$, are assumed to be non-overlapping. Therefore (7) is also valid for the whole scattering-density function:

$$F[\mathbf{h},\Gamma_1(\varrho)]F[\mathbf{h},\Gamma_2(\beta)]-F[\mathbf{h},\Gamma_2(\varrho)]F[\mathbf{h},\Gamma_1(\beta)]=0\,.$$

Substituting (5) we obtain:

$$0=\sum_{\mathbf{m}}\{G_{11}(\mathbf{m})G_{12}(\mathbf{h}-\mathbf{m})F[\mathbf{h},\Gamma_2(\beta)] \\ -G_{21}(\mathbf{m})G_{22}(\mathbf{h}-\mathbf{m})F[\mathbf{h},\Gamma_1(\beta)]\}F(\mathbf{m},\varrho)F(\mathbf{h}-\mathbf{m},\varrho)\,. \tag{8}$$

The Fourier transform of $G_{\mu v}(\mathbf{m})F(\mathbf{m},\beta)$ is a function $\beta_{\mu v}$ with the property:

$$F(\mathbf{m},\beta_{\mu v})=G_{\mu v}(\mathbf{m})F(\mathbf{m},\beta)\,. \tag{9}$$

From (5) we have:

$$F[\mathbf{h},\Gamma_\mu(\beta)]=F(\mathbf{h},\beta_{\mu1}\beta_{\mu2})\,. \tag{10}$$

Substituting (4*a*), (9) and (10) into (8) we obtain the structure factor equation for the case of point scatterers with known minimum distance:

$$0=\sum_{\mathbf{m}}[F(\mathbf{m},\beta_{11})F(\mathbf{h}-\mathbf{m},\beta_{12})F(\mathbf{h},\beta_{21}\beta_{22}) \\ -F(\mathbf{m},\beta_{21})F(\mathbf{h}-\mathbf{m},\beta_{22})F(\mathbf{h},\beta_{11}\beta_{12})]F(\mathbf{m},\tau)F(\mathbf{h}-\mathbf{m},\tau)\,. \tag{11}$$

The minimum distance between the point scatterers limits the extent of the functions $\beta_{\mu v}$. We notice that the derivation of the convolution-type equation (11) is similar to that for the case of spherical symmetric parts (Rothbauer, 1975). In both cases we have a degenerate solution of the system of equations:

$$F[\mathbf{h},\Gamma_0(\varrho_\mu)]=\sum_v a_vF[\mathbf{h},\Gamma_v(\varrho_\mu)]\,,\quad \mu=1,2,\dots,p\,,$$

with specific types of generating mappings, Γ, which are in the present case defined by (5).

We can also deduce (11) in a somewhat simpler way without making explicit use of generating mappings, Γ, and the usual formalism of deriving structure-factor equations.

From (2) and (3) we have:

$$(\beta_{j1}*\tau)(\beta_{j2}*\tau)=\sum_{\mu v}\sum_{\alpha\gamma}f_\mu f_\alpha\beta_{j1}(\mathbf{x}-\mathbf{x}_{\mu v})\beta_{j2}(\mathbf{x}-\mathbf{x}_{\alpha\gamma})\,,$$

If the bases of the functions β are not more extensive than a sphere of diameter equal to the minimum distance between the point scatterers, the above equation becomes:

$$(\beta_{j1}*\tau)(\beta_{j2}*\tau)=\sum_{\mu v}f_\mu^2\beta_{j1}(\mathbf{x}-\mathbf{x}_{\mu v})\beta_{j2}(\mathbf{x}-\mathbf{x}_{\mu v})$$

and hence

$$(\beta_{j1}*\tau)(\beta_{j2}*\tau)=(\beta_{j1}\beta_{j2})*[\sum_{\mu v}f_\mu^2\delta(\mathbf{x}-\mathbf{x}_{\mu v})]\,.$$

The Fourier transform of this is:

$$F[\mathbf{h},(\beta_{j1} * \tau)(\beta_{j2} * \tau)] = F(\mathbf{h},\beta_{j1}\beta_{j2})[\sum_{\mu\nu} f_\mu^2 \exp(2\pi i\mathbf{h}\mathbf{x}_{\mu\nu})] .$$

