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Fine Structure Within the Diffraction Maxima from Chrysotile

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A previously predicted fine structure has been observed within the sharp reflections of an electron-diffraction pattern of chrysotile. The fringe spacing of this fine structure is interpreted in terms of the size of the fibrils, and the observed configurations of the fine structure are used to show that the cylindrical layers of the structure cannot be both perfect and circular.

1. Introduction

It has been pointed out previously (Whittaker, 1954) that although the diffraction pattern of a cylindrical lattice resembles that of a rotating crystal, when two reflections from a cylindrical lattice occur in the same direction they must interfere with one another, because they occur simultaneously and not successively as with a rotating crystal. It was shown theoretically that such multiplicity, as, for example, of the $h00$ and $\bar{h}00$ reflections, must be expected to lead to a fine structure within the reflection profile, and this expectation has been confirmed for the corresponding optical diffraction from circular and spiral lattices in the optical diffractometer (Whittaker, 1955*a*). The phenomenon may be understood physically by considering the correspondence between a cylindrical lattice and a symmetrical arrangement around an axis of a large number of blocks of material having a conventional crystal lattice. The $h00$ and $\bar{h}00$ reflections would then be produced, respectively, by two of these blocks whose centres would be separated by the mean diameter of the arrangement. The diffraction pattern would therefore be expected to be modulated by a system of fringes with a spacing inversely related to this mean diameter; and furthermore, since the mean diameter must be larger than the wall thickness of the tube-like cylindrical lattice, the fringe spacing must be less than the breadth of the reflections, and would therefore appear as a fine structure within them.

Such a fine structure has never been observed in

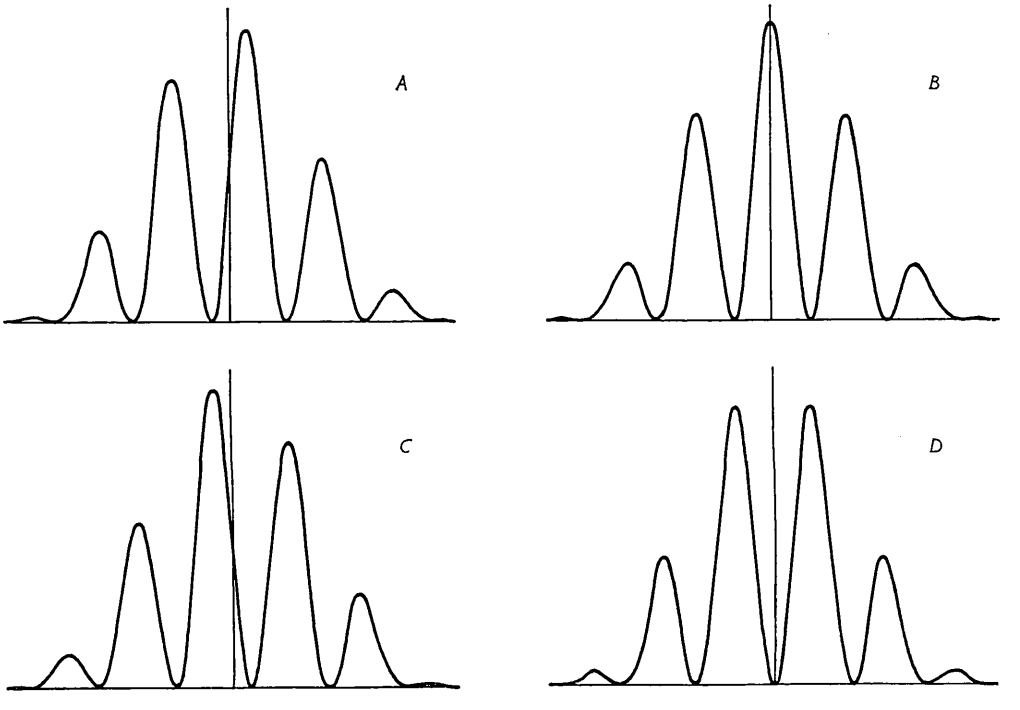

Fig. 1. Four configurations of the calculated profile of the 1st order reflection from the radial spacing of a cylindrical lattice with radial spacing a', internal radius $a'(8+x)$ and external radius $a'(15+x)$. Configurations A, B, C, D result when $x=0$, 0·125, 0·25, 0·375 respectively.

