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Diffraction Intensities from Bent Crystals

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Simple expressions are derived for the diffraction intensities given by coherently diffracting regions of a crystal in which the lattice is elastically bent, on the assumption that the amount of bending within such a region is small. Evidence is provided that under normal experimental conditions the geometric coherence of the incident radiation is usually such that coherent diffraction cannot take place between atoms more than a few hundred Ångström units apart, and the assumption of small amounts of bending in the coherently diffracting region gives a good approximation even for highly bent clay-mineral crystals.

The profiles of the broad *hk* bands observed in X-ray powder patterns of metahalloysite were calculated. The assumption that the crystallites are bent about a single axis improved the agreement with the measurements of Brindley & Robinson (1948).

It is shown that some results obtained in electron-diffraction structure analyses of single crystals may be explained on the assumption of very small amounts of bending and that such an assumption may provide an explanation for the apparent discrepancy between theoretical prediction and experimental evidence on the range of application of electron-diffraction structure-analysis methods for both polycrystalline and single-crystal samples.

1. Introduction

In the course of the electron-diffraction observations of clay minerals which are reported in another paper (Cowley & Goswami, 1961) the intensities observed showed some surprising features. The *hk*0 spot patterns obtained from single silicate-layer sheets of montmorillonite, or from aggregations of a small number of silicate layers, often showed hexagonal symmetry whereas the structure of montmorillonite which has been proposed on the basis of the X-ray data available should give no more than a two-fold symmetry in such patterns. It is possible to postulate stacking sequences of silicate layers of the montmorillonite type which would give a hexagonal spot pattern but the relative intensities calculated from such models show poor agreement with those observed. Also there is little evidence that any regular stacking of the silicate layers exists in the montmorillonite samples used.

An explanation of these observations has been found by assuming that the crystallites are appreciably bent within the range for which the diffracted radiation is effectively coherent. On the same basis we have been able to provide adequate explanations for some apparent discrepancies in previous X-ray-diffraction observations on clay minerals and some earlier electron-diffraction results. In the present paper we discuss these latter points and give the theoretical basis for our interpretations.

Detailed theoretical treatments of diffraction from simple cylindrically-bent crystals have been made by a number of authors including Fock & Kolpinsky (1940), Wilson (1949), Blackman (1951), Whittaker (1955, and previous papers mentioned there), Waser (1955) and Kunze (1956). All of these treatments involve considerable mathematical complexity particularly if, for comparison with experiment, some sort of averaging of the results over a range of radii of curvature of the crystals were required. Even greater complexity would result if bending about two axes were considered. The question arises whether under normal experimental conditions some simplification of the system is justifiable so that the mathematics may be simplified and the computation involved may be less formidable.

An assumption which is common to the above treatments is that the ratiation incident on the diffracting system is completely coherent. This is not necessarily so. Whether we consider X-rays or electrons, chromatic coherence of the radiation may usually be assumed, but the diameter of the source of radiation and its distance from the object are usually such that only partial geometric coherence can be assumed. From the discussion in a subsequent paragraph and Fig. 2 we deduce that for most cases of interest the dimensions of the regions over which the incident radiation can be considered coherent are smaller than the radii of curvature for the bending of the crystals. It is then possible to make the assumption that only small bending angles need be considered. This leads to a simplified mathematical treatment which allows ready evaluation of diffraction intensities. It also provides the basis for a concept, that of a limited coherence length in the beam direction due to the bending, which allows a rapid qualitative appreciation of the nature of changes to be expected in any particular circumstances when crystals are bent.

2. Diffraction by bent crystals

We consider coherent diffraction from a portion of a bent crystal such as that shown in Fig. 1. The extent of the crystal portion considered, if not limited by crystal boundaries, may be taken as the region for which the incident radiation may be assumed coherent with that passing through the centre of the crystal portion. We assume that within this crystal portion the total angle through which the lattice planes are bent is small, i.e. sufficiently small to allow us to neglect higher powers of the angle than the second and, if necessary, to take an average of terms of power two. Then the variation in length of the vectors between neighboring atoms will be negligible, but the variation of direction of such vectors will be important.

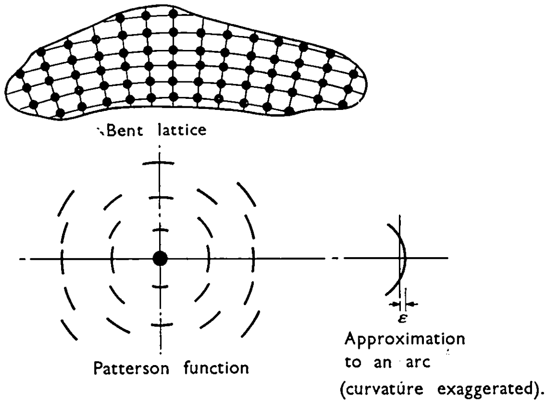

Fig. 1. An elastically bent portion of a crystal lattice, its Patterson function, and the approximation to an arc used in calculations.

