

Evaluation of Paracrystalline Distortions from Line Broadening

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If the units building up a three-dimensional lattice have different sizes and/or shapes and are randomly distributed the long-range order of the point lattice is destroyed. The integral widths δb of the Debye-Scherrer lines increase quadratically with $\sin \theta$ for a given set of netplanes. Studying the slopes for the reflexions $h00$, $hh0$ and hhh one obtains quantitative information on the paracrystalline distortions in the lattice. In the present paper these slopes are calculated for p.c., b.c.c. and f.c.c. lattices and identical coordination statistics with cylindrical symmetry and two fluctuation parameters α, β . The slopes can be conveniently normalized to the fluctuation Δx_a of a lattice cell. In a logarithmic Δx_a versus $\beta^2/(\alpha^2 + \beta^2)$ plot of all these types of paracrystalline lattices, observed Δx_a values of manganese-rich spinels are fitted as well as possible. A body centred paracrystalline lattice is observed with $\alpha/\beta = 0.7 \pm 0.1$. This example may illustrate how to analyse reasonably paracrystalline lattices.

1. Introduction

Under certain circumstances in solid state physics compounds exist which are crystal-like but have lost the long range order of the lattice points. Within a crystalline lattice the n th neighbour in the direction of the lattice constant \mathbf{a}_r can be found at $\mathbf{x}_{rn} = n\mathbf{a}_r \pm \delta\mathbf{x}_{rn}$. $\delta\mathbf{x}_{rn}$ is of the order of 0.3 \AA or less and depends on the amplitude of thermal vibration. Hence the whole probability function, $z(\mathbf{x})$, of the lattice points is a lattice point function (Ewald, 1940), where the points are somewhat smeared out by the distance statistics, $H_c(\mathbf{x})$, of thermal vibration. A single atom n displaced by $\delta\mathbf{x}_n$ from its ideal position has now *a priori* another distance statistic relative to all other atoms such as the atom m with a displacement $\delta\mathbf{x}_m$, if $\delta\mathbf{x}_m \neq \delta\mathbf{x}_n$.

In Table 1 + denotes a crystal which has both lattice and long range order, and - denotes a crystal where the single lattice points have not the same *a priori* distance-distribution.

In the conventional theory of liquids of Ornstein & Zernike (1918), Zernike & Prins (1927) and Debye (1927) no lattice is discussed, all atoms having the same distance statistics (pair distribution functions) with respect to the other atoms and, as a consequence, long range order is lost. Hence in Table 1 the signs of the last column are opposite to those of the first.

The concept of a paracrystal (Hosemann, 1950a) introduces the possibility of solid or liquid structures existing within the limits of paracrystals. The lattice function $z(\mathbf{x})$ is now defined by a three-dimensional convoluting polynomial (see, for details, Hosemann &

Bagchi, 1952, 1962). The fluctuation widths $\delta x_{r,n}$ are now proportional to $1/\sqrt{n}$. So from a certain distance, $\delta x_{r,n}$ and $\delta x_{r,n+1}$ are so large that the distance statistics of adjacent lattice points totally overlap and the long range order is lost. Only for the special case of point-like next neighbour distance statistics $z(\mathbf{x})$ degenerates to the well known lattice point function of crystals (Ewald, 1940). In the second line of Table 1 the + - sign in the second column indicates that the paracrystalline theory contains the concepts of both crystals and liquids with regard to the existence or nonexistence of long range order.

As long as $z(\mathbf{x})$ is defined by a convoluting polynomial all lattice points have the same *a priori* distance statistics (+ sign in column 2) but on the introduction of lattice vibrations other than paracrystalline distortions this is no longer valid. Hence both possibilities (+ and -) (the same or not the same distance statistics) have been considered in the theory of paracrystals.

The last line of Table 1 shows that the atomic density distribution of a conventional liquid is taken to be spherically symmetric, while from the theory of paracrystals the possibility is introduced of analysing such distance statistics in terms of paracrystalline microdomains with very small lattice compounds (- sign). Averaging over all atoms of the liquid the expected value of the distance statistic of the liquid becomes spherically symmetric, as in an isotropic crystalline powder (+ sign).