X-ray diffraction patterns of chrysotile, but this is not unexpected. The position of a maximum of the fine structure with respect to the centre of a reflection is exceedingly sensitive to the mean diameter of the lattice, and it changes through two complete cycles while this diameter is changed by an amount equal to the radial spacing a'. Calculated reflection profiles over one such cycle are shown in Fig. 1 for a succession of increments of radius of $0{\cdot}125a'$. Since a specimen of chrysotile for X-ray diffraction will normally contain of the order of 10^7 fibrils, variations in their diameters would be expected to lead to a complete smoothing out of the fine structure. However, it might be expected that in favourable circumstances the fine structure might be observable in selected-area electron diffraction in the electron microscope, and the present paper reports what is believed to be its detection for the first time.

2. Experimental

The photograph on which the fine structure was observed was one of a number taken for the author by Aeon Laboratories Ltd., using a Siemens Elmiskop I Electron Microscope at 80 kV. The fibres were mounted on the support grid by evaporation of a drop of a dilute suspension in absolute alcohol. The diffraction pattern of a selected area was recorded on the plate at a scale of 20 mm per $Å^{-1}$ in reciprocal space. On this scale the fine structure fringes had a spacing of only 0·12 mm, and were invisible to the naked eye. They were revealed on examination of the plate with a low-power optical microscope.

The specimen was from a slip-fibre seam from Mashaba District, S. Rhodesia.

3. Evaluation of the evidence

Before it can be established that the fine structure observed arises from the mechanism discussed in § 1 it is necessary to consider it in some detail. The diffraction pattern is shown in Fig. 2 at a magnification of $2\frac{1}{2}$ times. There are two superimposed chrysotile diffraction patterns present making an angle of about 40° with each other, corresponding with two fibres (or fibre bundles) which were visible in the micrograph. Each of these patterns consists further of several components making small angles with each other over a range of about 6°. This may be due in part to a composite character in the two fibres visible in the micrograph, and also either partly or wholly to the presence of sections within each fibre which make small angles with each other and which are joined at low-angle kinks. The diffraction patterns are all weak, and do not extend beyond the 2nd order of the radial spacing on the zero layer line. The zero layer line of one of the two patterns is entirely missing at one side of the photograph. From the extension of the spots along the 2nd layer lines it may be concluded that the fibres contain a disordered stacking sequence of mixed ortho- and clino-type.

Owing to the weakness of the photograph and to the presence on it of a number of dust marks, it does not reproduce well at a magnification sufficient to show the fine structure. However the effect is shown in Fig. 3 which shows two components of the best resolved group of the 200 reflections (the 1st order from the radial spacing), at a magnification of 20 times. A rather less clearly resolved 400 reflection (the 2nd order from the radial spacing) is also visible at the end of the photograph. Fig. 4 shows all the configurations of the fine structure that have been observed in sufficiently clearly associated 1st and 2nd order reflections.

The correspondence between the observed appearance and the various types of calculated spot profiles is obvious, but it is worth pointing out that two conceivable alternative explanations can be ruled out as follows:

(*a*) Replication of the diffraction pattern with a shift as a result of some instrumental aberration or vibration. This would shift the whole of the pattern in some particular direction, whereas the observed sub-spots are in every case spaced out along the layer line on which the main spot lies, irrespective of the direction of the layer line.

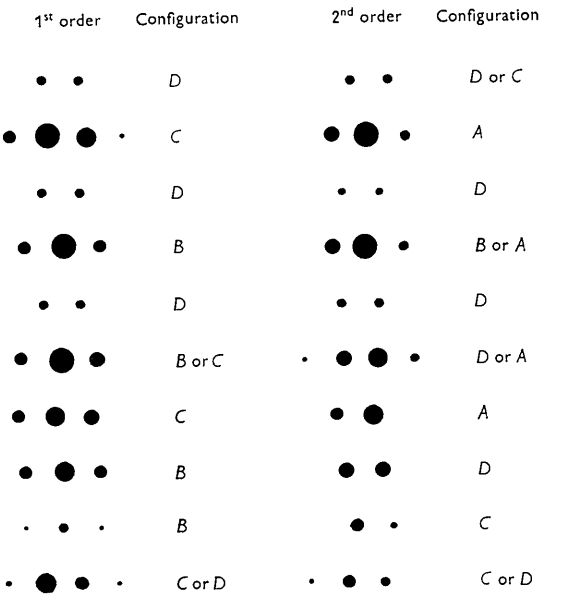

Fig. 4. Schematic representation of the observed configurations of the fine structure of associated 1st and 2nd order reflections from the radial spacing. The scale of the fine structure is exaggerated ×3 with respect to the distance between the orders. The resolution of the fine structure is also much exaggerated. The letters indicate the most nearly corresponding configuration in Fig. 1.

