direction cannot be defined except for its angle with the unique axis of the magnetic structure.

This is not an unexpected result, especially if we realize the fact that q^2 is a function of second order terms of the direction cosines of e and k, and the summation over equivalent reflections may cancel the cross terms and leave only the terms referring to the unique axis. It may be pointed out here that considerable similarity exists between the expression for $1/d^2$ and $\langle \cos^2 \eta \rangle$, especially in the cases of tetragonal, hexagonal and orthorhombic symmetries. We may examine some of the known magnetic structures (see, for example, Bacon, 1955, and Shull & Wollan, 1956), in the light of the present results (see Fig. 1).

In most of the cases of uniaxial crystals the spin lies in a direction parallel or perpendicular to the unique axis. When it coincides with the unique axis ($\varphi = 0$), the spin direction can be given by the powder data unambiguously. This is not true, however, when it is perpendicular to the unique axis ($\varphi = 90°$). Although in some cases special directions were assumed within the plane, it must be recognized that any other direction within this plane satisfies the powder data equally well.

One known case with φ not equal to $0°$ or $90°$ is tetragonal NiF_2, in which the spin direction was found to be $10°$ off the tetragonal axis (Erickson, 1953). In this case, Erickson stated clearly that the data could not be interpreted to give more information than the inclination of the moment with respect to the tetragonal axis.

The spin configuration of the MnO-type antiferromagnetics shown in Fig. 1(a) presents an interesting example. In this case, the configurational symmetry is rhombohedral although the chemical symmetry is cubic. It can thus be concluded that the spin direction cannot be defined except for its angle with the [111]

direction. The spin directions of this group of compounds were first studied by Shull, Strauser & Wollan (1951) and recently reexamined by Roth (1958). Although the uncertainty of the spin direction within the (111) plane was recognized, the general uncertainty associated with rhombohedral symmetry was overlooked and the spin directions were obtained by a trial-and-error method. A simple formula for $\langle q^2 \rangle$ can be obtained from equation (13) by assuming $\cos \alpha^* = 0$

$$\langle \cos^2 \eta \rangle = \{(n-r)\sin^2 \varphi + (n+2r)\cos^2 \varphi\} \frac{a^{*2} d^2}{3} .$$

Then the problem becomes a one parameter problem to determine φ from the observed intensities.

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X-ray Scattering by Bundles of Cylinders

By R. E. BURGE

Wheatstone Physics Laboratory, University of London King's College, Strand, London, W. C. 2, England

The effects of interparticle interference on the low-angle scattering by a bundle of parallel cylinders in close-packed hexagonal array are calculated. The application of the results to the elucidation of the sizes of coherent hexagonal aggregates from X-ray scattering measurements obtained from both solid samples and solutions of long chain molecules is discussed; the calculations may also be of value in the interpretation of light-scattering results from similar solutions.

Introduction

Interference effects in X-ray scattering at small angles are well known and theoretical and experimental

discussions have been published both for scattering by spheres (e.g. Lund & Vineyard, 1949; Oster & Riley, 1952a; Guinier, Fournet, Walker & Yudowitch,

1955) and cylinders (e.g. Oster & Riley, 1952*b*; Heyn, 1955*a*, *b*; Guinier *et al.*, 1955). The correlation in phase between the X-ray scattering by the component units of a regular assembly of particles reduces the scattered intensity per particle below the value for an isolated particle and is responsible for the observed maxima and minima in the scattering curves at small angles. There are two methods by which the properties of an assembly may be deduced from the observed scattering. The first method involves the fitting of the experimental curve by the calculation of the scattering curves of trial assemblies of particles of given size and shape arranged in a particular array. The second method requires a knowledge of the scattering envelope for a single particle on the same scale as that observed for the assembly. By a Fourier-integral method the probability of finding centres of particles cylindrically symmetrically disposed (for assemblies of cylinders) at a given radial distance from the centre of any reference particle may then be determined.

The first method is applied here to cylindrical units (of a helical form or otherwise) packed in centred hexagonal lattices of finite size. The application of the results to any practical case assumes the presence within a given specimen of a number of coherent assemblies of the cylindrical units of essentially the same size separated by regions where the packing of the units is disordered.

