

ing bands obtained by Taylor's method. These diagrams indicate that for the reflexion 530, condition (2) above is approximately obeyed and a narrow band is obtained, but for 220 the band is wide and not very useful in restricting the possible position of the molecular centre. The curves of Figs. 2(a) and 2(b) however are much more useful in limiting the possible positions since the molecular centre must lie at one of the intersections of the sets of curves for 220 and 530, and by adding further reflexions all but one were eliminated. This procedure was simplified considerably in this case by using the reflexions 400 and 020 which have small observed structure factors, give only a few *straight lines*, and so restrict the possible positions very greatly.

When the position of the molecular centre had been determined approximately, allowance was made for the small observed values of the structure factors, and narrow bands were drawn with boundaries corresponding to the reasonable maximum and minimum values of the structure factors (for both positive and negative signs), allowing quite a large variation in possible scale factor. For example:

	$F_{\text{relative}}$	$F_{\text{max.}}$	$F_{\text{min.}}$	$F_{\text{Final}}$ $F_{\text{obs.}}$
220	1.71	2	5	3.5
530	1.07	1	3	2.2
400	2.54	3	7	5.3
020	1.96	2	6	4.1

The position giving best agreement for the planes was obtained, giving for the coordinates of the molecular centre  $X = -1.602 \text{ \AA}$ ,  $Y = +0.599 \text{ \AA}$ . Structure factors were calculated for all the  $hk0$  reflexions and

the value of  $R$ , the usual discrepancy factor, was 27%. After refinement the mean centre of the benzene ring was at  $X = -1.600 \text{ \AA}$ ,  $Y = +0.601 \text{ \AA}$ , so that the value determined initially was quite accurate.

### Further extensions

The method is not of course confined to plane group  $pgg$ , but can be applied to any plane group, centrosymmetric or non-centrosymmetric, by writing the structure factor expression for a given plane with the coordinates of the  $j$ th atom as  $(x_j + X, y_j + Y)$ , expanding as a trigonometric function of  $X$  and  $Y$ , and evaluating the function over the unit cell. The curves of  $F = F_{\text{obs.}}$  are then the loci of possible positions of the molecular centre. The method could also be used in three dimensions, but three-dimensional methods are generally used for molecules which are too complex for the shape and orientation to be easily determined. Since the shape and orientation must be deduced initially, the method is of course limited to relatively simple molecules.

The procedure described by Taylor & Morley (1959) is a further extension of the method given here, and it presents the data for all the reflexions very conveniently on one contour map.

### References

- TAYLOR, C. A. (1954). *Acta Cryst.* **7**, 757.  
 TAYLOR, C. A. & MORLEY, K. A. (1959). *Acta Cryst.* **12**, 101.  
 TROTTER, J. (1959). *Acta Cryst.* **12**, 173.

*Acta Cryst.* (1959). **12**, 341

## Interpretation of Some $\gamma$ -MnO<sub>2</sub> Diffraction Patterns

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The analysis of three line-rich  $\gamma$ -MnO<sub>2</sub> patterns leads to the conclusion that the position of the sharper lines is in perfect accordance with a ramsdellite-type lattice. Certain broad lines, however, are shifted away from the positions consistent with the sharper lines in the same pattern.

Both the anomalous broadening and the shift are satisfactorily accounted for by a structure model consisting of randomly alternating layers of two kinds, derived from the known structures of ramsdellite and pyrolusite, respectively. It appears that each pattern can be characterized by one parameter  $p$ , the 'pyrolusite concentration', in addition to the apparent unit-cell and crystallite dimensions as derived from the sharper lines. However, the simplified theoretical treatment used here holds for small  $p$  only, corresponding to line-rich patterns. It is suggested that an exact treatment might be able to explain poor types of  $\gamma$ -MnO<sub>2</sub> patterns as well.

