1. At the exit surface a second strong diffracted wave appears, the wave E_{hd}. This leads, in comparison with the conventional theory, to smaller amplitudes E_h (Härtwig, 1978*b*). But, on the other hand, the diffracted wave E_h has a considerable amplitude still in the range of an extremely asymmetric Laue case with grazing emergence (Kishino, Noda & Kohra, 1972; Bedyńska, 1973, 1974), where the conventional theory predicts no E_h. Therefore, in the conventional theory the integrated reflectivity tends to zero for $\alpha - \theta_B$ tending to zero, whereas the theory for the extremely asymmetric case provides a non-zero value for $\alpha - \theta_B$ tending to zero.

2. The definition of the emerging-beam direction cosine changes from $\gamma_h = \sin(\theta_B - \alpha)$, which is also an approximation holding as long as $|\theta_B - \alpha| \gg |\Delta\theta|$, to that given in (2). But in the case of grazing emergence this change leads to an increase of the integrated reflectivity compared with the result of the conventional theory. So two opposite tendencies act now on the integrated reflectivity.

The consequences of the changes of the form of the dispersion surface are not so important now, because in the case of grazing emergence the departures from the exact Bragg law for the physically interesting region (*i.e.* for the maximum of the reflection curve) are much smaller than in the case of grazing incidence (now $\Delta\theta \simeq 10^{-5}$ rad and not $\sim 10^{-3}$ rad), but they too cannot be neglected (Härtwig, 1978*b*).

Despite the fact that the calculations were carried out for a special case, the obtained results may be generalized, because the discussed properties are independent of the chosen conditions.

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X-ray Diffuse Scattering in Dicalcium Barium Propionate

By S. Singh and A. M. Glazer

*Clarendon Laboratory, Parks Road, Oxford OX*1 3*PU, England*

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Abstract

Diffuse X-ray intensities have been measured in the *hk*0 reciprocal plane of cubic dicalcium barium propionate, $Ca_2Ba(C_2H_5COO)_6$, with a diffractometer. The observed streaks run parallel to [$\bar{1}$10], passing through reciprocal-lattice points with $h + k = 8n$. Intensity profiles in two directions perpendicular to the streaks were measured and fitted theoretically under the assumption of one-dimensional Markov-chain-type correlations; the agreement between theory and experimental data is excellent, particularly for the [110] direction, giving correlation lengths of 24·5 (5) Å along [110] and 4·6 (1) Å along [001]. These lengths are compared with the crystal structure and suggest a model in which there are ordered domains elongated along [110] but rather short along [001].

Introduction

Recently, Stadnicka & Glazer (1980), hereafter SG, reported an accurate structure determination of di-

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calcium barium propionate (DBP). The space group is *Fd*3*m* (O_h^7), with $Z = 8$ and $a = 18{\cdot}178$ Å. It was shown that it is physically impossible to form a fully ordered structure in this space group; instead, the propionate groups are found to lie in two orientations about pseudo-two-fold axes along [100] and equivalent directions, with limited correlation (static or dynamic) along [110] and [001]. The evidence for these correlations was in the observation of X-ray diffuse streaks, elongated along [$\bar{1}$10] and passing through reflections on $l = 0$ and 4 layers with $h + k + l = 8n$, and on $l = 2$ with $h + k + l = 4n$. For such a streak the intensity distribution is narrowest along [110], corresponding to the direction of longest short-range-order correlation, but wider along [001], corresponding to a shorter correlation in this direction. From the intensity distribution of the streaks and the fact that the temperature factors for Ca and Ba were normal, it was felt that these streaks might be connected with short-range correlations between the propionate groups. On the basis of these observations, SG proposed that in DBP there was limited two-dimensional ordering of domains lying perpendicular to ⟨001⟩. It was suggested that these 'platelets' of local order were of opposite chirality and give a clue to the mechanism of ferrogyrotropic switching of chiral regions in the related strontium compound, DSP. [Glazer, Stadnicka & Singh (1981) discuss the relationship between DSP and DBP and the importance of the disordered chiral regions in explaining the switching of the optical activity in DSP.] The diffuse scattering in DBP was observed on stationary-crystal X-ray photographs and no attempt was made to measure the intensity distribution, except in a qualitative way by eye. Nevertheless, SG estimated the mean correlation lengths of the short-range order to be roughly 9 Å along ⟨001⟩ (*i.e.* about one half a unit cell), and 55 Å along ⟨110⟩.