Interest in the interparticle interference effects in finite hexagonal lattices was stimulated by the observation by North, Cowan & Randall (1954) of fine structure in the low-angle equatorial region and near the meridian on the third layer-line of the X-ray diagram from fibres of native rat-tail collagen. The presence and size of the aggregates of helical molecules in this collagen have been qualitatively discussed by McGavin, Harrison & North (1956).

Scattering by assemblies of parallel cylindrical units

Consider an assembly of identical parallel cylinders (or helices) of length $L \gg \lambda$. Let each cylinder be in a fixed position relative to any other and let the separation of the centres of the *p*th and *q*th cylinders in the equatorial plane be u_{pq}. If all rotational orientations of the cylinders about their long axes are equally probable the normalized intensity of scattering of X-rays incident normally to the long axes is given by

$$I(kR) = \frac{1}{n^2} F^2(kR) \sum_p^n \sum_q^n J_0(ku_{pq}) , \qquad (1)$$

where $k = 4\pi(\sin \theta/\lambda)$, $2\theta = \varepsilon$ is the angle of scattering, θ the Bragg angle, the n rods in the assembly have radius R and J_0 is a Bessel function of zero order. $F^2(kR)$ is the normalized cylindrically averaged intensity of scattering by a single cylinder (or helix). Expressions for $F^2(kR)$ have been given by Oster & Riley (1952*b*) for hollow and solid smooth cylinders

and cylinders with radial structure and by Franklin & Klug (1955) for a helix. $F^2(kR)$ is measured experimentally for specimens in which there is no systematic phase relationship between the scattering from the component units.

Equation (1) may be conveniently written in the form

$$I(kR) = F^2(kR)T(u) , \qquad (2)$$

where

$$T(u) = \frac{1}{n^2} \sum_p^n \sum_q^n J_0(ku_{pq}) \qquad (3)$$

represents the interference between the contributions to the total scattering from the n units in the assembly. For any given material $F^2(kR)$ is usually known to a good approximation either from direct measurements made on the scattering curve from a specimen where the lateral organization of the units is minimal or by physical measurements made on monodisperse solutions of the material. For example, in the case of collagen the cylindrically averaged molecular transform of the helix in the equatorial plane is fitted quite well by the scattering curve for a smooth solid cylinder of radius 6 Å; the radius of the hydrated molecule in solution is about 6·7 Å (Boedtker & Doty, 1956).

The changes in the detailed profile of the equatorial scattering observed in fibres when e.g. the relative humidity of the atmosphere in the X-ray camera is varied essentially represent variations in the interference function i.e. changes in the sizes of the regions over which coherent scattering extends. The interference function is calculated below for a number of centred hexagonal lattices.

The interference function

For regular lattices u_{pq} is readily expressible in terms of the separation s of cylinders which are nearest neighbours where s is measured in any plane parallel to the equatorial plane. Equation (3) may be written

$$T(x) = \frac{1}{n^2} \left[n + \sum_{j=1}^{j_{max.}} b_j J_0(r_j x) \right] , \qquad (4)$$

where $x = ks$ and the number of vectors between cylinders in any plane parallel to the equatorial plane of length $r_j s$ is b_j. Here $\sum_j b_j = n(n-1)$ and if there are t complete rings of cylinders surrounding the cylinder defining the centre of the array making up the hexagonal lattice then $j_{max.} = (t+1)^2 - 1$ and $n = 3t^2 + 3t + 1$.

It is convenient to set up a co-ordinate system by which any vector between cylinders may be described by the two integers (l, m) where $l \geq m \geq 0$; it is also convenient to replace the subscript j by (l, m). The co-ordinate system is shown in Fig. 1.

The separations AB and CD are respectively $r_{22}s$ and $r_{21}s$ and the general separation is given by

$$r_{l,m}^2 = l^2 + ml + m^2 .$$

Table 1. *Number of inter-cylinder vectors for the hexagonal lattices $t = 1$ to $t = 8$*

