in the experimental work and in the preparation of drawings.

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The Interference Theory of Ideal Paracrystals

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The concept of a distorted lattice, 'ideal paracrystal', and its diffraction theory lead to a generalization of other well known interference theories and, in particular, under certain special conditions, degenerate to the theory of crystals by von Laue and Bragg, to that of liquids by Debye & Menke and Zernicke & Prins, and to that of amorphous matter by Guinier–Warren–Hosemann.

No single comprehensive theory of X-ray diffraction by matter of all kinds exists at present. There are three principal theories, namely the theory of X-ray diffraction by crystals by Laue (1913) and Bragg (Bragg & Bragg, 1913), that of liquids by Zernicke & Prins (1927) and Debye & Menke (1931), and that of 'amorphous' matter by Guinier (1939*a*, *b*) and Hosemann (1939), but the exact domain of validity of each of these is not clearly defined. Often for a single substance, e.g. a high polymer, the simultaneous existence of 'crystalline', 'liquid' and 'amorphous' features of the material is suggested. Various authors (Kratky, 1933, 1946; Hermans, 1944; Hermans & Weidinger, 1948; Warren, 1941; Bear & Bolduan, 1951; Fournet & Guinier, 1949) have tried to explain the X-ray diagrams by using additional hypotheses, but unfortunately no single theory explains satisfactorily all the characteristic features of the interference phenomena.

The concept of the 'ideal paracrystal' and the theory of its X-ray diffraction as given by Hosemann (1950*a*, *b*) is a step to fill up the gap in this direction. This theory uses the convolution or *Faltung* of Fourier transformation, the importance of which in the interference theories was first pointed out by Ewald (1940) and Hermans (1944).

Let there be N particles, each containing M electrons. According to the crystal theory, the scattered intensity at any angle is proportional to N^2M^2, whereas in the interference theory of liquids it is proportional to NM^2. 'Particle' in the first case stands for the total number of atoms in a lattice cell, and in the second case for the liquid molecules themselves. Moreover, there are many substances whose scattered intensity is proportional to $Nf^2(2\theta)$, where $f^2(2\theta)$ denotes the scattered intensity of each particle and 2θ is the scattering angle. Gases and vapours scatter according to this law where N represents the number of gas molecules. Guinier (1939*a*, *b*) and Hosemann (1939) have, however, shown that such 'amorphous' scattering is also obtained in the small-angle scattering of colloidal substances where N represents the number of colloid particles. Riley (1944, p. 232), therefore, classifies substances such as amorphous coals as 'solid bodies of gas type'. In view of this diversity in the behaviour of matter with regard to its diffraction power, it is desirable to develop a theory which gives the general phase relations between the scattered amplitudes of the individual particles and yields simultaneously the two extreme cases, namely $J \sim Nf^2$ and $J \sim N^2M^2$, as well as the intermediate case of 'liquids', namely $J \sim NM^2$. This theory is fundamentally one of the statistical problem of order–disorder.

Let $a_k (k = 1, 2, 3)$ be the three fundamental vectors of a distorted space lattice, and $H_k(x)$ be the frequency of meeting the vector $a_k = x$ in the lattice, so that $\int H_k(x)dv_x = 1$ and $H_k(x)dv_x$ is the probability of finding the vector $a_k = x$ ending in the volume dv_x. $\varrho(y-x)$ is the electron-density function of the lattice cell, whose origin lies at the point x. ϱ fluctuates purely statistically from cell to cell and is independent of the special values of a_k.

The Fourier transform $G(b)$ of any space function $g(x)$ in physical space is defined by

$$G(b) = \mathfrak{F}(g) = \int g(x) \exp\,[-2\pi i(bx)]dv_x\,.$$

The integral is to be taken over the whole of physical space. dv_x is the volume element in this space. b is called the 'reciprocal vector' in Fourier space and is given by

$$b = (s-s_0)/\lambda, \quad |b| = 2\sin\theta/\lambda\,,$$

where s, s_0 are unit vectors in the direction of the scattered and incident beams respectively, λ is the wave length and 2θ is the scattering angle. (bx) is the dimensionless scalar product of the vectors b and x in the two spaces. Further, let the following 'structure factors' be defined as

$$f(b) = \mathfrak{F}(\varrho); \quad F_k(b) = \mathfrak{F}(H_k); \quad S(b) = \mathfrak{F}(\sigma)\,.$$

Following Ewald, $\sigma(x)$ is called the shape function of a single paracrystallite; it has the value 0 for all vectors except those ending in the paracrystallite, where it has the value 1. Finally let $f_e(2\theta)$ denote the scattered amplitude of a single electron.

For ideal paracrystals which have sufficient numbers of lattice cells ($\gtrsim 5$) in all three directions the mean scattered intensity is given by

$$J = f_e^2(J_1+J_2)\,, \tag{1}$$

where

$$J_1 = N\left(\overline{f^2}-\bar{f}^2\right)\,, \tag{2}$$

$$J_2 = \frac{1}{v_r}\bar{f}^2\cdot\widehat{|S|^2 Z^{1/v_r}}\,. \tag*{(3)*}$$

$Z^{1/v_r}(b)$ is called the lattice factor of ideal paracrystals† and is given by

$$Z^{1/v_r}(b) = \prod_{k=1,2,3} \mathrm{Re}\,\frac{1+F_k}{1-F_k}\,, \tag{4}$$

where v_r is the mean value of the volume of a cell of the distorted lattice in physical space.

Equations (3) and (4) hold good also for one-dimensional and two-dimensional lattices.