In the present paper we report a quantitative study of the X-ray diffuse scattering from DBP in the *hk*0 reciprocal-lattice plane, demonstrating that

(i) the arrangement of streaks is indeed as described by SG,

(ii) the intensity distributions normal to the streaks are typical of short-range order,

(iii) the mean correlation lengths along ⟨110⟩ and ⟨001⟩ are $24{\cdot}5 \pm 0{\cdot}5$ and $4{\cdot}6 \pm 0{\cdot}1$ Å respectively, approximately one-half the values reported earlier.

Experimental details

The intensity data were collected on a Stoe Stadi-2 two-circle diffractometer with Mo *Kα* radiation. The beam was monochromated by plane pyrolytic graphite and pulse-height discrimination reduced the effect of harmonics. The crystal dimensions were approximately 1 × 0·8 × 0·8 mm; the diameter of the collimator was 0·8 mm, and the detector slit was 1 mm² at 120 mm from the crystal.

To investigate the general disposition of the diffuse scattering, measurements were made in the *hk*0 plane at intervals of $\frac{1}{25}\mathbf{a}^*$, $\frac{1}{4}\mathbf{b}^*$, with the diffractometer in the ω–2θ mode; measurements were made for 90 s at each point. A fast scan was performed in *h*, slow in *k*. After every few rows in *k*, the minimum and maximum values of *h* were changed by appropriate amounts to cover an octant of the *hk*0 layer, of radius 20$\mathbf{a}^*$; an octant is all that is necessary to provide complete information about 00*l* layers because of the presence of four-fold axes along ⟨100⟩ and mirror planes perpendicular to ⟨110⟩ in *Fd*3*m*. The numbers of counts obtained at each point were rounded off to the nearest 10 and plotted on a large-scale map of the *hk*0 section; a value of 100 counts was taken as the cut-off value above background. Typically, 200 counts were obtained near the centres of the stronger streaks. Contouring was carried out at intervals of 50 counts (except near Bragg peaks) and the map was reflected across the (110) plane for convenience.

In Fig. 1 long streaks can easily be seen parallel to [$\bar{1}$10], and weaker ones (such as that marked *C*) parallel to [110]; the latter are equivalent to continuations of the stronger streaks into the adjoining quadrants, folded back according to the symmetry. The streaks pass through reciprocal-lattice points given by $h + k = 8n$.

In order to provide a more quantitative study of the diffuse scattering, the intensity was remeasured across the width of the strong streaks, *i.e.* along [110]. To do this it was necessary to choose regions well away from the reciprocal-lattice points, so that normal Bragg scattering was not included. It was found that measure-

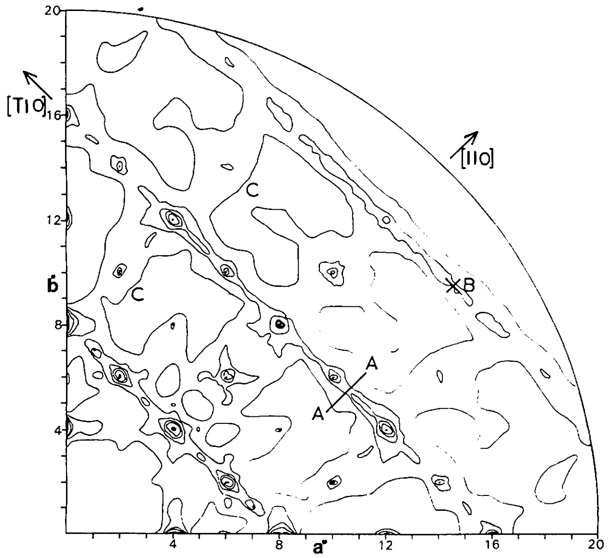

Fig. 1. Diffuse scattering in the *hk*0 reciprocal-lattice plane of DBP.

ments made across two separate portions of the streak through 880 gave similar profiles. As a further check that all the regions of the streaks between Bragg points had similar profiles, we also integrated the intensities in Fig. 1 *along* the 880 streak and then plotted these out as a function of distance *across* the streak (again omitting the Bragg-reflecting regions). Once more, a similar profile was found. A careful set of measurements (see Fig. 2) was then made along the section *AA* in Fig. 1. This was chosen so that it did not pass through a Bragg position, nor would be contaminated by any $\lambda/2$ component. The time spent at each point was 30 min, and several complete scans were subsequently added together to improve the counting statistics and to ensure that any variations in the incident intensity were averaged out. A similar set of scans (see Fig. 3) was also made along [001] through the point *B* (Fig. 1) lying on the $[\bar{1}10]$ streak through 12,12,0. As can be seen from the scales at the tops of Figs. 2 and 3 the thickness of the $[\bar{1}10]$ streaks is considerably greater along [001] than along [110].