### 1. Introduction

Gamma-MnO<sub>2</sub> is at present used (Brenet (1956)) as a collective name for a series of phases, characterized

mainly by their diffraction pattern. The poorest patterns consist of a strong diffuse background with some lines (Fig. 1C), the greater part of which happen

to match certain lines of pyrolusite, or  $\beta$ -MnO<sub>2</sub> (Fig. 1 *A*). The most line-rich patterns, on the contrary, show a striking resemblance with the pattern of a rare MnO<sub>2</sub>-mineral called ramsdellite. This situation is bound to cause—and has indeed caused—some confusion in the nomenclature of different types. Indeed the mere need for a systematic classification of  $\gamma$ -MnO<sub>2</sub> varieties would be sufficient to justify a study of the structure of this product.

The present analysis originated from a comparison of three patterns of the line-rich type called  $\gamma^{\text{II}}$ -MnO<sub>2</sub> by Cole *et al.* (1947), to whom we refer for a review of the earlier literature on the subject. One pattern, remarkable for its purity, is described by values of  $d$  and of  $q = 10^4/d^2$  in Table 1. This we shall designate as pattern *D*, the other two—which contain weak lines of  $\alpha$ -MnO<sub>2</sub>—being termed *E* and *F*.

## 2. The 'sharp lines'

Upon comparing the three patterns (Fig. 1 *D-E-F* and *D'-E'-F'*) it is observed that they contain many comparatively sharp lines in almost identical positions. Certain broad lines (notably Nos. 1, 2, 9 and 12), however, show considerable differences in position.

It was found that the first group of lines, which we shall call the 'sharp lines', have observed  $q$ -values,  $q_o$ , which agree very well with a quadratic form  $q_c = 505h^2 + 115\frac{1}{2}k^2 + 1231l^2$  (for *D*), corresponding to an orthorhombic unit cell with  $a = 4.450$ ,  $b = 9.305$ ,  $c = 2.850$  Å. The unbiased unit-cell determination led to an *A*-centered cell with half the above length for  $b$ ,  $a$  and  $c$  being the same. For reasons to be given later, we choose the above unit cell, which is very similar to that of ramsdellite. Accordingly, the sharp lines all have  $l + \frac{1}{2}k$  even.

This result is further confirmed by the fact that, between *D*, *E* and *F*, small but significant differences in the positions of these sharp lines were accurately accounted for by suitable changes in the axes:

	$a$ (Å)	$b$ (Å)	$c$ (Å)	
<i>D</i>	4.450	9.305	2.850	
<i>E</i>	4.470	9.336	2.848	
<i>F</i>	4.489	9.391	2.848	
Ramsdellite	4.533	9.27	2.866	(Byström (1949))
Ramsdellite	4.46	9.32	2.850	(Kondrashev <i>et al.</i> (1951))

Actually the 'sharp lines' are not very sharp. There are marked differences in line width among them, which can be explained qualitatively by assuming platy crystallites || (100) with the longest dimension in the  $c$ -direction (500–1000 Å), a width of some 300 Å, and a thickness of around 150 Å. On the whole, however, these 'sharp lines' are much less broadened than the lines which we shall deal with in the next section.

Table 1. Observed\* values of  $d$  and  $q = 10^4/d^2$  for pattern *D*; calculated  $q = q_c$  for indices  $hkl$ ; observed ( $q_o - q_c$ ) and calculated ( $\Delta q$ ) shifts

Note that an error of  $\pm 0.1$  mm. on the film or  $\pm 1/40^\circ$  in  $\theta$  corresponds to an error in  $q$  of  $\pm 0.10/q$  for lines Nos. 1–13 (Fe  $K\alpha$ ), and  $\pm 0.25/q$  for the remaining lines (Mo  $K\alpha$ )