(*b*) Each sub-spot might be a reflection from a separate fibril, the different fibrils having slightly different a-parameters. However the sharpness of

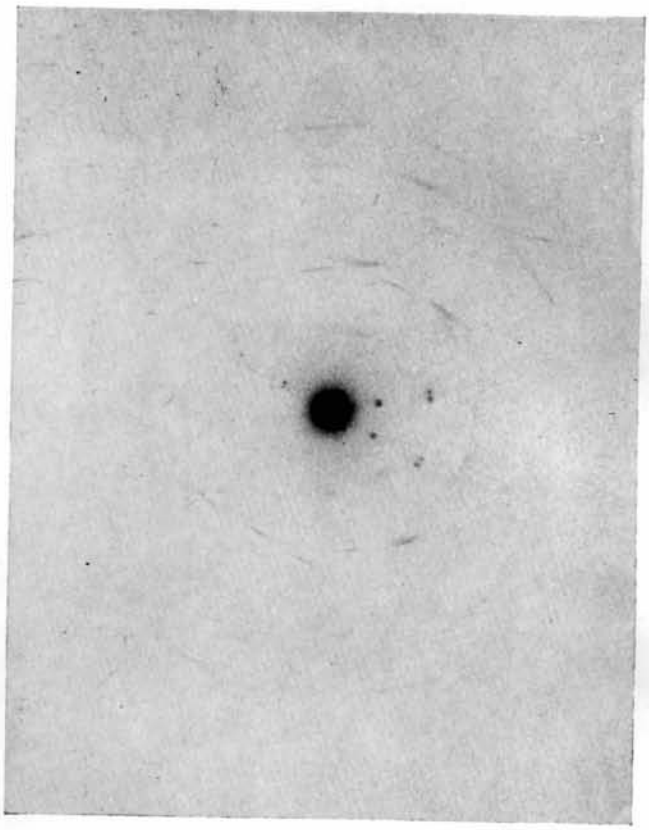

Fig. 2. Electron diffraction pattern of the specimen. (×2·5).

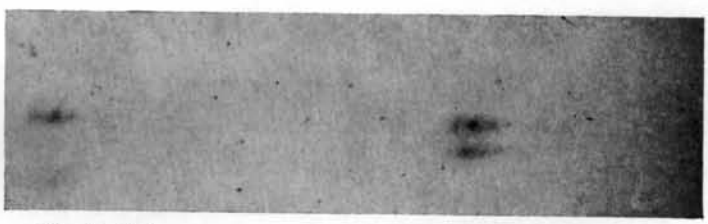

Fig. 3. Enlargement of a zero layer line from Fig. 2. (×20).

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reflexions interpreted in this way would indicate a fibril wall thickness of the order of 400 Å, and hence a fibril diameter in excess of 800 Å, and there would have to be an appreciable number of such abnormally thick fibrils present to account for all the spots. It seems unlikely that such an interpretation could be compatible with the appearance of the micrograph, or that it could account for the regular modulation of intensity of the sub-spots along each group on each zero layer line.

4. The diameter of the fibrils

The profiles of reflections have been calculated for cylindrical lattices with a variety of values of $\bar{r}$, the mean radius, and n, the number of co-operating layers. Provided that the hole in the centre of the lattice is not too small compared with the wall thickness, the spacing of the fringes (q) is related to $\bar{r}$ as

$$\bar{r}=1/(2q)\,.$$

This simple relationship ceases to apply when the central hole in the lattice becomes small relative to the wall thickness. Fig. 5 shows the ratio of $\bar{r}_{\text{calc}}/\bar{r}_{\text{true}}$ as a function of $2\bar{r}/[(n+1)a']$ where a' is the radial spacing of the lattice. This parameter is unity if the