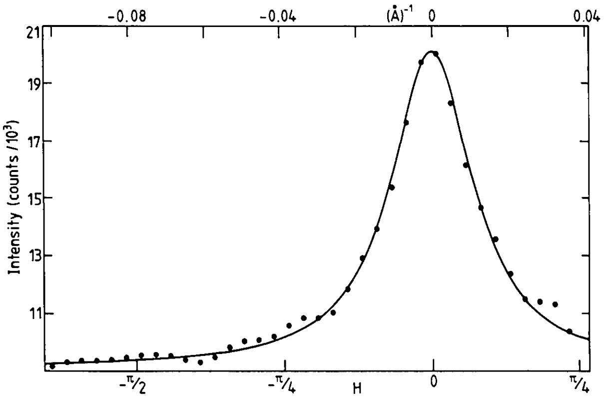

Fig. 2. Section through the 880 streak parallel to [110]: . experimental point; – theoretical fit, α = 0·116 (background 9 × 10^3 counts).

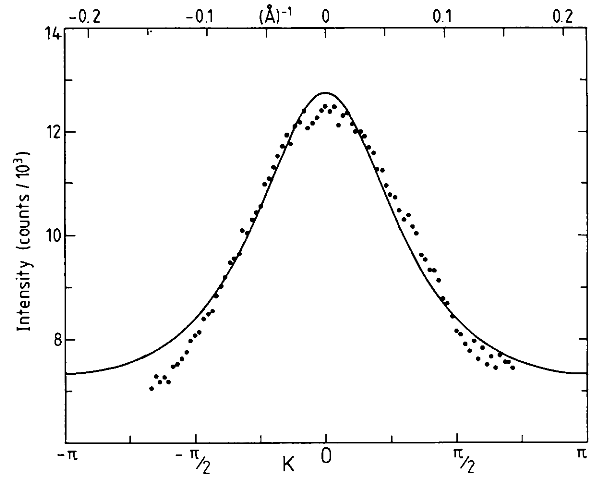

Fig. 3. Section through the 12,12,0 streak parallel to [001]: . experimental point; – theoretical fit, β = 0·332 (background 5·5 × 10^3 counts).

Lorentz–polarization correction factors were calculated, but the maximum correction was found to be small, within the statistical fluctuations, and so they were ignored. No absorption correction was applied, as this too was calculated to be negligible. The profile was corrected for the effect of the detector slit width by deconvolution with the method of Stokes (1948).

Interpretation of the profiles

SG proposed a short-range-order model of the structure in which there were long-range correlations between the propionate groups along [110], shorter correlations along [001] and almost no correlations along $[\bar{1}10]$, thus giving rise to the observed type of streak.

In order to analyse this scattering we can assume that because of the extreme length of the streaks along $[\bar{1}10]$, in real space one is dealing with two-dimensional ordering perpendicular to $[\bar{1}10]$. If the cross section of such a streak were small and circular (so that the diffuse streaks would be 'rod-like'), the problem could be treated in terms of parallel, equally spaced, infinite planes perpendicular to $[\bar{1}10]$ but with each plane randomly out of register as in a normal stacking-fault sequence. However, the anisotropic nature of the cross section of the streak and its large area suggests that we must consider short-range order *within* these planes.