Line No.	$d_o$	$q_o$	$q_c$	$hkl$	$q_o - q_c$	$\Delta q$ , theory (shift = $b^*/7$ )
1	3.93	645	620	110	25	35
2	2.624	1452	1545	130	-93	-97
3	2.430	1694	1693	021	1	0
4	2.346	1817	1851	111	-34	-31
5	2.328	1846	1848	040	-2	0
6	2.225	2020	2020	200	0	0
7	2.133	2197	2198	121	1	0
8	2.064	2348	2353	140	-5	0
9	1.863	2880	2776	131	104	102
10	1.642	3710	3713	221	-3	0
11	1.609	3864	3868	240	-4	0
12	1.497	4462	4614	151	-152	-163
13	1.426	4918	4924	002	-6	0
14	1.361	5395	5391	061	4	0
15	1.341	5558	5544	112	14	35
16	1.303	5888	5896	161	-8	0
17	1.252	6380	5891	122	-3	0
18	1.214	6780	6469	132	-89	-97
19	1.199	6956	6672	042	8	0
20	1.161	7415	6944	202	12	0
21	1.066	8795	7400	261	15	0
			8792	242	3	0

\* The lines were measured from photometer records of the films reproduced in Fig. 1. Thereby an accuracy of the order of  $\pm 0.1$  mm. was achieved even for very broad lines, as well as for the incompletely resolved doublet (nos. 4–5).

## 3. The 'broad lines'

At first sight the remaining lines ('broad lines') seem to match strong ramsdellite lines with  $k = \text{odd}$  (cf. *X-Ray Powder Data*, 1957). Such an assignment was made for (110), (131) and (151) by Byström (1949).\* (Our line Nos. 1, 9 and 12). In Table 1, these tentative indices as well as those for Nos. 2, 4, 15 and 17 are listed in italics.

For all these lines the discrepancy  $q_o - q_c$  is very much larger than the possible error of measurement. Moreover, samples *E* and *F* yielded quite different values of  $q_o - q_c$  (smaller, but still significant).

Now abnormal shifting and broadening of diffraction lines are known to occur for certain types of random layer structures (Hendricks & Teller, 1942). In view of the similarities mentioned in the introduction, which have been noted by numerous authors, we therefore attempted to devise a structure model which could be considered as a random stacking of ramsdellite and pyrolusite layers.

## 4. Random layer model

Both ramsdellite and pyrolusite contain well-defined

\* Byström's 'very weak' line (120) does not appear on our patterns. Its  $\sin^2 \theta$ -value of 0.13 for Cr  $K\alpha$ , however, points to the strongest line of pyrolusite ( $d = 3.11$  Å), which is also mentioned as an impurity by Cole *et al.* (1947).