Instead of attempting a Fourier transform of the bent crystal portion, we consider the (non-periodic) Patterson function of this portion and calculate the diffraction intensity from the Fourier transform of that. The form of the Patterson function corresponding to a simple lattice bent about one axis is illustrated in Fig. 1. Each Patterson peak is spread out over an arc, centred on the origin, the length of the arc being proportional to the distance from the origin. The exact distribution along the arc will depend on the dimensions of the crystal portion and the nature of the bending which is not necessarily uniform. Since the total angle of bending is small, each arc may be approximated by a straight line segment parallel to the central part of the arc and very slightly nearer the origin, as is suggested by the small sketch in Fig. 1.

Suppose that the Patterson function for the unbent crystal consists of a set of peaks of weight and form given by $w_i(\mathbf{r})$ at positions defined by the vectors, $\mathbf{r}_i$, of magnitude r_i, i.e.

$$P(\mathbf{r})=\Sigma_i w_i(\mathbf{r}) * \delta(\mathbf{r}-\mathbf{r}_i)\,. \qquad (1)$$

If the lattice is bent about the x axis (with unit vector $\mathbf{i}$) of a set of orthogonal axes, each Patterson peak is spread along an arc which may be approximated by a line segment in the direction of $(\mathbf{r}\times\mathbf{i})$. The distribution of relative weight along this line segment may be represented by a normalized function $g_{i,x}(p/r_i)$ where p is the distance along the arc. Then the Patterson function for the bent crystal is given by

$$\begin{aligned}P(\mathbf{r}) = \Sigma_i w_i(\mathbf{r}) &* \delta(\mathbf{r}-\mathbf{r}_i)\\ &* \int g_{i,x}(p/r_i)\,.\,\delta\{\mathbf{r}-(\mathbf{r}_i\times\mathbf{i})p/r_i\}\,.\,dp\,. \qquad (2)\end{aligned}$$

The reciprocal-space intensity function is given by the Fourier transform of the Patterson function, thus:

$$\begin{aligned}I(\mathbf{s}) &= \int P(\mathbf{r})\,.\exp\{2\pi i\mathbf{r}\,.\,\mathbf{s}\}\,.\,d\mathbf{r}\\ &= \Sigma_i W_i(\mathbf{s})\exp\{2\pi i\mathbf{r}_i\,.\,\mathbf{s}\}\\ &\quad\times \int g_{i,x}(p/r_i)\,.\exp\{2\pi i((\mathbf{r}_i\times\mathbf{i})\,.\,\mathbf{s})p/r_i\}\,.\,dp\\ &= \Sigma_i W_i(\mathbf{s})\,.\,r_iG_{i,x}((\mathbf{r}_i\times\mathbf{i})\,.\,\mathbf{s})\,.\exp\{2\pi i(\mathbf{r}_i\,.\,\mathbf{s})\}\,, \qquad (3)\end{aligned}$$

where $W_i(\mathbf{s})$ is the Fourier transform of $w_i(\mathbf{r})$ i.e. the scattering factor corresponding to a Patterson peak, and $G_{i,x}(s)$ is the Fourier transform of $g_{i,x}(p)$. Thus the contribution of the Patterson peak at $\mathbf{r}_i$ to the intensity at a reciprocal-lattice point defined by $\mathbf{s}$ is modified according to its position relative to the x axis.

If the lattice is also bent about the y axis, the Patterson function of (2) is further convoluted with a term of the form

$$\int g_{i,y}(q/r_i)\,.\,\delta(\mathbf{r}-(\mathbf{r}_i\times\mathbf{j})\,.\,q/r_i)\,.\,dq\,,$$

where $\mathbf{j}$ is the unit vector along the y axis and $g_{i,y}(q/r_i)$ gives the spread of the ith Patterson peak in a direction perpendicular to the y axis in terms of the parameter q.