It can be shown that for ideal crystals equation (4) degenerates into the well known 'peak-function' of the reciprocal lattice

$$Z^{1/v_r}(b) \rightarrow \frac{1}{v_r}\sum_h P^1(b-b_h)\,,$$

where b_h is the radius vector of the point h of the reciprocal lattice and $P^1(b)$ is the normalized point function, which completely corresponds to Dirac's δ-function and is defined by

$$P^1(b) = 0 \text{ for all } b \neq 0 \text{ and } \int P^1(b)dv_b = 1\,.$$

Since

$$\widehat{|S|^2 P^1}(b-b_h) = |S(b-b_h)|^2\,,$$

equation (3) degenerates for a crystal into the well known formula

$$J_2 = \frac{1}{v_r^2}\bar{f}^2\sum_h |S(b-b_h)|^2 \quad \text{('crystalline' case)}. \tag{3a}$$

In the general case of paracrystalline lattices equation (4) represents a 'lattice hump function'; individual humps lying at the points b_h are more and more broadened with increasing $|b_h|$. Thus the 'amorphous' case is realised at sufficiently great scattering angles where the limiting condition

$$\lim_{|b|\rightarrow\infty} Z^{1/v_r}(b) = 1$$

is practically fulfilled.

The intensity of the scattered radiation is then given by (cf. equations (2) and (3))

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* The folding (in German *Faltung*) of the functions $G_1(b)$ and $G_2(b)$ in Fourier space is defined by

$$\widehat{G_1G_2} = \widehat{G_2G_1} = \int G_1(c)G_2(b-c)dv_c\,,$$

where c is also a reciprocal vector, ending in the volume element dv_c, and the integration runs over the whole of the Fourier space.

† $1/v_r$ denotes an index and not a power of Z (cf. Ewald, 1940) where $\int\limits_{\text{lattice cell}} Z^{1/v_r}dv_b = 1/v_r$ and dv_b is the volume element in Fourier space.

$$J = Nf_e^2 \,.\, \overline{f^2} \qquad \text{(‘amorphous’ case)}, \quad (3b)$$

since $\int |S|^2 dv_b = v$ (v is the volume of the paracrystal) and $v/v_r = N$ the number of ‘particles’.

For all b_h humps of $Z^{1/v_r}(b)$ which are relatively broad compared to the shape factor $|S(b)|^2$, equation (3) degenerates into

$$J = Nf_e^2\{\overline{f^2}+\bar{f}^2(Z^{1/v_r}(b)-1)\} \qquad \text{(‘liquid’ case)}. \quad (3c)$$

It can generally be proved that for all reflexions $b_h \neq 0$, equation (3*c*) holds then, and then only, when the interaction zone* of a particle (i.e. lattice cell) is small compared to the volume v of a paracrystal. Thus, except for the ‘central spot’ $b_h = 0$, there appears no scattering component proportional to N^2. For a powder diagram equation (3*c*) degenerates further into the well known form of the equation in Debye's theory of liquids (Debye & Menke, 1931):

$$J = f_e^2(\overline{f^2}+\bar{f}^2 \frac{2\lambda^3}{pv_r}\int_0^\infty W(q)q \sin 2\pi pq\, dq) \,, \qquad (3d)$$

where $p=|b|\lambda$, $q=|x|/\lambda$ and $W(q)$ is Debye's spherical ‘*a priori*’ distance statistics of liquid molecules. If, on the contrary, the interaction zone of a lattice cell is large compared to the mean value v of the volume of a paracrystal, then each hump of $Z^{1/v_r}(b)$ is small compared to the shape factor $|S|^2$, and equation (3) degenerates into the crystalline case, equation (3*a*), for all reflexions.

In all other cases however—and they are quite frequently encountered in nature—where the interaction zone is of the same order of magnitude as the mean volume v of the paracrystal, both the crystal reflexions of the form (3*a*), and liquid and amorphous reflexions of the forms (3*c*) and (3*b*), respectively, appear on the X-ray diagram. Thus all types of reflexions, whether they are proportional to N^2 or to N, can be satisfactorily interpreted with the help of equations (2) and (3). These equations cover not only the cases of crystals, liquids and amorphous substances but also of special types of lattice models, e.g. the ‘mixed perfect and imperfect fibril’ models of Bear & Bolduan (1951) or the ‘random layer lattice’ model of carbon black proposed by Warren (1941). So, in general, depending on the relative magnitude and form of the fluctuation statistics, H_k, and on the statistics of particle size of paracrystals, the X-ray diagram may show purely ‘amorphous’, ‘liquid’ or ‘crystalline’ reflexions as well as reflexions which have intermediate character. Moreover, in certain states of statistical distributions it is possible to obtain individual reflexions which in Fourier space show in one direction crystalline habit, in another liquid, and in yet another amorphous features. Such reflexions were found to be present in the small-angle scattering diagrams of fibrous proteins (Hosemann, 1951).

Thus this theory of ideal paracrystals has the advantage that for the interpretation of the X-ray diagrams special lattice models are not at all necessary. Further, if the lattice is not too much distorted, the quantitative study of the X-ray diagrams permits one to calculate unambiguously the statistics of the cell edges a_k and, in special cases, the mean electron-density distribution and its fluctuations in the cells (Hosemann, 1951).

The present note is a summary of work that will be communicated in full at an early date.

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* It corresponds, for example in Debye's theory of liquids, to the region around a particular molecule where $W(q)$ (see equation (3*d*)) has not yet reached its final value 1.

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