l, m	$b_{l,m}$							
	$t=1$	$t=2$	$t=3$	$t=4$	$t=5$	$t=6$	$t=7$	$t=8$
0, 0	7	19	37	61	91	127	169	217
1, 0	24	84	180	312	480	684	924	1200
2, 0	6	54	138	258	414	606	834	1098
3, 0		24	96	204	348	528	744	996
4, 0		6	54	150	282	450	654	894
5, 0			24	96	216	372	564	792
6, 0			6	54	150	294	474	690
7, 0				24	96	216	384	588
8, 0				6	54	150	294	486
9, 0					24	96	216	384
10, 0					6	54	150	294
11, 0						24	96	216
12, 0						6	54	150
13, 0							24	96
14, 0							6	54
15, 0								24
16, 0								6
1, 1	12	60	144	264	420	612	840	1104
2, 1		72	216	432	720	1080	1512	2016
3, 1		24	144	336	600	936	1344	1824
4, 1			72	240	480	792	1176	1632
5, 1			24	144	360	648	1008	1440
6, 1				72	240	504	840	1248
7, 1				24	144	360	672	1056
8, 1					72	240	504	864
9, 1					24	144	360	672
10, 1						72	240	504
11, 1						24	144	360
12, 1							72	240
13, 1							24	144
14, 1								72
15, 1								24
2, 2		18	78	174	306	474	678	918
3, 2			96	264	504	816	1200	1656
4, 2			36	180	396	684	1044	1476
5, 2				96	288	552	888	1296
6, 2				36	180	420	732	1116
7, 2					96	288	576	936
8, 2					36	180	420	756
9, 2						96	288	576
10, 2						36	180	420

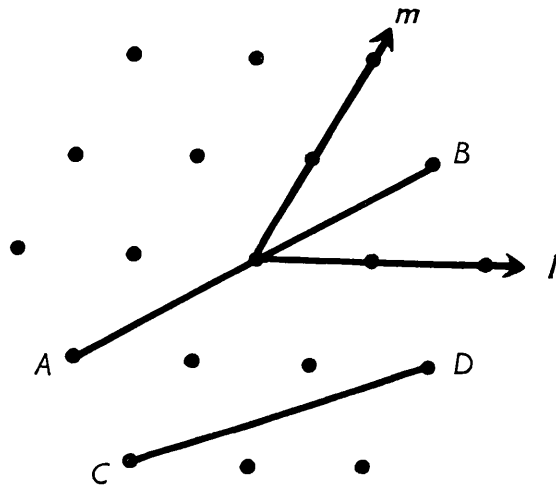| l, m	$b_{l,m}$					
	$t=3$	$t=4$	$t=5$	$t=6$	$t=7$	$t=8$
11, 2					96	288
12, 2					36	180
13, 2						96
14, 2						36
3, 3	24	96	204	348	528	744
4, 3		120	312	576	912	1320
5, 3		48	216	456	768	1152
6, 3			120	336	624	984
7, 3			48	216	480	816
8, 3				120	336	648
9, 3				48	216	480
10, 3					120	336
11, 3					48	216
12, 3						120
13, 3						48
4, 4		30	114	234	390	582
5, 4			144	360	648	1008
6, 4			60	252	516	852
7, 4				144	384	696
8, 4				60	252	540
9, 4					144	384
10, 4					60	252
11, 4						144
12, 4						60
5, 5			36	132	264	432
6, 5				168	408	720
7, 5				72	288	576
8, 5					168	432
9, 5					72	288
10, 5						168
11, 5						72
6, 6				42	150	294
7, 6					192	456
8, 6					84	324
9, 6						192
10, 6						84
7, 7					48	168
8, 7						216
9, 7						96
8, 8						54

Fig. 1. Co-ordinate system used to define the inter-cylinder vectors.

The number $b_{l,m}$ of vectors of length $r_{l,m}s$ may be shown to be given by the expression

$$b_{l,m} = 12 \sum_{r=0}^{r=\min.(t-m,\,2t-l-m)} [2t-l-m+1-r] + 12 \sum_{r=1}^{m-1} [2t-l-m+1]$$

$$+ 12 \sum_{r=\max.(m,1)}^{t} [2t-r-l+1] \quad (5)$$

or alternatively

$$b_{l,m} = 12(R+1)(2t-l-m+1-\tfrac{1}{2}R)_{R=\min.(t-m,\,2t-l-m)}$$
$$+12(m-1)(2t-l-m+1)$$
$$+12(t-R+1)[2t-l+1-\tfrac{1}{2}(t+R)]_{R=\max.(m,1)}. \quad (6)$$