Then the intensity becomes

$$\begin{aligned}I(\mathbf{s}) = \Sigma_i W_i(\mathbf{s})\,.\,r_i^2\,.\,G_{i,x}&((\mathbf{r}_i\times\mathbf{i})\,.\,\mathbf{s})\\ &\times G_{i,y}((\mathbf{r}_i\times\mathbf{j})\,.\,\mathbf{s})\,.\exp\{2\pi i(\mathbf{r}_i\,.\,\mathbf{s})\}\,. \qquad (4)\end{aligned}$$

Similarly, if bending also occurs about the z axis (unit vector $\mathbf{k}$), we multiply by a further term,

$$r_iG_{i,z}((\mathbf{r}_i\times\mathbf{k})\,.\,\mathbf{s})\,.$$

Usually the volume of specimen irradiated is very much greater than the coherently diffracting crystal portion considered above. The intensity is then given by summing the intensities corresponding to all such crystal portions, and the functions $G_{i,x}$, etc. may be replaced by averaged functions. The coherence function, defined below, will usually have a form for which a Gaussian curve is a fair approximation. The averaging involved when the crystals are bent in an irregular manner or have irregular shape makes this approximation still more appropriate. We therefore make the assumption that the functions $g_{i,x}$ have the same form for all $\mathbf{r}_i$ and may be approximated by a Gaussian distribution

$$g_{i,x}(p/r_i) = (c/\pi^{\frac{1}{2}}r_i).\exp(-c^2p^2/r_i^2)\ .$$

The half-width of this distribution, proportional to r_i/c, is a measure of the amount of bending within a coherently diffracting region and so depends on both the distortion present in the crystals and the conditions of irradiation.

Then

$$r_iG_{i,x}((\mathbf{r}_i\times\mathbf{i}).\mathbf{s}) = \exp\{-(\pi^2/c^2)((\mathbf{r}_i\times\mathbf{i}).\mathbf{s})^2\}\ .$$

In some special cases the average bending may be considered as being the same about all axes. For equal bending about each of three perpendicular axes

$$\begin{aligned} I(\mathbf{s}) &= \Sigma_i W_i(\mathbf{s}).\exp\{2\pi i\mathbf{r}_i.\mathbf{s}\} \\ &\quad \times\exp[-(\pi^2/c^2)\{((\mathbf{r}_i\times\mathbf{i}).\mathbf{s})^2 \\ &\quad +((\mathbf{r}_i\times\mathbf{j}).\mathbf{s})^2+((\mathbf{r}_i\times\mathbf{k}).\mathbf{s})^2\}] \\ &= \Sigma_i W_i(\mathbf{s}).\exp\{2\pi i\mathbf{r}_i.\mathbf{s}\}.\exp\{-(\pi^2/c^2)(\mathbf{r}_i\times\mathbf{s})^2\}\ . \end{aligned} \tag{5}$$

For thin sheet-like crystals, such as those of many clay minerals, we may usually assume that bending takes place principally about two axes in the plane of the crystal sheets. The appropriate intensity formula is thus

$$\begin{aligned} I(\mathbf{s}) &= \Sigma_i W_i(\mathbf{s})\exp\{2\pi i\mathbf{r}_i.\mathbf{s}\} \\ &\quad \times\exp[-(\pi^2/c^2)\{((\mathbf{r}_i\times\mathbf{i}).\mathbf{s})^2+((\mathbf{r}_i\times\mathbf{j}).\mathbf{s})^2\}]\ . \end{aligned} \tag{6}$$

If we are concerned with the *hk*0 single-crystal electron-diffraction spot patterns obtained with the beam approximately perpendicular to the crystal sheets, and the **s** vector lying in the x–y plane, this reduces to

$$\begin{aligned} I(\mathbf{s}) &= \Sigma_i W_i(\mathbf{s}).\exp\{2\pi i\mathbf{r}_i.\mathbf{s}\} \\ &\qquad \times\exp[-(\pi^2/c^2)(s^2r_i^2\cos^2\alpha)]\ , \end{aligned} \tag{7}$$

where α is the angle made by $\mathbf{r}_i$ with the z axis. Thus the contribution of a Patterson peak to the intensity function depends on its z-coordinate, z_i. If the unit cell is not too small in the c direction, the bending may introduce changes of effective weight of the Patterson peaks which are appreciable within the unit-cell dimensions. The intensity of the *hk*0 reflections will then be appreciably changed.

In powder patterns from assemblies of small plate-like crystals which are bent in this way, equation (7) may be applied to the *hk*0 lines. For *hkl* reflections with l small we may consider that **s** makes a small angle, γ, with the x–y plane. Then it is readily shown that the final exponential of equation (7) becomes, approximately,

$$\exp\{-(\pi^2/c^2)s^2r_i^2\cos^2\alpha(1+2\gamma\tan\alpha.\cos\nu)\}\ , \tag{8}$$

where ν is the angle between the projections of $\mathbf{r}_i$ and **s** on the x–y plane. The additional term may be interpreted as implying that the contributions of the Patterson peaks to the intensity depend on their distances from a plane tilted through an angle γ with respect to the x–y plane, rather than on their distances from the x–y plane itself. Taking into account that contributions to any one diffraction ring usually come from several Patterson peaks with different values of the angle ν, this additional term may be neglected if the angle γ is small and if the accuracy required in intensity calculations is not great.