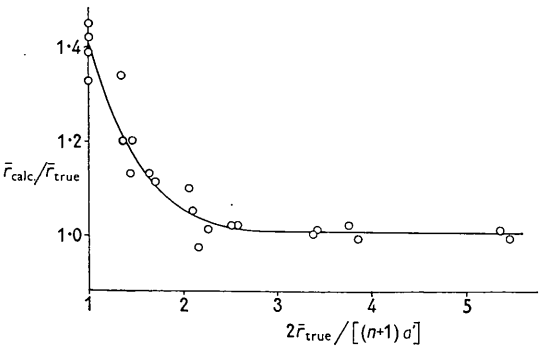

Fig. 5. The ratio $\bar{r}_{\text{calc}}/\bar{r}_{\text{true}}$ as a function of $2\bar{r}_{\text{true}}/[(n+1)a']$. The latter parameter is unity when the radius of the innermost layer of the lattice is a', *i.e.* when the central hole can be regarded as non-existent. Each point is derived from measurement of a graph of the calculated intensity distribution in the fine structure for a particular combination of internal and external radii. Scatter of the points about the line is due partly to graphical errors, and partly to the fact that $\bar{r}_{\text{calc}}/\bar{r}_{\text{true}}$ is only approximately a unique function of the parameter $2\bar{r}_{\text{true}}/(n+1)a'$.

radius of the innermost layer of the lattice is a' (when the central hole can be regarded as non-existent), and under these conditions $\bar{r}_{\text{calc}}/\bar{r}_{\text{true}}=1{\cdot}4$. However $\bar{r}_{\text{calc}}$ gives a reasonable estimate of $\bar{r}$ (within 10%) down to $2\bar{r}/[(n+1)a']=1{\cdot}8$.

Some estimate of $2\bar{r}/[(n+1)a']$ may be obtained from the appearance of the fine structure, since this parameter is closely related to the number of fringes which will occur within the confines of a reflection, although this number also depends on the disposition of the fine structure with respect to the centre of the reflection as shown in the following table.

	Reflection of type B		Reflection of type D	
$2\bar{r}/[(n+1)a']$	No. of fringes	Intensities	No. of fringes	Intensities
1·3	3	3–10–3	2	10–10
1·6	3	4–10–4	4	1–10–10–1
2·2	5	1–6–10–6–1	4	4–10–10–4
2·8	5	$2\frac{1}{2}$–7–10–7–$2\frac{1}{2}$	6	1–6–10–10–6–1

A and C type reflections can be regarded as intermediate between types B and D. As the reflections observed contain two, three, or four fringes if they are strong and two if they are weak, it may be concluded that $2\bar{r}/[(n+1)a']$ is near 1·6 and that the value of $\bar{r}$ calculated from the fringe spacing is up to about 15% high.

The observed fringe spacing of 0·006 Å^{-1} corresponds to a value of $\bar{r}_c$ of about 85 Å so that the true value of $\bar{r}$ is about 75 Å. When these figures are combined with the estimated value of $2\bar{r}/[(n+1)a']$ one obtains inside and outside diameters of about 60 Å and 240 Å respectively. This value of the inside diameter is at the extreme lower end of the distribution deduced by Whittaker (1957) from the diffuse-reflection profiles of a specimen from Quebec, and is very similar to values obtained by Jagodzinski (1961) from low-angle scattering. The outside diameter is in the middle of the range deduced by Whittaker but lower than most of Jagodzinski's values. It is not suggested that the present results either support or conflict with previous measurements, as the specimen was appreciably different from those studied previously, but the comparison with results obtained by quite different methods shows that the interpretation of the fine structure as suggested here does lead to reasonable results.

5. The configuration of the fine structure

The form of the fine structure can be shown to be given by

$$I(h)=\{\sum_m m^{\frac{1}{2}}\cos 2\pi(mh-\tfrac{1}{8})\}^2/\{\sum_m m^{\frac{1}{2}}\}^2 \qquad (1)$$

which is a slight simplification of equation (9) of Whittaker (1954). Here h is the order of reflection from the radial spacing (a') treated as a continuous variable and

$$m=r_j/a'$$

where r_j is the radius of the jth layer.