The question is whether or not the mathematical approach is somewhere realized in nature. The first examples found were the macro-lattices of biological

Table 1. Notation for the extent of order

| Concept | Conventional crystal | Paracrystal | Conventional liquid |
|---|----------------------|-------------|---------------------|
| Lattice | + | + | - |
| Long range order | + | + - | - |
| Same <i>a priori</i> distance statistics | - | - + | + |
| Spherically symmetric distance distribution | - | - + | + |

fibres (Hosemann, 1950b) and later the molecular lattices of synthetic fibers (Hosemann, Balta-Calleja & Wilke, 1966) and atomic lattices in the ammonia catalyst (Hosemann, Preisinger & Vogel, 1966). The more Debye-Scherrer lines could be studied, the more interesting it became to find an adequate technique for evaluating the paracrystalline distortions from line broadening. The following sections give some results of these studies (cf. Vogel, 1967).

2. Basic equations

According to the theory of paracrystals by Hosemann & Bagchi (1962) the integral width δb of a certain Debye-Scherrer line hkl (netplane distance d) and its higher orders increases quadratically with the distance b in reciprocal space

$$\delta b = \pi^2 d_{hkl} g_{hkl}^2 b^2 \quad (1)$$

with

$$\mathbf{b} = (\mathbf{s} - \mathbf{s}_0) / \lambda, \quad b = 2 \sin \theta / \lambda. \quad (2)$$

\mathbf{s}, \mathbf{s}_0 are unit vectors in the direction of the primary and scattered beams, θ is the Bragg angle and λ is the wave length. g_{hkl} is the relative paracrystalline distance fluctuation of the family of netplanes $\{hkl\}$ (bars denote average values)

$$g_{hkl} = \sqrt{\overline{d^2} - \overline{d}^2} / \overline{d}. \quad (3)$$

This characteristic line broadening occurs if the nearest neighbour distances \mathbf{a}_k in the lattice are given by *a priori* probability functions $H_k(\mathbf{x})$ which are not point-like, and fluctuate without statistical correlation with each other. The distance statistics between two lattice points (000), (p, q, r) can then be described by a convoluting product of the nearest neighbour's distance statistics $H_k(\mathbf{x})^*$ ($k = 1, 2, 3$)

$$H_{pqr}(\mathbf{x}) = \overbrace{P \widehat{H_1 H_1} \dots}^{p \text{ times}} \overbrace{\widehat{H_2 H_2 H_2} \dots}^{q \text{ times}} \overbrace{\widehat{H_3 H_3 H_3} \dots}^{r \text{ times}} H_3. \quad (4)$$

P is a pointfunction at $\mathbf{x} = 0$ (Dirac's delta function).

The mean distance vector, $\bar{\mathbf{a}}_r$, of the so-called coordination statistic H_r and its statistical fluctuation, Δx_{ri} , in the direction of the unit vector \mathbf{s}_i is defined by

$$\bar{\mathbf{a}}_r = \int \mathbf{x} H_r(\mathbf{x}) d v_x; \quad (5)$$

$$\Delta^2 x_{ri} = \int (\mathbf{x} \cdot \mathbf{s}_i)^2 H_r(\mathbf{x} + \bar{\mathbf{a}}_r) d v_x.$$

If the $\bar{\mathbf{a}}_r$ are orthogonal as in the p.c. lattice, then the fluctuation of H_{pqr} in the direction \mathbf{i} is given by

$$\Delta^2 x_{pqr i} = p \Delta^2 x_{1i} + q \Delta^2 x_{2i} + r \Delta^2 x_{3i}. \quad (6)$$

* This corresponds to the model of an 'ideal paracrystal', which neglects correlations between the different $H_r(\mathbf{x})$.

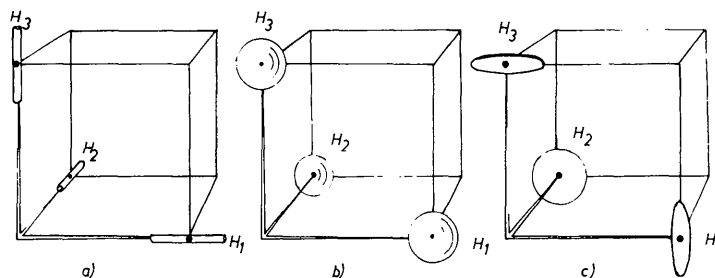


Fig. 1. Coordination statistics of the same shape in a primitive-cubic lattice cell; (a) rod-like, (b) sphere-like, (c) disc-like.