From equation (7) it is seen that Patterson peaks with z coordinates greater than a certain value, say z_0, determined by the average bending or disorientation of the crystals, give a negligible contribution. Hence the relative positions of a pair of atoms with z coordinates differing by more than z_0 do not influence the intensity distribution. Such pairs of atoms may then be regarded as diffracting incoherently. We may therefore say that the effect of bending or misorientation of crystals by small rotations about the x and y axes is to introduce a limitation to the range in the z direction over which coherent diffraction can take place. By use of this concept it is easy to obtain a rapid appreciation of the effect of bending on the symmetry and relative intensities of diffraction patterns.

As an example we consider the case in which the bending and misorientation causes the Patterson peak to be spread over an arc subtending ten degrees at the origin so that, in equation (7) we put $c\approx 10$. Then for a reflection with $s_0 = 1$ Å^{-1} the Gaussian term in equation (7) has a half width of about 6 Å, and a Patterson peak has very little influence on the intensity distribution if its z coordinate is more than 3 Å. Thus layers of atoms separated by more than 3 Å in the z direction will, in effect, diffract incoherently.

For montmorillonite, the silicate layer consists of a layer of Al–O octahedra sandwiched between two layers of Si–O tetrahedra. Each of these sub-layers has hexagonal symmetry, but in the composite layer they are so stacked that they give a monoclinic structure with, at best, a plane of reflection. The concentrations of scattering matter of the three sub-layers are about 3 Å apart in the z direction. Hence under the above conditions we can assume, as a first approximation, that the three sub-layers will diffract independently. Each will give a hexagonal diffraction pattern. Hence the total diffraction pattern will have hexagonal symmetry.

3. Coherence of illumination

It is now necessary to demonstrate that our small-bending-angle approximation is justified under normal experimental conditions because of the limited range over which the incident radiation may be regarded as coherent. This may be done by estimating the coherence either approximately by elementary methods or more exactly by using, for example, the method of Cowley & Moodie (1959*a*).

For the purposes of diffraction experiments we may define the coherence of the radiation used as its ability to produce diffraction effects. As a measure of coherence we consider the contrast of the diffraction fringes produced in an idealized Young's fringe experiment. If the relative coherence of the radiation at two points, separated by a distance X in a direction perpendicular to the beam, is to be found we imagine that the incident radiation is blocked by screens except for two δ-function apertures at these two points. The contrast of the fringes given by interference of the radiation from these two apertures is then a measure of the relative coherence. If the radiation is uniform over the whole diffracting system the contrast so measured will be a function of X only, and not of the positions of the two points.

It is therefore possible to define a coherence function giving the relative coherence as a function of X for any two points. The range of X values over which their coherence function has an appreciable value we call the 'lateral coherence range'.

It can readily be shown that this coherence function is identical with the correlation function, for the points x and $X+x$, of the wave function, $\psi(x)$, of the incident wave, given by $\langle\psi(x).\psi^*(X+x)\rangle$.

The coherence function for the experimental arrangements treated by Cowley & Moodie (1959*a*) or for any more elaborate arrangement may be obtained either by replacing the diffracting object, $q_2(x)$, by a pair of apertures of variable spacing or by finding the auto-correlation function for the wave function at the $q_2(x)$ position. In particular if we assume that the effective source of radiation has a Gaussian distribution of intensity with a width σ measured at $1/e$ of the maximum intensity, and this irradiates a specimen at a distance R, with no intermediate apertures or lenses, the coherence function at the specimen is again a Gaussian function with a width, which may be taken to represent the coherence range, given by

$$\Delta = 2R\lambda/\pi\sigma\,. \tag{9}$$

This formula was derived for forward scattering from two-dimensional objects and is not immediately applicable to the high-angle scattering from three-dimensional crystals met in X-ray diffraction experiments. Since we are here dealing only with very thin crystals it may be assumed to apply reasonably well.

For most X-ray and electron-diffraction experiments it will be sufficient to take the effective source size σ to be the diameter of either the source or of a limiting aperture, whichever subtends the smaller angle at the specimen. In Fig. 2 we have plotted the relation between source diameter and coherence range for 50 kV. electrons and Cu $K\alpha$ X-rays for various source-to-specimen distances. The regions which correspond approximately to the experimental arrangements most commonly employed are shown shaded. From this figure it appears that, for the experimental arrangements normally used for powder or single-crystal X-ray diffraction work, for the usual low-resolution electron-diffraction and for electron-probe micro-diffraction methods of single-crystal studies (Cowley, 1953*a*), the coherence range is of the order of 100 to 1000 Å. Only when special attempts are made to obtain high-resolution conditions is the coherence range appreciably greater than this. For some high-resolution X-ray diffraction experiments, coherence ranges approaching 100μ are possible.