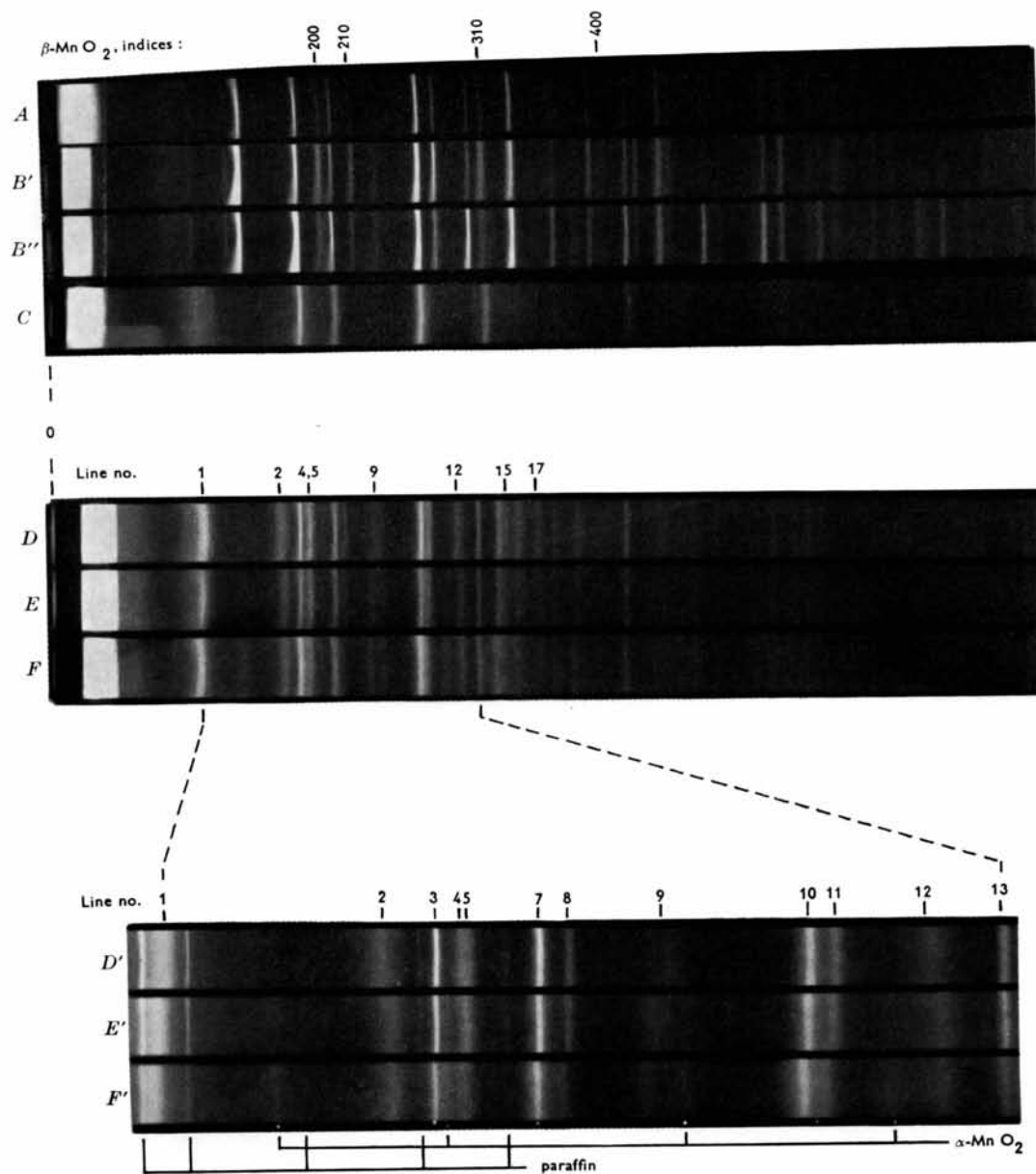


Fig. 1. Samples:

- A: artificial pyrolusite.
  - B: mineral pyrolusite. The paste obtained by mixing with vaseline was smoothed out vertically (*B'*) and horizontally (*B''*).
  - C:  $\gamma$ -MnO<sub>2</sub>, made electrolytically.
  - D, E, F:  $\gamma$ -MnO<sub>2</sub>, mode of preparation unknown.
- Exposures taken with a fourfold camera of the Guinier focusing type,  $\varphi = 114.6$  mm.

Radiation:  
 A-F: Mo  $K\alpha$ , monochromatized by (202) quartz reflection;  
 0.1 mm. Al before film, 40 kV., 26 mA., 5 hr.  
 D', E', F': Fe  $K\alpha$ , (101) quartz reflection, 40 kV., 9 mA.,  
 4 hr.  
 Film: Ilfex.

structural units. For pyrolusite the unit is an infinite chain of  $MnO_6$ -octahedra, each octahedron sharing two opposite edges with its neighbours, while neighbouring chains merely share corners.

In ramsdellite the structure determination by Byström (1949) shows the presence of units consisting of two such chains, each octahedron sharing two edges with those of the other chain. Again neighbouring units share corners. These units will be termed double chains.

The chains run in the  $c$ -direction for both minerals. Viewed in this direction, the outline of the units is a rhomb for the single chain, and roughly a parallelogram for the double chain, as indicated by dashed lines in Fig. 2(a). The left part of that figure shows schematically a portion of the ramsdellite structure, one unit cell being drawn in. To the right thereof, single chains have been introduced in what we think is a plausible way to obtain a 'pyrolusite layer' in a ramsdellite matrix. This layer is seen to be parallel to (010). Correspondingly, we may define layers of double chains, four of which are indicated in Fig. 2. Layers of both single and double chains occur in two orientations related by a screw-axis.