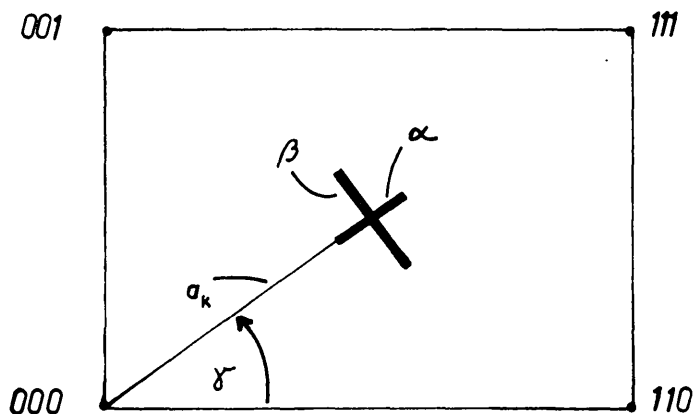


Fig. 2. The fluctuation parameters, α, β , of a coordination statistic with cylindrical symmetry in a b.c.c. lattice cell.

According to the nature of the convolution operation $H_{pqr}(\mathbf{x})$ becomes more and more broadened with increasing $|p|$, $|q|$, $|r|$; this means that the long range order is disturbed (Table 1).

The Bragg-like intensity is then proportional to the paracrystalline lattice factor (Hosemann & Bagchi, 1962)

$$Z(\mathbf{b}) = \prod_{r=1}^3 \operatorname{Re} \frac{1 + F_r(\mathbf{b})}{1 - F_r(\mathbf{b})}. \quad (7)$$

The $F_r(\mathbf{b})$ are called 'statistical amplitudes' and are the Fourier transforms of the $H_r(\mathbf{x})$:

$$F_r(\mathbf{b}) = \mathcal{F} H_r(\mathbf{x}) \quad (\mathcal{F}: \text{Fourier transform operator}). \quad (8)$$

In a primitive cubic lattice the $H_r(\mathbf{x})$ of the paracrystalline lattice are given by the cell edges \mathbf{a}_r . For b.c.c. and f.c.c. lattices the \mathbf{a}_r between next-neighbours are given by the vectors from 000 to $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and 000 to $0\frac{1}{2}\frac{1}{2}$ respectively.

Since the coordination statistics $H_r(\mathbf{x})$ have a physical meaning (they describe the statistical properties of chemical binding between next neighbours) the paracrystalline lattice cell can no longer be described by the conventional b.c.c. and f.c.c. lattice cells.

It is important to realize that from a quantitative study of paracrystalline distortions one can obtain directly the information: which atoms are the next neighbours and which atoms form the distorted lattice. This will be demonstrated in § 4.

The g_{hkl} values defined by (3) depend on the order of reflexion. For the $2h\ 2k\ 2l$ reflexion for instance, according to (6) the netplanes are separated by $\bar{d}/2$; their fluctuation is

$$\frac{1}{\sqrt{2}} \sqrt{\bar{d}^2 - d^2} \text{ hence } g_{2h2k2l} = \sqrt{2} g_{hkl}. \quad (9)$$

In this way it is possible to transform all g_{hkl} values of the different families of netplanes to those of families with the same netplane distance a : if Δx_a and g_a are the respective fluctuations, one obtains

$$\begin{aligned} \Delta^2 x_a &= (d^2 - \bar{d}^2) a / \bar{d}; \\ \Delta x_a / a &= g_a = g_{hkl} \sqrt{\bar{d} / a}; \\ \delta b &= \pi^2 / a^3 \cdot \Delta^2 x_a h^2. \end{aligned} \quad (10)$$

(h is the order of reflexion).

As will be shown below there is a characteristic mutual dependence of the g_a values for the (100), (110), (111) netplanes which permits one to obtain information on the Δx_{rl} values [equation (5)] and hence the type of Bravais lattice (see below).