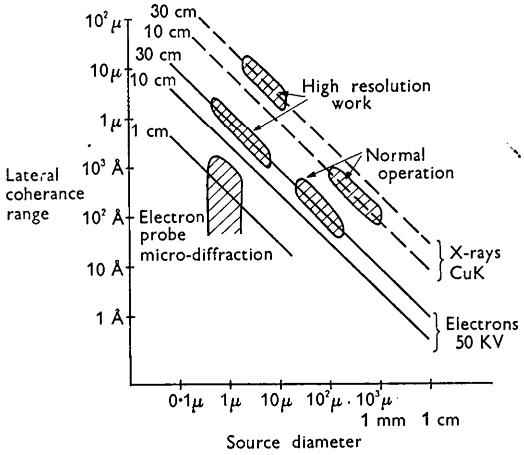

Fig. 2. Indicating the approximate values for the lateral coherence range under various experimental conditions.

For clay minerals, electron microscopy provides evidence that the thin crystals are frequently bent. An extreme example is provided by the observation by Honjo & Mihama (1954), Taggart, Milligan & Studer (see Waser, 1955) and others, that thin halloysite silicate sheets appear to be rolled into cylinders with diameters of the order of 1000 Å. If such crystals are illuminated with radiation having a coherence range of only a few hundred Å, the angle of bending will be of the order of 10–30°. Hence even in this case our methods will be adequate to give at least an approximate account of the diffraction patterns. If we assume that, in general, the radii of curvature of the bent or distorted silicate layers are not less than in the case of halloysite our method should be applicable for most diffraction studies of clay minerals. For other better-ordered crystals the curvature is much less, the bending within the coherence range will be no more than a few degrees and our method should be quite accurate.

4. Application to metahalloysite

The clay minerals for which the bending should be greatest are those with very little apparent order in the stacking of the silicate layers. Such minerals give X-ray powder patterns consisting of relatively sharp

$00l$ reflections and broad hk bands. The only detailed measurements of the intensity distribution of the bands seem to be those of Brindley & Robinson (1948) on metahalloysite. These authors calculated theoretical band profiles using the method of Warren (1941) assuming that the sample consisted of small plate-like crystals, one silicate layer thick, in random orientation. They obtained a fair measure of agreement with their observations, but marked anomalies remained. The width of the 06,33 band, for example, appeared to be nearly twice that predicted by the theory.

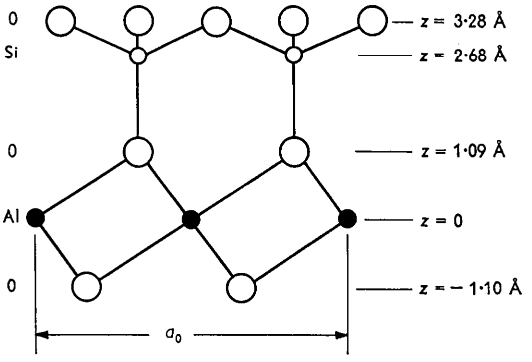

Fig. 3. A projection of the lattice structure assumed for metahalloysite.

It seems clear that the anomalous width of the 06,33 band is readily explained on the assumption of bending of the crystals. This would have the effect of decreasing the effective layer thickness and so lead to a more gradual fall-off of scattering power with l' along the $06l'$ and $33l'$ reciprocal-lattice lines. We have therefore repeated Brindley & Robinson's calculations, taking the possibility of bending into account.

The lattice dimensions assumed, $b=8{\cdot}90$ and $a=b/3^{\frac{1}{2}}=5{\cdot}14$ Å are those of Brindley & Robinson. For purposes of calculation an artificial c' axis of 30 Å, perpendicular to the a and b axes, was used. The z coordinates of the atoms, shown in Fig. 3, were taken to be equivalent to the mean z coordinates for each layer of atoms found by Newnham & Brindley (1956) for dickite. The x and y coordinates taken were those corresponding to an idealized structure with no distortion of the oxygen layers from perfect hexagonal nets, since no distortions of the oxygen layers have been established for metahalloysite and any such distortion would give relative intensity changes within any one line profile which were small compared with the bending effects. The assumption that the crystals were unbent and only one silicate layer in thickness gave the intensity profiles shown by the continuous line in Fig. 4, and the dotted lines in Figs. 5 and 6. For the 02,11 profile, Fig. 4, and the 06,33 profile, Fig. 5, our calculations agree with those of Brindley & Robinson. For the 20,13 profile, although the calculated variation of scattering power with l' is the same, our profile is much narrower than theirs. It does, however, agree with theirs in failing to predict the observed clear division of the profile into one sharp and one broad maximum. In our calculations we assume the average crystal size $L=150$ Å which seemed to give the best fit for the low-angle part of the 02,11 profile.