The second term in equations (5) and (6) is valid for those vectors where $m-1 > 0$. If $m = 0$ or $l = m$, the vectors are counted twice and equations (5) and (6) give $2b_{l,m}$. Equation (6) gives $b_{0,0} = 12(3t^2+3t+1) = 12n$ instead of n; the multiplicity factor of 12 corresponding to the symmetry of the hexagonal lattice is not valid for the identity vectors (0, 0) and
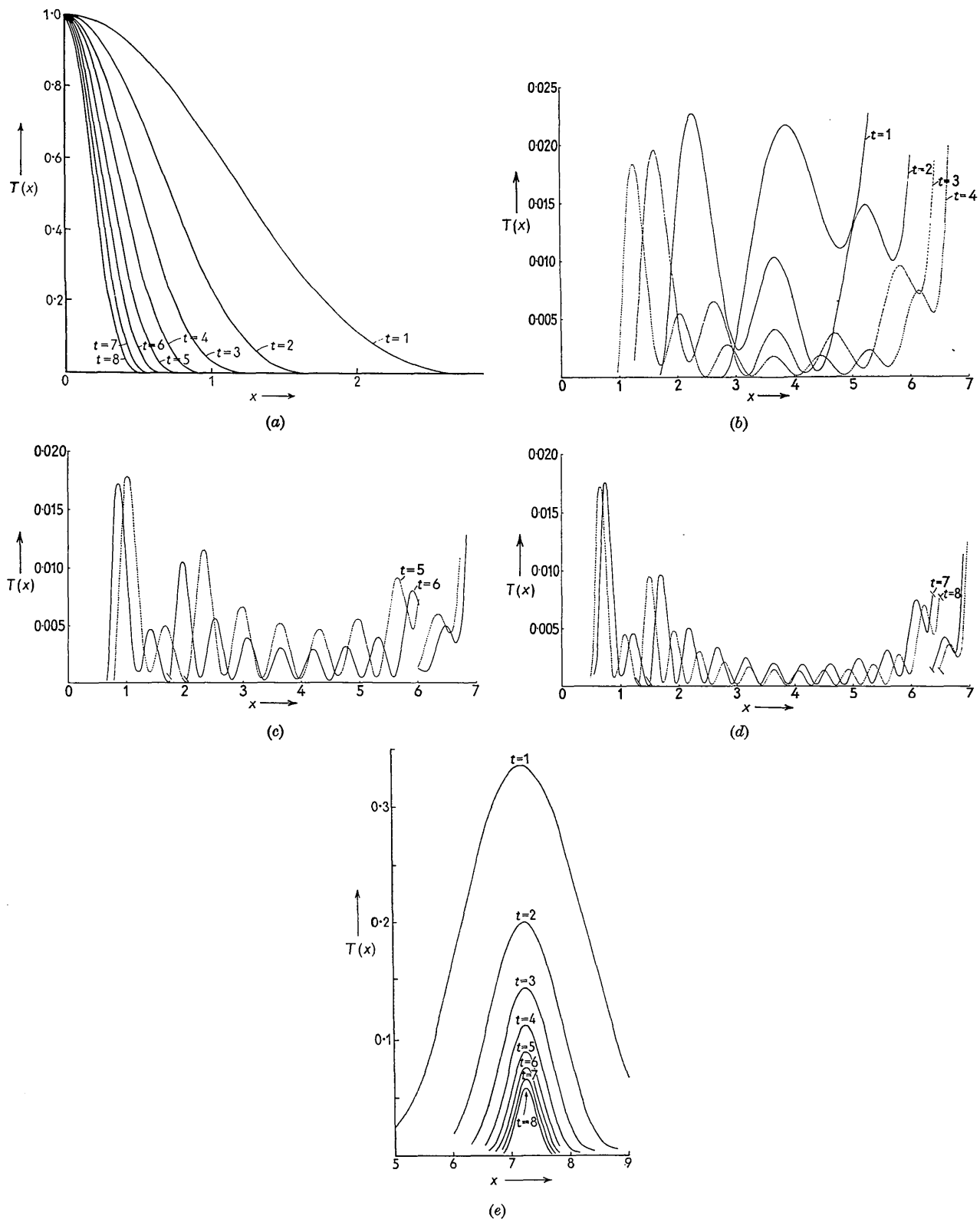
Fig. 2. (a) to (e). The variation of $T(x)$ with x for $t = 1$ to $t = 8$ is shown at intervals of x in the range $x = 0$ to $x = 9$.

In (b) the numerical values of the ordinate should be multiplied by 2 for the curve $t = 1$.

In (c) the scale of $T(x)$ has been changed in the range from $x = 2$ to $x = 6$. In this range the numerical values of the ordinate should be divided by 5.