For a finite crystal, introducing the shape function

$$s(\mathbf{x}) = \begin{cases} 1 & \text{inside the crystal} \\ 0 & \text{outside the crystal} \end{cases} \quad (11)$$

and its Fourier transform

$$S(\mathbf{b}) = \mathcal{F} s(\mathbf{x}) \quad (12)$$

Table 2. Statistical fluctuations $\Delta^2 x_{p_1 p_2 p_3}$ of the edges, a , and diagonals, $\sqrt{2}a$, $\sqrt{3}a$, of the conventional lattice cell in the directions in which they lie, and their fluctuations $\Delta^2 x_a$ normalized to the distance a [equation (10)] for different Bravais lattices

| | c.p. $a_r = a$ | | | b.c.c.; $a_r = \frac{1}{2}\sqrt{3}a$ | | | f.c.c.; $a_r = \frac{1}{\sqrt{2}}a$ | | |
|---------------|---------------------------|----------------------------|---|---|----------------------------------|--|---|----------------------------|--|
| | $H_{p_1 p_2 p_3}$ | $\Delta^2 x_{p_1 p_2 p_3}$ | $\Delta^2 x_a$ | $H_{p_1 p_2 p_3}$ | $\Delta^2 x_{p_1 p_2 p_3}$ | $\Delta^2 x_a$ | $H_{p_1 p_2 p_3}$ | $\Delta^2 x_{p_1 p_2 p_3}$ | $\Delta^2 x_a$ |
| $p_1 p_2 p_3$ | | | | | | | | | |
| 001 | H_{001} | α^2 | α^2 | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $\frac{2\alpha^2 + 4\beta^2}{3}$ | $\frac{\Delta^2 x_a}{3}$ | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $\alpha^2 + \beta^2$ | $\alpha^2 + \beta^2$ |
| 011 | $H_{001} H_{010}$ | $\alpha^2 + \beta^2$ | $\sqrt{\frac{1}{2}(\alpha^2 + \beta^2)}$ | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $\frac{4\alpha^2 + 2\beta^2}{3}$ | $\frac{4\alpha^2 + 2\beta^2}{3\sqrt{2}}$ | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $2\alpha^2$ | $\sqrt{2}\alpha^2$ |
| .111 | $H_{001} H_{010} H_{100}$ | $\alpha^2 + 2\beta^2$ | $\sqrt{\frac{1}{3}(\alpha^2 + 2\beta^2)}$ | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $2\alpha^2$ | $\frac{2}{\sqrt{3}}\alpha^2$ | $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ | $2\alpha^2 + \beta^2$ | $\frac{2\alpha^2 + \beta^2}{\sqrt{3}}$ |

we obtain for the Bragg-like intensities the convolution product:

$$I(\mathbf{b}) \sim Z(\mathbf{b}) |S(\mathbf{b})|^2. \quad (13)$$

The 'shape factor' $|S(\mathbf{b})|^2$ alone gives a new line broadening, δb_{size} , independent of the order of reflexion:

$$\delta b_{\text{size}} = 1/\bar{L} \quad (14)$$

where \bar{L} is the mean linear crystallite size perpendicular to the reflecting netplane. As a result of the convolution product (13), the integral widths (10) and (14) sum in different manner, depending on the shapes of the two functions $Z(\mathbf{b})$ and $|S(\mathbf{b})|^2$. Since the shape for $Z(\mathbf{b})$ is always a 'Cauchy-like' function $f(b) \sim 1/(1+k^2b^2)$ we may write:

$$\begin{aligned} \delta b &= \frac{1}{\bar{L}} + \pi^2 g_{hkl}^2 d_{hkl} b^2 \\ &= \frac{1}{\bar{L}} + \frac{\pi^2}{a^3} \Delta^2 x_a h^2 \end{aligned} \quad (15)$$

if the shape factor itself does not deviate too much from a Cauchy function. Integral widths of Cauchy functions sum linearly on convolution.

Equation (15) often holds to within the measurement errors if pure size broadening is low compared with paracrystalline broadening, especially for the high order reflexions (large h).

In a plot of δb versus h^2 , for $\delta b \gg \frac{1}{\bar{L}}$ we should obtain

practically straight lines for reflexions which are parallel in the reciprocal lattice. These lines differ in slope, for instance for $00h$ or $0hh$ or hhh type reflexions, depending on the shape of the coordination statistics $H_r(\mathbf{x})$ and the lattice type. Examples are given below.