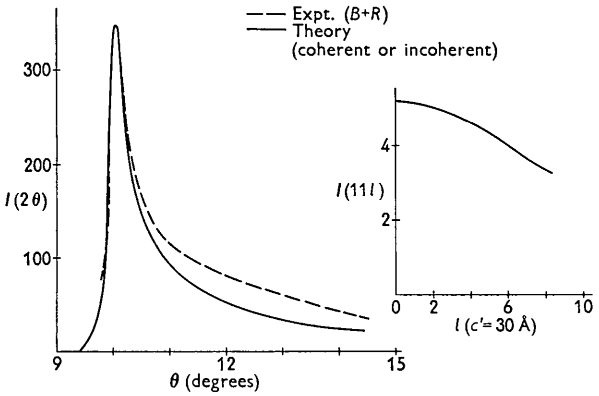

Fig. 4. The variation of scattering power with l' and the profile for the 02,11 band of metahalloysite.

In the pattern from randomly oriented crystallites the h, k bands contain contributions from crystals at all angles to the incident beam. If we neglect the high-angle tails, however, we can say that the principal portions of the profile correspond to vectors **s** making only small angles with the plane of the silicate sheets. Equation (7) may thus be used as a basis for the intensity calculations as a first approximation, bearing in mind that agreement with observation cannot be expected for the high-angle tails of the bands.

If it is assumed that, within the lateral-coherence range of the illumination the average deviation in orientation from the average is of the order of 10°, the maximum distance between two layers of atoms which can diffract coherently is about 3 Å for the 02,11 reflections and about 1 Å for the 06,33 reflections. Calculation shows that for the 02,11 reflections the intensities are very nearly independent of the amount of bending unless the distances between coherently diffracting planes is less than about 2 Å. Hence the variation of scattering power with l' and the line profile shown in Fig. 4 as continuous lines apply equally to bent and unbent crystals. Assuming an average size $L=150$ Å gives good agreement with the measurements of Brindley & Robinson except on the high-angle side.

For the 20,13 profile, the assumption that the bending is the same in all directions does not give good agreement with the experimental profile. As for unbent crystals the profile is not resolved into two distinct maxima; in order to account for the observed features it is necessary to make a more specific assumption concerning the nature of the bending. Electron-microscope observations indicate that metahalloysite crystals are usually bent about a single axis, sometimes forming complete cylinders. If we assume

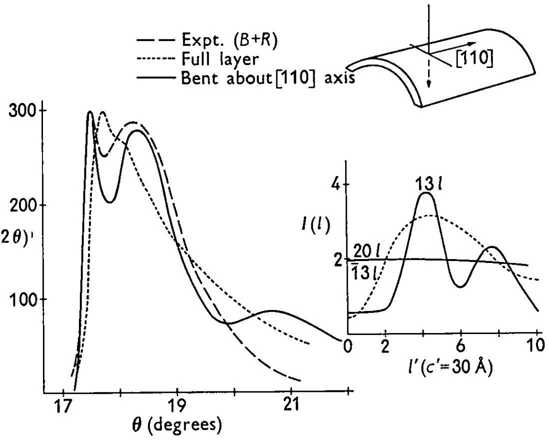

Fig. 5. The type of bending assumed, the variation of scattering power with l' and the profile for the 20,13 band of metahalloysite.

that the axis of bending is, for example, the [110] axis of our imaginary orthorhombic cell the bending will be effectively zero for the (130) planes but great for the $(20l')$ and $(\bar{1}3l')$ planes. The variation of scattering power with l' is therefore almost constant for $20l'$ and $\bar{1}3l'$ but more like that for an unbent layer for $13l$. Adding separately the contributions from the different type of planes then gives fair agreement with the experimentally obtained profile. The agreement is improved still further if it is assumed that some order exists between adjacent silicate layers so that the maximum due to $13l'$ is sharpened. The full-line profile of Fig. 5 is calculated on the assumption that the silicate layers are ordered in pairs with a shift of $a/6$ between them. This gives, in fact, too definite a separation of the two maxima in the profile.