In (d) the scale of $T(x)$ has been changed in the range from $x = 1.5$ to $x = 6.5$. In this range the numerical values of the ordinate should be divided by 5.

thus equations (5) and (6) are applicable only for $l > m \geq 0$. Values of $b_{l,m}$ for $t = 1$ to $t = 8$ are given in Table 1.

It is of interest to examine the behaviour of $T(x)$ near the origin, as $x \to 0$ equation (4) becomes

$$T(x)_{x \to 0} \to 1 - \frac{x^2}{4n^2} \sum_j b_j r_j^2 \,,$$

and

$$I(kR)_{\varepsilon \to 0} \to 1 - \frac{\pi^2}{\lambda^2} R^2 \varepsilon^2 \left[1 + \frac{4\gamma^2}{n^2} \sum_j b_j r_j^2 \right] , \quad (7)$$

where $\gamma = s/2R$ is the 'swelling' parameter introduced by Oster & Riley (1952b).

An International Business Machines Type 650 Electronic Data Processing Machine was programmed to calculate $T(x)$ and the computations carried out for the eight hexagonal lattices in the range $x = 0$ to $x = 9$ at intervals of 0·06. The zero order Bessel functions were computed by means of an expansion in Tchebychev polynomials (Hitchcock, 1958) and a modified form of the summation procedure adopted by Langridge, Barnett & Mann (1958). The minimum accuracy of the results for $T(x)$ (at the minima for $t = 8$) was 1%; the complete calculation took 8 hr. The values of $T(x)$ are plotted against x for $t = 1$ to $t = 8$ in Fig. 2.

The main maximum in the $T(x)$ curves shown in Fig. 2(e) moves progressively from $x = 7·205$ towards the value $x = 7·255$ corresponding to an infinite hexagonal lattice. The number of maxima in the range of x considered is $2t$.

Discussion

Coherent assemblies of long chain molecules are produced in fibres by inter-chain bonds such as the –S–S– bridge and the OH $\cdots$ OC hydrogen bond together with Van der Waals forces and weak Coulomb forces. In concentrated solutions of polyelectrolytes e.g. proteins and nucleic acids, aggregation is produced by Coulomb interactions between the ionized groups which impose restrictions on the spatial distribution of the charged molecules. The $T(x)$ curves may be used to deduce the size of the coherent scattering units (for the hexagonal case) from the small-angle X-ray scattering produced by either solid samples or solutions. The mean size of the regions where ordered packing exists is directly related to the gradient of the scattering curve at the origin since from equation (7) we have to a good approximation that

$$n^2 / \left(\sum_j b_j r_j^2 \right) \sim -8\pi^2 \gamma^2 R^2 \varepsilon \Big/ \left(\lambda^2 \left(\frac{dI}{d\varepsilon} \right)_{\varepsilon \to 0} \right)$$

When the $T(x)$ functions are used to analyse an experimental curve functions $T(k)$ and $F^2(k)$ are evaluated from $T(x)$ and $F^2(kR)$ by using the appropriate values of s and R. Since $F^2(k)$ decreases rapidly as k increases when R is in the range found for long chain molecules the maxima in $I(k) = F^2(k)T(k)$ are displaced to lower k values. If a Gaussian shape is assumed for a maximum in $T(k)$ at $k = k_0$ given by $T(k) = T_0 \exp[-\alpha^2(k-k_0)^2] + \Delta T_0$, then the shift Δk in the position of the corresponding maximum in $I(k)$ is given for Δk small by

$$\Delta k \simeq \left[\frac{d}{dk} (F^2(k)) \right]_{k=k_0} T(k) / [2\alpha^2 F^2(k_0) T_0] \,.$$

The scattering of aggregates of cylindrical units has been dealt with above with particular reference to the X-ray case but the results may be applied to the interpretation of intensity data obtained by light-scattering (visible radiation) from solutions of long chain molecules providing that the conditions $\Delta n_0 \ll 1$ and $4\pi L \Delta n_0 \ll \lambda$ (e.g. Oster, 1948) are satisfied. Here L is the length of a single cylindrical unit and Δn_0 is the difference between the refractive indices of the solution and the solvent for light of wavelength λ. The second condition is usually satisfied for solutions of high polymeric materials while the first can be satisfied by addition of highly refractive substances to the solution.

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