The obvious model for gamma- $MnO_2$ , then, is a random succession of layers of single and double chains, with the condition that the orientation of each layer must be opposite to that of its neighbours. If in this model  $p$  is the probability for an arbitrary unit to be a single chain, then  $p = 0$  for ramsdellite and  $p = 1$  for pyrolusite.

Now a rigorous treatment of this model involving correlation with first neighbours, is rather cumbersome. An approximate simplified treatment suggests itself by looking at Fig. 2(a).

We can see that the disturbance in the ramsdellite lattice caused by one layer of single chains can be described as a local shortening of the  $\mathbf{b}$ -translation to  $\frac{3}{4}$  of its normal value. The side view (Fig. 2(b)) shows that  $\mathbf{b}'$  also differs from the ramsdellite  $\mathbf{b}$ -axis in having a transverse component:

$$\mathbf{b}' = \frac{3}{4}\mathbf{b} + \frac{1}{2}\mathbf{c}. \quad (1)$$

This interpretation fails if two or more layers of single chains occur in succession. So we must expect the result to be valid only for small 'pyrolusite concentrations'.

The ensuing simplified model has a defect lattice, in which only  $\mathbf{a}$  and  $\mathbf{c}$  are true translations, whereas  $\mathbf{b}$  is replaced by  $\mathbf{b}'$  at arbitrary places in the succession of (010)-planes. Obviously in these places there is not only an abnormal phase shift, but an abnormal layer form factor as well. We shall disregard the latter, which may be expected to have little influence on the peak positions.

### 5. Predicted and observed shifts

We have now reduced our model to an almost trivial case: layers of constant form factor separated by two

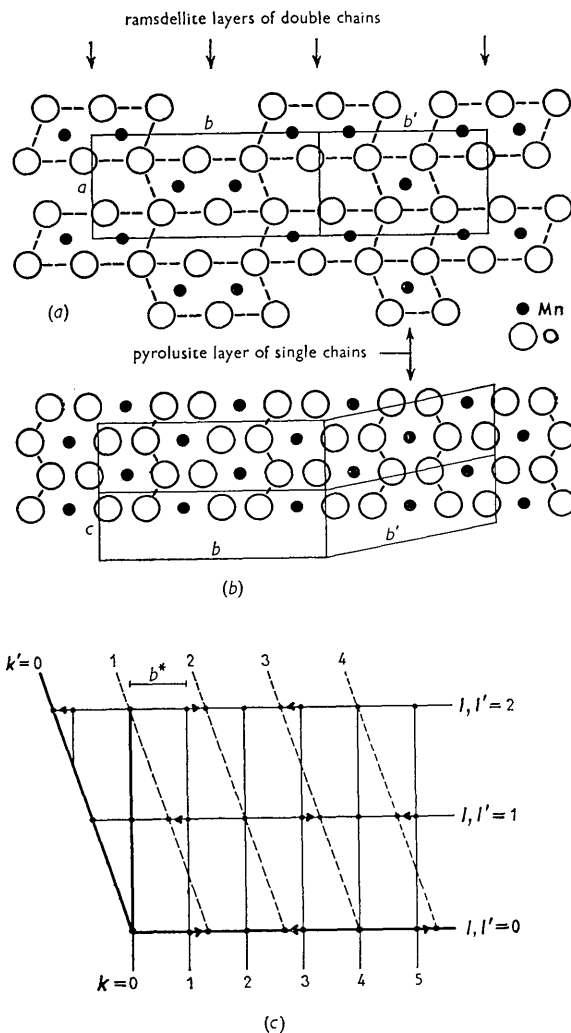


Fig. 2. (a) Schematic drawing of part of the proposed random layer model for  $\gamma$ - $MnO_2$ , viewed along  $c$ . (b) Same, viewed along  $a$ . (c) Section  $h = \text{constant}$  of the reciprocal lattice of this model. Lines with  $k = \text{odd}$  are shifted in the direction of the arrows.

translation vectors  $\mathbf{b}$  and  $\mathbf{b}'$  in random succession. The diffraction phenomena for this case have been stated very clearly by Méring (1949), to whom we refer for a simple derivation of what follows.