3. The calculation of $\delta b-h^2$ plots for different lattice types and shapes of coordination statistics

Beginning for convenience with a onefold primitive lattice we discuss these important cases (Fig. 1), when all the coordination statistics H_r have the same shape. Let Δx_{ri} again be the standard fluctuation of the lattice cell edge a_r in the direction of \mathbf{s}_i (equation 5), then

$$\begin{aligned} \text{rod-like means:} & \quad \Delta x_{ri} \ll \Delta x_{rr} \quad (i \neq r) \\ \text{globular means:} & \quad \Delta x_{r1} \sim \Delta x_{r2} \sim \Delta x_{r3} \\ \text{disc-like means:} & \quad \Delta x_{ri} \gg \Delta x_{rr} \quad (i \neq r). \end{aligned} \quad (16)$$

Equal shapes of all $H_r(\mathbf{x})$ means that

$$\Delta x_{ri} = \begin{cases} \alpha & \text{for } i=r \\ \beta & \text{for } i \neq r. \end{cases} \quad (17)$$

Fig. 1 gives an example for p.c. lattices.

To calculate the slopes of the integral width δb of a certain family of reflexions from the $\Delta^2 x_{ri}$ values, we start with a lattice point $\mathbf{x}_{p_1 p_2 p_3}$ which lies on the normal to the family of netplanes $(h_1 h_2 h_3)$ under consideration:

$$p_1 = h_1; p_2 = h_2; p_3 = h_3.$$

Let \mathbf{s}_h be an unit vector perpendicular to the netplane $(h_1 h_2 h_3)$ and a the length of the cubic lattice cell, then

$$\mathbf{x}_{h_1 h_2 h_3} = a h \mathbf{s}_h; h = \sqrt{h_1^2 + h_2^2 + h_3^2}.$$

The squared standard deviation of $\mathbf{x}_{h_1 h_2 h_3}$ in the direction of \mathbf{s}_h is then, according to equation (5), given by

$$\begin{aligned} \Delta^2 x_{h_1 h_2 h_3} &= \int (\mathbf{x} \cdot \mathbf{s}_h)^2 H_{h_1 h_2 h_3}(\mathbf{x} + \mathbf{x}_{h_1 h_2 h_3}) d v_x, \\ \Delta^2 x_{h_1 h_2 h_3} &= \int \frac{1}{h^2} (x_1 h_1 + x_2 h_2 + x_3 h_3)^2 \\ &\quad \times H_{h_1 h_2 h_3}(\mathbf{x} + a h \mathbf{s}_h) d v_x. \end{aligned}$$

Since $\int x_i x_r H_{h_1 h_2 h_3}(\mathbf{x} + a h \mathbf{s}_h) d v_x = 0$, if $i \neq r$, the bracket

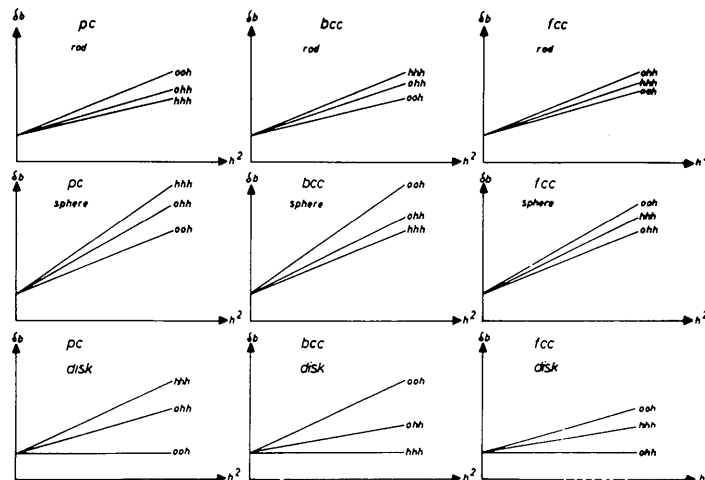


Fig. 3. Relative slopes of line widths δb in a $\delta b-h^2$ plot for different lattice types and cylindrical symmetric coordination statistic shapes. A mean broadening δb_{size} has been added according to equation (15).