A possible way of proceeding is to treat the problem in a manner akin to a stacking-fault model. Wilson (1962) has given a formula for the intensity distribution across a streak when there is one-dimensional short-range order:

$$I(H) = I_0 \frac{1-(1-2\alpha)^2}{1-2(1-2\alpha)\cos H + (1-2\alpha)^2}.$$

Here α is the probability of a molecular unit being correlated with (or having its orientation determined by) the previous one in a one-dimensional (Markov) chain. $H = 2\pi\mathbf{A}.\mathbf{S}$, where $\mathbf{A}$ is the repeat vector along the chain and $\mathbf{S}$ is the scattering vector ($|\mathbf{S}| = 2\sin\theta/\lambda$). I_0 represents the intensity derived from the difference in molecular transform of the disordered species responsible for the diffuse scattering. It is not clear, however, how to apply this formula to the case where short-range order occurs in more than one direction. Flack (1970) and Glazer (1970) demonstrated that, when dealing with short-range order within a plane, a good approximation could be made by multiplying two separate Wilson-type formulae, with two independent probabilities α and β referring to the two major short-range-order directions:

$$I = I_0 \frac{1-(1-2\alpha)^2}{1-2(1-2\alpha)\cos H+(1-2\alpha)^2} \times \frac{1-(1-2\beta)^2}{1-2(1-2\beta)\cos K+(1-2\beta)^2}.$$

Similar proposals were made by Hosemann & Bagchi (1962) for 'paracrystals'.

We have applied the same model to DBP. Since the anisotropic shape of the cross sections of the streaks indicated that the correlation lengths along [110] and [001] were quite different, the assumption of independent probability functions should be good. We therefore chose α and β to represent short-range order along [110] and [001] respectively.

Each probability function rises to a maximum half-way between reciprocal-lattice points for $\alpha,\beta > 0{\cdot}5$ and on reciprocal-lattice points for $\alpha,\beta < 0{\cdot}5$. Since the streaks in DBP pass through Bragg peaks, $\alpha,\beta < 0{\cdot}5$ and the period of H and K is $\pm\pi$.

For the [110] direction, the repeat distance between streaks is $4\mathbf{a}^*\sqrt{2}$ (successive streaks pass through 440, 880, 12,12,0). The value of α was determined by least-squares refinement; excellent agreement was obtained for $\alpha = 0{\cdot}116 \pm 0{\cdot}002$, as shown in Fig. 2.

For the direction along [001], the repeat distance can be inferred to be $8\mathbf{a}^*$ from the pattern of diffuse streaks given by SG; this leads to a least-squares value of $\beta = 0{\cdot}332 \pm 0{\cdot}003$ (assuming a background at 5500 counts in Fig. 3).

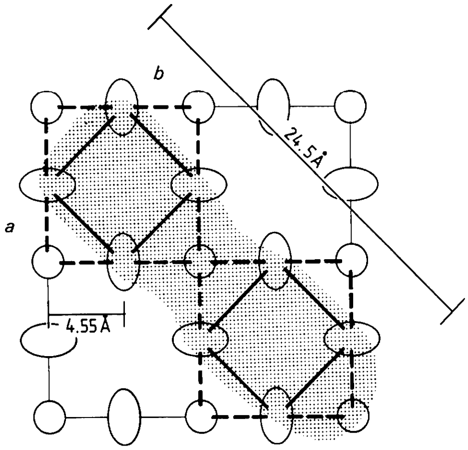

Fig. 4. Schematic diagram of propionate groups in a (001) section of the DBP structure. Ellipses represent propionates with their long axes lying in the (001) plane, and circles those with their long axes along [001]. Heavy lines indicate strong links; dashed lines indicate weak links. The shading approximately denotes a typical short-range domain and corresponds to one of the two-dimensional 'platelets' mentioned in the *Introduction*, *i.e.* the correlation (along [001]) perpendicular to the plane of the diagram is very short.

The values of α or β can be interpreted in terms of mean domain sizes or correlation lengths in the appropriate directions. For example, for the [110] direction, the number of correlated molecules (or molecular planes) $= 1/\alpha = \langle n\rangle$ and thus the number of correlation steps (repeat distances) $= \langle n\rangle - 1 = (1-\alpha)/\alpha$ and the correlation length $= [(1-\alpha)/\alpha] \times$ real-space repeat distance.

For the [110] direction the repeat distance is $\mathbf{a}/4\sqrt{2}$ and the correlation length = 24·5 ± 0·5 Å. For the [001] direction the repeat distance is $\mathbf{a}/8$ and the correlation length = 4·6 ± 0·1 Å. We see then that the intensity profiles normal to the streaks are consistent with the model of short-range order proposed by SG, although the correlation lengths are found to be approximately half their eye estimates. The agreement between the theoretical fits and the experimental points, especially for the [110] direction, is particularly good, and seems to justify our approach of using independent one-dimensional probability distributions.