Eliminating $\sum f_\mu^2 \exp(2\pi i\mathbf{h}\mathbf{x}_{\mu\nu})$ from two equations of this kind with $j=1$ and $j=2$, respectively, we obtain:

$$0 = F[\mathbf{h},(\beta_{11} * \tau)(\beta_{12} * \tau)]F(\mathbf{h},\beta_{21}\beta_{22}) - F[\mathbf{h},(\beta_{21} * \tau)(\beta_{22} * \tau)]F(\mathbf{h},\beta_{11}\beta_{12}) .$$

Substituting

$$F[\mathbf{h},(\beta_{j1} * \tau)(\beta_{j2} * \tau)] = 1/V \sum_{\mathbf{m}} F(\mathbf{m},\beta_{j1})F(\mathbf{h}-\mathbf{m},\beta_{j2})F(\mathbf{m},\tau)F(\mathbf{h}-\mathbf{m},\tau)$$

we obtain again equation (11).

The functions β of this equation can be chosen arbitrarily with the only restriction that their bases are not allowed to be more extensive than a sphere of diameter equal to the minimum distance of the point scatterers. Therefore, the knowledge of the minimum atomic distance is essential for the formulation of (11), whereas this information is irrelevant for the formulation of the matrix equations for a structure consisting of point scatterers (Rothbauer, 1974).

We may transform Sayre's (1952) equation by (4) into a structure-factor equation for structures consisting of identical point scatterers with a known minimum distance, and obtain:

$$F(\mathbf{h},\beta)F(\mathbf{h}) = A(\mathbf{h}) \sum_{\mathbf{m}} F(\mathbf{m},\beta)F(\mathbf{h}-\mathbf{m},\beta)F(\mathbf{m})F(\mathbf{h}-\mathbf{m}) \quad (12a)$$

$$A(\mathbf{h}) = F(\mathbf{h},\beta)/[\sum_{\mathbf{m}} F(\mathbf{m},\beta)F(\mathbf{h}-\mathbf{m},\beta)] , \quad (12b)$$

where β is an arbitrary density function not more extensive than a sphere with the diameter of the known minimum distance. While (11) is valid for a structure consisting of arbitrary different point scatterers, (12) is valid for a structure consisting of identical point scatterers.

In those cases where structure analysis can be reduced to the localization of point scatterers, all distance vectors between the scattering centres can in principle be obtained from a Patterson map, provided one has enough intensities to calculate a resolved one, and provided there is additional information, *e.g.* $f_\mu > 0$, $\mu = 1,2,\ldots$, which excludes the possibility that Patterson peaks may annihilate each other. In particular, the minimum distance can be obtained in this case from the empty region of the Patterson map around the zero point, and a necessary and sufficient condition for the minimum distance can be formulated in terms of intensities as was shown by Goedkoop, MacGillavry & Pepinsky (1951). Hence the information about minimum distance does not add constraints to the phases that are not already contained in the knowledge of the lattice constants, of a sufficient number of intensities and that the structure under consideration consists of point scatterers with $f_\mu > 0$.

In practice, one mostly cannot get enough intensities from a diffraction experiment to calculate a resolved Patterson map, and in this situation the knowledge of the minimum distance becomes more important in structure analysis as fewer intensities are known. This may be shown by the following example.

Suppose we have a cubic crystal with lattice constant a consisting of point scatterers with $f_\mu > 0$. Now, if we know in addition that the minimum distance exceeds $(\frac{3}{4})^{1/2}a$, we can conclude immediately that the elementary cell contains only one atom and that all the phases of the invariants must be zero. To complete the structure analysis in this case, we have to determine the unknown scattering amplitude of this atom, which may be done by measuring the intensity of only one reflexion on an absolute scale.

Besides the additional restriction which the knowledge of the minimum atomic distance may impose on the phases, this kind of *a priori* information about direct space is of value for structure analysis because it can be translated, in the case of point scatterers, in a simple way into structure factor equations *e.g.* equations (11) and (12). In the more general theory of structure-factor equations dealing with continuous scattering-density functions, the information about the minimum distance must be replaced by knowledge of the non-overlapping of the atoms.

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