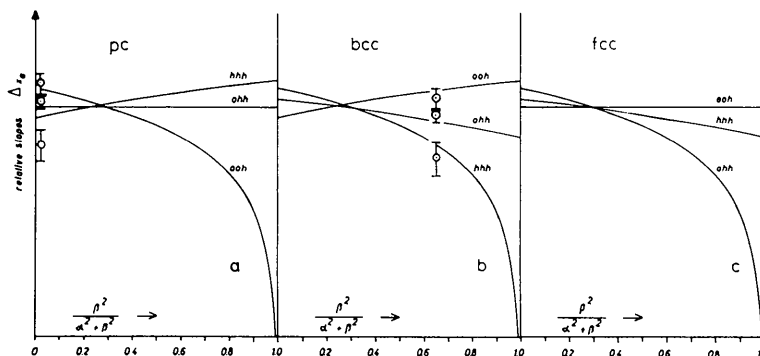


Fig. 4. The normalized fluctuations Δx_a (equation 10) of the netplanes ($h00$), ($hh0$), and (hhh) calculated for different lattice types and α , β -values of coordination statistics. The observed values of a manganese-rich spinel are fitted into the respective plots as well as possible.

can be replaced by $(x_1^2 h_1^2 + x_2^2 h_2^2 + x_3^2 h_3^2)$.^{*} Now substituting equation (6) we get:

$$\Delta^2 x_{h_1 h_2 h_3} = \frac{1}{h^2} \sum_i \sum_r h_i^2 h_r \Delta^2 x_{ri}; \quad (18)$$

for like-shaped coordination statistics especially one obtains from equation (17):

$$\Delta^2 x_{h_1 h_2 h_3} = h \left[\alpha^2 \left(\frac{h_1^3 + h_2^3 + h_3^3}{h^3} \right) + \beta^2 \left\{ \frac{h_1 + h_2 + h_3}{h} - \frac{h_1^3 + h_2^3 + h_3^3}{h^3} \right\} \right]. \quad (19)$$

According to equation (10) the slope of the integral width δb of order parameter h is proportional to

$$\Delta^2 x_a = \frac{a}{x_{h_1 h_2 h_3}} \Delta^2 x_{h_1 h_2 h_3} = \frac{1}{h} \Delta^2 x_{h_1 h_2 h_3}.$$

Hence from (19) one obtains

$$\Delta^2 x_a = \alpha^2 \left(\frac{h_1^3 + h_2^3 + h_3^3}{h^3} \right) + \beta^2 \left(\frac{h_1 + h_2 + h_3}{h} - \frac{h_1^3 + h_2^3 + h_3^3}{h^3} \right). \quad (20)$$

The expressions inside the brackets are angle-dependent factors of order of magnitude 1.

Equation (20) is built on the statistical fluctuations Δx_{rr} , Δx_{ri} of the conventional lattice cell a . As mentioned above, in non-primitive paracrystalline lattices the coordination statistics $H_r(\mathbf{x})$ are given by next-neighbour statistics and not by those of the conventional cell edges. For a body centred cubic lattice (b.c.c.) for instance, the next neighbours lie at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, hence the cell-edge statistic H_{001} is given by $H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}\frac{1}{2}} H_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}^{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$, and so on.

Introducing the α, β -values of the coordination statistics defined by (17) one obtains for the fluctuation $\Delta^2 x_{33}$ of the conventional cell edge (see Fig. 2)

$$\Delta^2 x_{33} = 2 \cdot (\beta^2 \cos^2 \gamma + \alpha^2 \sin^2 \gamma) \quad (21)$$

^{*} We propose a centre of symmetry for the functions $H_r(\mathbf{r})$. The same is then true for $H_{pr}(\mathbf{x})$.

where $\sin \gamma = 1/\sqrt{3}$. In Table 2 the dependence of the fluctuation of the conventional lattice edges, body diagonals and face diagonals from those of the coordination statistics is given for p.c., b.c.c. and f.c.c. lattices.

4. Analysis of the paracrystalline lattice type and the shape of the coordination statistics

Since according to equation (15) the slope of the line width in a $\delta b - h^2$ plot is proportional to $\Delta^2 x_a$, such plots can easily be constructed for given lattices and coordination statistic shapes: Fig. 3 gives an example for rod-like, sphere-like, and disc-like coordination statistics. The relative fluctuations of the coordination statistics have been chosen as follows:

| | | |
|--------|--------------------------|-------------------------|
| Rod | $\alpha/\bar{a}_r = 1\%$ | $\beta/\bar{a}_r = 0$ |
| Sphere | $\alpha/\bar{a}_r = 1\%$ | $\beta/\bar{a}_r = 1\%$ |
| Disc | $\alpha/\bar{a}_r = 0$ | $\beta/\bar{a}_r = 1\%$ |

If the statistics are sphere-like, we see that those netplanes belonging to next neighbours ($h00$ for p.c., hhh for b.c.c. and $hh0$ for f.c.c.) have the smallest slope. Thus, from a study of line broadening information on the lattice type can be obtained if the shape of the coordination statistics is known.