Successive values of m always differ by unity, so that if $m=p+x$ where p is the nearest integer to m, (1) becomes

$$I(h)=\{\sum_p (p+x)^{\frac{1}{2}}\cos 2\pi(ph+hx-\tfrac{1}{8})\}^2/\{\sum_p (p+x)^{\frac{1}{2}}\}^2\,. \qquad (2)$$

This form of the expression permits one to derive

by inspection the configuration of the fine structure in terms of the types A, B, C, D of Fig. 1 as a function of the value of $(hx-\frac{1}{8})$ at integral values of h. If $(hx-\frac{1}{8})$ is zero at any particular integral value of h then that reflection will be of type B since every term in (2) will have a maximum at the centre of the reflection. Similarly if $(hx-\frac{1}{8})=\frac{1}{4}$ the reflection will be of type D since every term will be zero at this point. The A and C types will occur at $-\frac{1}{8}$ and $+\frac{1}{8}$ respectively. Because the summation in (2) is squared the same configurations A, B, C, D will also occur when $(hx-\frac{1}{8})=\frac{3}{8}, \frac{1}{2}, \frac{5}{8}$ (or $-\frac{3}{8}$), and $\frac{3}{4}$ (or $-\frac{1}{4}$) respectively.

There is of course no reason to suppose that x need be restricted to integral multiples of $\frac{1}{8}$, but the four reflection types of Fig. 1 provide a simple way of classifying observed configurations and one which is as precise as is practicable in absence of intensity measurements. One can assign the configuration to be expected for any particular values of h and x to that one of these four types to which it most nearly approximates.

If the chrysotile structure consists of perfectly circular coaxial cylindrical layers each containing an integral number of unit cells in its circumference, then it follows from the values of a' and b that x can take only the values 0, 0·2, 0·4, 0·6 and 0·8. These give rise to the following spot configurations in the first two orders:

x	0	0·2	0·4	0·6	0·8
$h=1$	A	C	D	B	$C(D)$
$h=2$	A	D	$C(D)$	C	B

where $C(D)$ indicates a configuration which is only slightly nearer to C than to D.

If the fibrils have a helical lattice (Whittaker, 1955*b*) then the layers might be perfectly circular with half integral numbers of unit cells in their circumference, and in this case x could take the values 0·1, 0·3, 0·5, 0·7 and 0·9. However these values lead only to configurations included above, so that there are only five possible configurations AA, CD, $DC(D)$, BC and $C(D)B$, which can arise from perfectly circular cylindrical layers.

There were six pairs of configurations observed which could be classified fairly definitely as

$$BC,\ BD,\ CA \text{ (twice) and } DD \text{ (twice)}$$

and four more in which the classification of the configuration was less certain, namely

$$B\ (B \text{ or } A),\ (B \text{ or } C)\ (D \text{ or } A),\ (C \text{ or } D)\ (C \text{ or } D) \text{ and } D\ (D \text{ or } C).$$

Thus of the ten observed pairs of configurations only one is certainly in accordance with the supposition that the layers are perfectly circular and contain integral or half integral numbers of unit cells in their circumferences. This supposition must therefore be regarded as very improbable.

Possible alternative structures are as follows:

1. *Spiral cylindrical layers.* It has been shown by optical diffraction that the transform of such a structure consists of a $2nh$-fold spiral in the hth order of diffraction, if the spiral structure is n-fold. Thus the configuration of a first-order diffraction maximum from such a structure would be entirely random and would depend on the orientation of the starting points of the spiral layers with respect to the incident electron beam.

2. *Distorted integral (or half integral) closed cylindrical layers.* If the layers, although closed and integral, are not perfectly circular it may be deduced from Fourier-transform theory that the circular ring in the transform which corresponds to the 1st order diffraction maximum will contain a fine structure whose shape will be reciprocal to that of the cross-section of the layers (with further modification if their shape is not centro-symmetrical). The observed configuration of the first order would again be entirely random and dependent on the orientation of the deformation directions with respect to the electron beam. Departure from circularity of less than 1% would be sufficient to upset completely the expected configuration from the perfect circular form. Such distortions are very probable. They might arise from stress during growth, or from incipient polygonization, and they might be either elliptical, regularly polygonal, or irregular in form.

3. *Non-integral circular cylindrical layers.* This is a possibility if the layers contain dislocations or other imperfections. However the stresses associated with such imperfections would probably introduce deformations leading to (2) above.

Even though these alternative structures would eliminate all restrictions on the configuration of the 1st order diffraction maximum, not all pairs of configurations would even then be possible for the first two orders. AC, BA, CC and DA are always forbidden. It may be noted that none of these forbidden pairs was certainly observed.

