limited when $\nu = 3$ or 4. This occurs because the rate of decrease of η with increasing U is equal to or less than that of $\Delta\eta$, and it confirms the suitability of these indices.

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Calculated Powder Patterns from Very Small Crystals: Body-Centered Cubic Cubes

BY CHANG MOROZUMI
Computing Service, Department of Mathematics, University of Wisconsin, Madison, Wisconsin, U.S.A.
AND H. L. RITTER*
Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

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The X-ray scattering patterns of several cubic arrays of points arranged on a body-centered cubic lattice have been computed according to the Debye scattering formula, $I = \sum_i \sum_j (\sin r_{ij}s)/r_{ij}s$ and plotted as a function of $t = as$, where a is the unit translation of the lattice.

The dependence upon the scattering angle of X-ray intensity scattered from an assemblage of crystals in the Debye–Scherrer arrangement may be described in terms of Bragg's Law; or alternatively in terms of the Debye scattering formula

$$I(s) = \sum_i \sum_j f_i f_j \frac{\sin r_{ij}s}{r_{ij}s} ,$$

where $s = (4\pi/\lambda) \sin \frac{1}{2}\theta$. When the discrete crystallites making up the assemblage are large (of the order of tens of thousands of unit cells or more), these two relations give identical positions of maximum intensity. As the crystallites become smaller, the familiar line-broadening effect appears. In addition to the actual broadening of the powder lines, this effect includes also a loss of resolution between adjacent lines, coalescence of adjacent lines, and disappearance of both the weaker lines and the lines occurring at high θ. Numerous investigations into the relation between amount of peak-broadening and size of crystallite have been published. The companion questions: of minimum crystallite size for the appearance of a given (weak) line; of minimum crystallite size for the resolution of two or more adjacent lines; of the size below which the finer details of the pattern are absorbed into the background scattering; and of the preferential suppression of diffraction detail as the crystallites are asymmetrically reduced in size or the preferential appearance of characteristic lines as the crystallites are enlarged in preferred directions: have been more neglected.

Probably the conceptually most satisfactory answer to these questions is obtained by actual calculation of the scattering patterns characteristic of crystalline assemblages of appropriate dimensions. It is then possible to inspect plots of the Debye scattering function for a series of crystallite sizes and shapes, and to form a coherent and detailed mental picture of the gradual transition from the diffuse and characterless haloes of the patterns from very tiny crystallites to the family of discrete lines characteristic of indefinitely large crystallites. The availability of high-speed computing machines makes the task of numerical evaluation of the Debye scattering function rather less formidable than it once was, even for relatively large crystallites.

The present communication presents the results of such calculations for the case of body-centered cubic homoatomic crystallites, cubic in shape, and ranging from one unit cell (nine atoms) to a cube of 1000 unit cells (2331 atoms). Plots of this kind have already been published by Germer & White (1941) and by James (1948). The results of Germer & White cover the case of face-centered cubic assemblages. Their calculations were spaced at considerably larger intervals than in the present paper, however, with the result that the background is not well-delineated; and

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* To whom inquiries concerning this article should be addressed at: Department of Chemistry, Miami University, Oxford, Ohio, U.S.A.

their largest assemblage is considerably smaller than reported here. The work of James is for the case of simple cubic assemblages and is still less extensive.

For the homoatomic case, the Debye scattering function is

$$I(\theta) = f^2 \Sigma\Sigma\, (\sin r_{ij}s)/r_{ij}s\ .$$

Because the function f^2 differs for each different kind of atom, and in any case is both monotonic and well-known, the purposes of our calculations are as well served by omitting it. Hereafter the term 'Debye scattering function' will mean

$$I = \Sigma\Sigma\, (\sin r_{ij}s)/\sin r_{ij}s\ .$$

The conversion to actual scattering pattern will then have to include the well-known behavior of f^2 as well as the effects of absorption, polarization and geometry of experimental set-up.