In order to analyse both the lattice type and the shape of the statistics Δx_a is plotted on a logarithmic scale against $\frac{\beta^2}{\alpha^2 + \beta^2}$ (Fig. 4). As an example the observed Δx_a values for the three families of netplanes ($h00$) ($hh0$) and (hhh) of a manganese-rich spinel are moved over the graph till they fit the calculated curves as well as possible. The procedure does not depend on the absolute values of the paracrystalline distortions but only on the relative values between the single netplanes. There are two possibilities:

1. Lattice: primitive cubic; coordination statistics: rod-like ($\beta \ll \alpha$). But as can be seen in Fig. 4, the observed values do not fit the calculated curves within the experimental error. Hence, this solution is improbable.

2. Lattice: body centred cubic; $\frac{\beta^2}{\alpha^2 + \beta^2} = 0.65 \pm 0.1$,
 $\frac{\alpha}{\beta} \sim 0.7 \pm 0.1$.

Hence the next neighbours (bricks) are placed along body diagonals. The fluctuation is less parallel to their mean coordination vector (20 XU) and greater at right angles to it (28 XU). ($\alpha < \beta$, see Fig. 2). It is known, that in a spinel oxygen ions build up a close packed f.c.c. lattice; the small spaces at tetragonal and octahedral sites between these large anions are filled up by the small cations. In the manganese-rich spinels under consideration obviously the cations in octahedral positions make 'bricks' with the surrounding oxygen ions and these molecular bricks themselves make up the crystalline lattice.

In another paper* the results from these spinels are dealt with in detail. The aim of the present paper is to illustrate that information relevant to the concept of paracrystals is available from line profile analysis.

* Červinka, Hosemann & Vogel (1970).

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Paracrystalline Lattice Distortions and Microdomains in Manganese Ferrites near the Cubic-to-Tetragonal Transition

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The line profiles of X-ray reflexions from different $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ samples were investigated. Sample I ($x = 1.66$) is cubic with no anomalies; small paracrystalline distortions, $g < 0.1\%$, cannot be excluded and are calculated to be of this magnitude from considerations of a simple volume effect of the larger Mn^{3+} ions. Samples II–IV ($x = 1.88$) show interesting effects which are closely connected with the development of the tetragonal structure, observed when $x > 1.80$. Sample II (quenched) shows paracrystalline distortions which can be quantitatively explained on the basis of the Jahn–Teller effect: the tetragonally deformed single $\text{Mn}^{3+}\text{O}_6^{2-}$ octahedra are statistically oriented and statistically distributed over B sites and have a mean tetragonality $\bar{\epsilon} = 0.014$. In sample III (cooling rate $20^\circ\text{C}.\text{min}^{-1}$) about 26% of the volume consists of microdomains which result from a correlation between the orientations and positions of Jahn–Teller octahedra; quantitative agreement with the theory can be obtained by introducing a correlation factor $\gamma = 2$. In sample IV (cooling rate $7^\circ\text{C}.\text{min}^{-1}$) this correlation proceeded in such a way that the crystal consisted of 74% tetragonal matrix which had already attained a value of $c/a = 1.056$, and about 22% of tetragonal microdomains oriented in two other directions with a value $c/a < 1.056$. In addition about 3 to 5% of a cubic phase is present. If the mean tetragonality of the microdomains is taken to be $\bar{\epsilon} = 0.020$ the experiments correspond quantitatively with the theory. The detailed study of sample III proves that $H_{\pm\pm\pm}$ are the paracrystalline coordination statistics with a fluctuation $\alpha = 27$ XU in the direction [111] and $\beta = 38$ XU perpendicular to it. This is explained by a model of the spinel structure having two kinds of blocks: a tetrahedral A -structure and Jahn–Teller affected octahedral subcubes at B sites; the separation distance is $\frac{1}{3}a = 3.7 \text{ \AA}$.

1. Introduction

It has been proved that tetragonally distorted octahedra of $\text{Mn}^{3+}\text{O}_6^{2-}$ exist locally in the macroscopic

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cubic lattice of the $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ system (Červinka, Krupička & Syneček, 1961; Červinka, 1965). This can be explained quantum mechanically by Mn^{3+} ions in an octahedral environment of O^{2-} anions. The eigen-