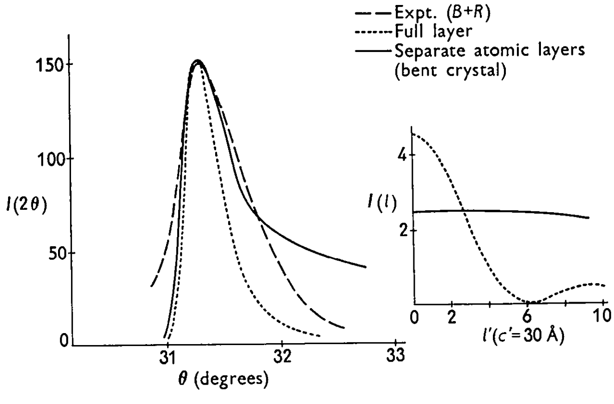

Fig. 6. The variation of scattering power with l' and the profile for the 06,33 band of metahalloysite.

If we make the same assumption of uniaxial bending for the 06,33 reflections we see that the effective degree of bending is high for all contributing planes, and for each an effective incoherence between layers of atoms only about 1 Å apart implies that each individual layer of oxygen or metal atoms must be considered as diffracting separately. The scattering power along the $06l'$ and $33l'$ reciprocal-lattice lines is therefore almost independent of l', whereas for the full layer it falls off very sharply with l', as shown in Fig. 6. The line profile is therefore much broader and agrees well with the experimental profile except in the higher-angle region.

By making suitable assumptions about the structure of the silicate layer, the ordering between the silicate layers and the amount and nature of the bending present it would be possible to fit the experimental curves at exactly as desired. This is true also if it is assumed that bending takes place about the [100] axis rather than the [110]. The limitations to the accuracy of the experimental data and the lack of precise information on the structure of the crystals and the nature of their deformations make any further calculations pointless. The calculations we have made indicate that even in this extreme case of bending our methods can give an adequate explanation for all the observed features of the band profiles without requiring any unreasonable assumptions.

5. Implications for structure analysis

From the above considerations it will be obvious that any attempt to derive detailed structural information from the band profiles of X-ray diffraction patterns from such highly disordered clay minerals must fail unless detailed information on the morphology of the crystals in the sample is available. For electron-diffraction patterns from oriented polycrystalline material and single-crystal patterns obtained by electron micro-probe techniques this is also true, although here the possibility exists of deriving some information concerning the variation in orientation and particle size from the diffraction patterns. The main source of morphological data, however, must always be electron-microscope observations such as those mentioned above. Even in the most favourable cases, if the bending is great enough to affect the relative intensities of reflections appreciably an additional variable has been introduced and allowance must be made for it in interpreting intensities.

It seems probable that relative intensities of reflections will be affected to the same extent as the relative heights of Patterson peaks within one unit cell of the Patterson function. If we assume that the height of a Patterson peak is appreciably changed if the centre of the peak is spread over an arc 0·1 Å long, for a unit-cell dimension of 10 Å the relative intensities may be changed by a bending of 10^{-2} radians or $\frac{1}{2}$ degree over a distance equal to the lateral coherence range i.e. usually less than 1000 Å. This corresponds to a radius of curvature of about 10μ. Under high-resolution conditions this radius may be increased to 1 mm. or more.

There seems to be little doubt that bending effects have been present and have influenced the results, sometimes favourably and sometimes unfavourably, in previous electron-diffraction structure analysis investigations by both the 'oblique texture' and the single-crystal methods. The crystals studied have frequently been in the form of very thin flakes, since the average crystal thickness in the beam direction must necessarily be limited to a few hundred Ångströms. For such crystals any form of mechanical support or overlapping can introduce bends of a few degrees.

As an example we consider the structure analysis of disordered boric acid crystals (Cowley, 1953*b*). Because some disorder exists in the stacking of layers the unit cell could be taken as including only one averaged layer of atoms perpendicular to the beam. The relative intensities of the *hk*0 spots were therefore not affected by any bending present. The effect of bending would have been to modify the distribution function which was used to define the set of relative translations between the origins of successive layers. Although the method used in deriving the average layer structure and distribution function is under review, and some details of the results may thereby be modified, it seems likely that the main conclusions drawn from them remain valid. From the distribution function it was deduced that a given origin layer gave coherent diffraction with only three or four layers on each side of it. It now appears likely that this limited range of coherent diffraction can be attributed almost entirely to a bending of the crystal. In this way we can avoid the rather unsatisfactory assumption that stacking disorders exist in which adjacent planes of atoms are displaced by arbitrary amounts but retain their relative orientations. The bending required to produce the observed effect is of the order of one degree within the lateral coherence range, which was probably a few hundred Ångströms.