The interatomic distances r_{ij} include every cell-corner-to-cell-corner distance, every cell-center-to-cell-center-distance, and every cell-center-to-cell-corner distance in the assemblage. Every such distance may be written as $\varphi_{ij}a$ where a is the unit cell edge and $\varphi_{ij} = (u^2+v^2+w^2)^{\frac{1}{2}}$, where u, v, w, are the orthogonal components of the analog of r_{ij} in a lattice having a unit cell edge of unity. Placing $s = at$ in the scattering function, we may now write

$$I(t) = \Sigma\Sigma\, (\sin \varphi_{ij}t)/\varphi_{ij}t\ .$$

The effect of this transformation is simply to remove from I its explicit dependence on the absolute size of the lattice.

In a cube consisting of m^3 unit cells, there are $m^3+(m+1)^3$ atoms and therefore $[(m+1)^3+m^3]^2$ φ_{ij}'s not all of them distinct. Reordering the φ_{ij}'s over a single index, i, and noting that any given φ_i will occur in the assemblage A_i times, we rewrite the Debye scattering function finally in the form in which it was actually used:

$$I(t) = \Sigma A_i\, (\sin \varphi_i t)/\varphi_i t\ .$$

The evaluation of $I(t)$ may conveniently be divided into two steps: (1) counting the frequency of occurrence, A_i, of each φ_i; and (2) numerical evaluation of the sum. The latter step may be reduced to a routine machine operation.

For the purpose of counting these frequencies, it is convenient to distinguish three kinds of φ: (1) those both of whose end points lie in the simple cubic 'outer' lattice formed by the cell-corners; (2) those both of whose end points lie in the simple cubic 'inner' lattice formed by the cell-centers; and (3) those having one end in the outer and one end in the inner lattice. The outer lattice contains $(m+1)^3$ points and the inner one m^3 points. The u, v, w associated with the first and second kinds of φ are always integral; those associated with the third kind are half-odd integers.

Consider a two-dimensional simple square lattice consisting of m cells in both directions. From the upper left lattice point, draw a φ having the horizontal component u and the vertical component v. This is the diagonal of a rectangle having dimensions $u\times v$, and it is required to find how many such diagonals can be drawn in the array. Each rectangle has two diagonals, and since the original double summation recognizes r_{ij} as distinct from r_{ji}, each of these is counted twice. Thus each rectangle has four identical φ's. Since there are $m+1$ lattice points in the horizontal direction, it is clear that the rectangle can be reproduced, by successive horizontal translations of one unit, $(m+1-u)$ times. Each of these may be reproduced $(m+1-v)$ times vertically. The array therefore contains $4(m+1-u)(m+1-v)$ repeated φ's. In three dimensions, the total is $8(m+1-u)(m+1-v)(m+1-w)$.

If, however, one of u, v, w becomes zero, then there are only half as many φ's since a rectangle of zero width has only one, not two, 'diagonals'. If two of u, v, w are zero, the number is halved again; and if all three are zero, halved once more. Thus

$$A_i = 8g(m+1-u)(m+1-v)(m+1-w)\ ,$$

where the index i refers to one permutation of integers u, v, w; and $g = 1$ when none of u, v, w is zero, $\frac{1}{2}$ if one of them is zero, $\frac{1}{4}$ if two of them, and $\frac{1}{8}$ if all three. The integers u, v, w may each range from 0 to m, and all distinct permutations of the three integers must be counted.

Similar formulae for the φ's of the second and third kinds may be developed. For the inner lattice,

$$A_i = 8g(m-u)(m-v)(m-w)\ ,$$

where u, v, w take all integral values from 0 to $m-1$. For the mixed φ's,

$$A_i = 16(m+\tfrac{1}{2}-u)(m+\tfrac{1}{2}-v)(m+\tfrac{1}{2}-w)\ ,$$

where u, v, w take all half-odd integral values from $\frac{1}{2}$ to $m-\frac{1}{2}$. There are a few cases, of course, where two different sets of integers, uvw and $u'v'w'$, have the same $\varphi_i = [u^2+v^2+w^2]^{\frac{1}{2}}$. In such cases the total A_i for that φ_i is the sum of the partial A_i's, not only for all permutations of u, v, w, but also for all permutations of u', v', w'. A convenient check on the accuracy of the count is provided by the evident fact that the sum of all the coefficients, A_i, must equal the square of the number of atoms; that is,

$$\Sigma A_i = [(m+1)^3+m^3]^2\ .$$

Using the several sets of A_i so calculated for $m = 1, 2, 3, 4, 5$ and 10, the Debye scattering function was computed in the range $3{\cdot}0 \leqslant t \leqslant 37{\cdot}0$. This range corresponds roughly to typical experimental conditions. Thus for a unit cell edge of 5 Å, the maximum observable t at 180° diffraction angle with Cu $K\alpha$ radiation is about 40. The computations were carried out on the International Business Machines' card-programmed electronic computer (CPC) using a wiring scheme designed specifically for this purpose.