The distinction between the above three possible types of structure cannot be made on the basis of the present results. It could be made in principle from a succession of diffraction patterns of a single fibril taken at a series of orientations about its own axis. The configurations from a spiral structure (1) would then change continuously in one direction or the other through the cycle $ABCDA\ldots$, whereas those from (2) would change in this way over a limited range and then reverse, and (3) would not vary. The practical difficulties of making such a distinction would, however, be very great.

6. Concluding remarks

The fine structure of the reflections which has been observed departs from theory in one respect, in that the configuration of corresponding spots on opposite

sides of the origin is not in general the same. No explanation is offered for this lack of centro-symmetry in the diffraction pattern. It presumably belongs to the same class of phenomena as that which often leads to a gross lack of such symmetry in intensity in electron-diffraction patterns, and even, as in the present instance, of complete suppression of a layer line at one side of the origin.

Since the observation of the fine structure in the present work, a review of earlier electron-diffraction photographs has revealed traces of the same phenomenon on some of them, but to a much less marked degree. In some cases it may be deduced from the heights of the spots perpendicular to the layer lines that the resolution was not sufficient to resolve such a fine structure, but this is certainly not always true, and it seems probable that the fine structure does not usually appear even when the resolution is high enough.

If the structure were spiral this would be explained if the edges of the spiral layers were not parallel to the fibril axis, and if the structure were of the distorted circular type if the distortions were twisted along the length of the fibril.

One possible special case of the fine structure is worth noting. A reflection of configuration *B* from a fibril with a very small central hole would consist of a single sharp spot, flanked by two very weak spots which might either be missed or mistaken for subsidiary Laue maxima. In either case, if the sharpness of the central spot were taken to be due to the wall thickness of the fibril this parameter would be overestimated by a factor of about two.

Thanks are due to the Directors of Ferodo Ltd., for permission to publish this paper.

References

JAGODZINSKI, H. (1961). *Z. Elektrochem.* **65**, 313.
WHITTAKER, E. J. W. (1954). *Acta Cryst.* **7**, 827.
WHITTAKER, E. J. W. (1955*a*). *Acta Cryst.* **8**, 265.
WHITTAKER, E. J. W. (1955*b*). *Acta Cryst.* **8**, 571.
WHITTAKER, E. J. W. (1957). *Acta Cryst.* **10**, 149.

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Diffraction by Face-Centered Cubic Crystals Containing Extrinsic Stacking Faults

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The diffraction pattern of a face-centered cubic crystal containing an arbitrary density of extrinsic faults is derived. The derivation is subject to the restriction that the crystal be infinite with infinitely extended faults distributed at random on one set of parallel close-packed planes.

Although both extrinsic and intrinsic stacking faults shift and broaden the same Bragg reflections, there are marked differences in behavior which make them readily distinguishable. The peak shift produced by a low density of extrinsic faults is in a direction opposite to the shift produced by intrinsic faulting. At higher extrinsic fault densities the shifted reflections show two peaks: a new peak arises near the hexagonal position, moving to the twin position as the density of faulting approaches unity. The broadening is asymmetric at all fault densities.

Introduction

A face-centered cubic crystal, considered as a layer structure produced by the appropriate stacking of close-packed (111) planes, can contain three essentially different types of stacking error (Read, 1953):

(1) Intrinsic fault, corresponding to the removal of a close-packed plane from the perfect crystal.
(2) Extrinsic fault, corresponding to the insertion of an extra close-packed plane into the perfect crystal.
(3) Twin (growth) fault, located at the interface between two perfect crystallites which are in twin relation.

The stacking patterns of these faults are shown in Fig. 1 in the usual *A*, *B*, *C* notation.

Although the presence of intrinsic stacking faults

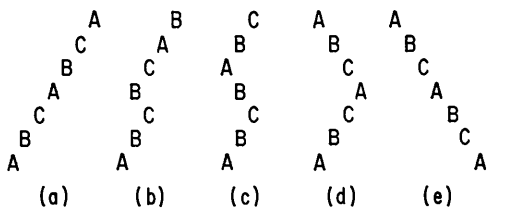

Fig. 1. Stacking sequences for: (*a*) Perfect crystal; (*b*) Intrinsic fault; (*c*) extrinsic fault; (*d*) twin fault; and (*e*) twin crystal.