In the structural study of SG, it was shown from an analysis of intermolecular contacts between the propionate groups that along ⟨001⟩ every other group formed a 'weak' link compared with stronger links along ⟨110⟩ (Fig. 4). The correlation length of 4·6 Å along ⟨001⟩ coincides exactly with $\frac{1}{4}\mathbf{a}$, the distance between successive propionates in the same direction (4·55 Å), and gives support to the 'weak-link' model proposed by SG. The value of 24·5 Å is close to the value of 25·7 Å ($\mathbf{a}\sqrt{2}$) for the linkage along ⟨110⟩ as shown in Fig. 4, thus indicating that the average domain length along ⟨110⟩ contains only one or two weak links with a break in correlation occurring at the second weak link on average. The very short correlation length along ⟨001⟩ lends strong support to the two-dimensional 'platelet' model of SG since, compared with the much greater correlation along ⟨110⟩, it corresponds to almost complete disorder along ⟨001⟩.

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Note added in proof: It is important to realize that the ordered 'platelets' proposed contain ordering also of the cations, so that the DBP structure is to be thought of as having microdomains of differing chirality for cations *and* organic molecules. Recent optical transform experiments by Welberry & Epstein (private communication) suggest that the cations are the major contributors to the diffuse scattering; however, because of the strong Ca—O bonds in the structure, and thus the effect of the cation positions on the organic molecules, the 'weak link' model may still apply.

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Can Intensity Statistics Accommodate Stereochemistry?

BY A. J. C. WILSON

Department of Physics, University of Birmingham, Birmingham B15 2TT, England

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Abstract

As pointed out by French & Wilson [*Acta Cryst.* (1978), A**34**, 517–525], central-limit theorems exist for the sums of non-independent as well as of independent variables [Bernstein (1922). *Math. Ann.* **85**, 237–241; (1927). *Math. Ann.* **97**, 1–59]. The finite size and stereochemical properties of atoms make the terms summed in the calculation of structure factors non-independent, but, if a central-limit theorem is applicable, then French & Wilson's postulate that the distribution parameter is $\langle I \rangle$ and not Σ has a theoretical base as well as empirical justification. The curve of $\langle I \rangle$ *versus* $(2 \sin \theta)/\lambda$ is correlated with the Patterson function, and the question of the existence of series expansions of the Gram–Charlier or Edgeworth type for sums of non-independent variables is raised.

Central-limit theorems

The expression for the structure factor in terms of the atomic positions and the indices of reflexion,

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp\{2\pi i(hx_j + ky_j + lz_j)\}, \qquad (1)$$

is of the form

$$S_n = u_1 + u_2 + \ldots + u_n \qquad (2)$$

considered in statistics in connexion with central-limit theorems. The usual theorem (see, for example, Cramér, 1945, pp. 213–220) depends on the assumption that the u's are independent variables, and Wilson (1949) used it to deduce the probability distribution of the structure factors and of the intensities of reflexion for crystals having the space groups $P1$ and $P\bar{1}$, though he realized that the finite size of atoms would prevent complete independence of the successive terms of (1). The assumption of complete independence implies that the mean intensity of reflexion is

$$\Sigma = \sum_{i=1}^{n} |f_i|^2 \qquad (3)$$

(Wilson, 1942). The expressions derived by Wilson have been found to apply with useful accuracy to many structures, but for large-molecule structures the average intensity does not decrease monotonely with $(2 \sin \theta)/\lambda$, as predicted by (3), but shows more or less marked oscillations. French & Wilson (1978), drawing attention to generalized central-limit theorems applicable when the u's of (2) are not independent, postulated that the functional forms of the Wilson (1949) distributions would remain valid, but that the distribution parameter [S in the notation of Wilson (1950)] would be $\langle I \rangle$, the actual local value of the mean intensity, averaged over values of hkl giving approximately the same value of $(2 \sin \theta)/\lambda$, instead of the sum given in (3). [In reading their paper it must be noted that they use the symbol Σ both for this sum and for the mean intensity $\langle I \rangle$.] Rogers (1965, 1980), Ladd (1978) and others have tacitly made the same assumption, without explicit reference to central-limit theory.

There are two main generalizations of the central-limit theorem for non-independent variables. The first applies when the u's are 'almost independent' (*presque indépendantes*; Bernstein, 1922), where 'almost independent' is given a precise mathematical definition whose physical meaning is not easy to grasp. The

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