It seems probable that the effective range or order has been reduced in the same way in the structural studies of ferric chloride–graphite compounds (Cowley & Ibers, 1956) and basic lead carbonate (Cowley, 1956). In the latter case the occurrence of a long effective *c*-axis probably led to a modification of the relative intensities, which may have given rise to the apparent differences in the details of the structure at the top and bottom of the complex layers.

In all the above considerations we have assumed purely kinematic diffraction conditions. Particularly for electron diffraction this is a serious limitation since the kinematic theory does not represent the true limiting case of diffraction theory for crystal thicknesses tending to zero, and gives a good approximation to the diffraction intensities for very thin crystals only if no heavy atoms are present. Our theoretical treatment may be applied to a limited extent if, instead of the kinematic theory, we use the phase-grating approximation of Cowley & Moodie (1959*b*) which represents a correct limiting form of the theory for small thicknesses, since the intensities may still be expressed in terms of the projection of a Patterson function in favourable circumstances. Careful intensity measurements on thin crystals of BiOCl, for which deviations from kinematic scattering are appreciable (Cowley & Kuwabara, 1961) confirmed that our treatment could be applied to that compound.

For thick crystals, the validity of our conclusion that the effective coherently-diffracting thickness of a crystal is reduced by bending could only be proved by use of the full dynamic theory applied to bent crystals. There is some limited experimental evidence from X-ray diffraction experiments that it may be at least approximately valid. For example White (1950) showed that bending of a quartz crystal increased the integrated intensity of an X-ray reflection from the perfect crystal value to very nearly the 'ideally imperfect' crystal, kinematic, value. Fukushima (1933) reported that elastic strain increases the intensity of reflection of an X-ray beam transmitted through a quartz crystal.

No equivalent observations seem to have been reported for the electron case. Perhaps the most valuable tests in this respect would be an extension of the observations of the 'shape transform' fine structure of electron-diffraction spots from bent lamellar crystals by Uyeda, Ichinokawa & Fukano (1954) and more recently by Hashimoto, Yoda & Mannami (private communication) to crystals with a much smaller radius of curvature.

If we can, in fact, make the assumption that bending can reduce the effective thickness so that the scattering approximates to kinematic instead of being dynamic in the electron-diffraction case, the implications for structure analysis experiments are considerable. Only a small amount of bending, of the order of a fraction of a degree over a range of 1000 Å or so, would be sufficient to reduce the effective crystal thickness to a few hundred Ångströms or less, i.e. to a value for which the kinematic theory or the phase-grating approximation should provide a reasonable account of the intensities of electron-diffraction patterns from polycrystalline specimens or single crystals.

The most important objection which was raised to the pioneer work on electron-diffraction structure analysis by Pinsker and his co-workers and later work in this field was that the apparent thickness of the crystals used was not always less than the limits set for kinematic diffraction by theoretical treatments such as those of Blackman (1939). The crystals investigated frequently had a layer-lattice structure and probably were very thin and flexible so that some bending seems probable. A sufficient amount of bending or equivalent mosaic disorientation is well within the spread in orientations deduced from the published patterns (usually at least one or two degrees). It may be that in the presence of such bending lies the justification for the use of the kinematic theory as a basis for some of these structure analyses.

While confirmation of these indications may have the effect of extending the range of the methods of electron-diffraction structure analysis beyond that admitted by earlier theoretical work, it must be born in mind that, as for montmorillonite, mentioned in the Introduction, excessive bending can render difficult or impossible a structure analysis in the conventional sense of the term. This provides an additional argument for the requirement that any quantitative electron-diffraction work should be accompanied by detailed and careful electron-microscope examination of the specimen.

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The Crystal Structure of Chromium(II) Chloride

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$CrCl_2$ is found to have an orthorhombic unit cell, *Pnnm*, with

$$a_0=6{\cdot}64\pm0{\cdot}01,\ b_0=5{\cdot}98\pm0{\cdot}01,\ c_0=3{\cdot}48\pm0{\cdot}01\ \text{Å}\,.$$

The cell contains the equivalent of two $CrCl_2$ groups in which chromium(II) is surrounded by an elongated octahedron of halogens. The structure consists of interacting planar chains in which chromium ions are bridged by two chloride ions.

Chromium(II) chloride is the only dichloride of the first row transition metals for which the crystal structure has not been reported. Handy & Gregory (1951) observed that X-ray powder diagrams could be indexed on the basis of an orthorhombic unit cell, $6{\cdot}65\times5{\cdot}99\times3{\cdot}48$ Å^3, and that the structure appeared to be of a deformed rutile type, similar to $CaCl_2$; however the atomic positions were not determined. It became known to the authors of the present paper that the structure had recently been determined independently and at practically the same time in four different laboratories; hence results will be reported under joint authorship.

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