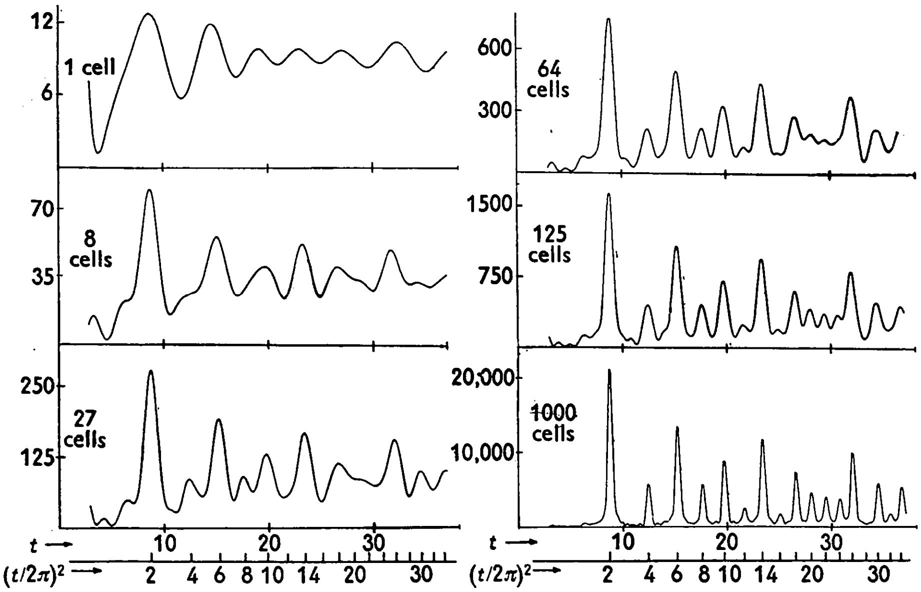

Fig. 1.

$I(t)$ was calculated at every 0·1 in t in order to assure correct detail for the larger values of m.

Fig. 1 shows plots of these functions. All have been plotted to the same horizontal scale of t and to such a vertical scale as to make the height of the first peak the same in each plot. As the assemblage becomes larger, the gradual suppression of background, sharpening and resolution of peaks, and appearance of new peaks at high scattering angle are all evident.

The lower horizontal scale shows those positions of t where, according to Bragg's law, a powder composed of indefinitely large crystals should show diffraction lines. These occur when $\lambda = 2d \sin \frac{1}{2}\theta$; i.e. when $t = 2\pi a/d$; for the cubic case, when $t = 2\pi(h^2+k^2+l^2)^{\frac{1}{2}}$, h, k, l being integers. Thus, in accordance with the theorem of Gauss (see e.g., Dickson, 1939), a diffraction line should show whenever $(t/2\pi)^2$ is integral, except for those integers of the form $4^p(8q+7)$ where p and q are positive integers including zero. For the body-centered cubic case, however, all odd integers are also missing because of lattice extinctions. The smallest even integer of forbidden form is 28. The plot of the Debye scattering function for 1000 unit cells shows very clearly a peak for every even integral value of $(t/2\pi)^2$ up to 34 with the single omission of 28.

It appears, then, that a powder sample will show all possible lines in the Debye–Scherrer pattern out to about $t = 37$ if the crystallites are as large as 1000 unit cell cubes; particles, say, 50 Å in diameter. Even crystallites as small as about 60 unit cells—say 20 Å in diameter—show all the diffraction lines of macrocrystals out to about $t = 25$. The width of the peaks at half-maximum is essentially constant for all peaks and is inversely proportional to m. This circumstance is in accord with the common formulae correlating line broadening with crystallite size. The patterns of non-cubical assemblages of points arranged on this same body-centered cubic lattice is currently being investigated.

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