First the reciprocal lattices for ramsdellite ( $a^*b^*c^*$ ) and for a 100% fault lattice ( $a^*b'^*c^*$ ) are drawn in the same reciprocal space. Since both sets of (100) lattice planes are parallel and have the same spacing, all sections  $h = h' = \text{constant}$  are geometrically identical. Such a section is shown in Fig. 2(c). The relations between  $hkl$  and  $h'k'l'$ -coordinates are found from (1):

$$h' = h, \quad k' = \frac{3}{4}k + \frac{1}{2}l, \quad l' = l \quad (2)$$

Upon introducing the  $\mathbf{b}'$  stacking faults in ramsdellite, one finds theoretically that the sharp intensity

Table 2. *Pyrolusite concentration p, width of lines with k odd (both calculated from the observed shift of these lines) and observed width for patterns D, E and F*

Pattern	Shift	Pyr. conc. <i>p</i>	Theory, from <i>p</i>	Line width in units of <i>b</i> *			
				Observed for lines No.			
				1	2	9	12
<i>D</i>	0.14 <i>b</i> *	0.25	0.19	0.50	0.20	0.34	0.18
<i>E</i>	0.05 <i>b</i> *	0.12	0.09	—	—	—	—
<i>F</i>	0.03 <i>b</i> *	0.08	0.06	—	—	—	—

peaks at the points (*hkl*) are shifted in the direction of the *k*-axis towards the nearest neighbouring (*h'k'l'*)-point. Simultaneously the peak is broadened, again in the direction of the *k*-axis. Both shift and broadening increase with increasing concentration (if < 50%) of faults.

For certain points (*hkl*) there will be neither shift nor broadening because they coincide with a (*h'k'l'*)-point. It follows from (2) that these are the points with  $l + \frac{1}{2}k$  even, in complete accordance with the very satisfactory agreement between  $q_o$  and  $q_c$  for the 'sharp lines' whose indices obey precisely this relation (cf. section 2).

Certain other points, namely those with  $l + \frac{1}{2}k$  odd, are situated midway between two points (*h'k'l'*). For such points, too, there should be no shift, but the theory predicts that they broaden and fade away rapidly with increasing pyrolusite concentration. No unambiguously indexed line of this category occurs in our patterns, whereas some do occur for ramsdellite.

The remaining points, for which *k* is odd, all have an unmistakable neighbour at a distance of  $\frac{1}{2}b^*$  in the *k*-direction. The sign of  $q_o - q_c$  in Table 1 is found to agree completely with a shift towards this neighbour for each of the 'broad lines', which indeed have odd *k*-indices.

Furthermore, if variations in continuous factors can be neglected, all these shifts should be equal (when measured in reciprocal space) because the distance to the (*h'k'l'*)-neighbour is the same. It is found that for pattern *D* a shift of  $\frac{1}{2}b^*$  gives a fair agreement between calculated ( $\Delta q$ ) and observed ( $q_o - q_c$ ) discrepancies for the 'broad lines', cf. Table 1. For patterns *E* and *F* the observed shifts are only about 0.05 and 0.03*b*\*, respectively. The agreement with calculated discrepancies for *E* and *F* is again fair. This gives additional support not only to our model, but also to the indices (*hkl*) assigned tentatively to the broad lines.

## 6. Pyrolusite concentration and line width

The average frequency of occurrence of *b'* translations is twice the pyrolusite concentration *p* as defined in section 4, since *b* stands for two double chains and *b'* for a double chain plus a single chain. This quantity is related to the shift  $rb^*$  (as measured in reciprocal space) of reflections with *k* odd by the condition that Mering's  $|1 - Q|$ , or in our case

$$|1 - (1 - 2p) \exp \{2\pi i(1 + r)\} - 2p \exp \{\frac{3}{2}\pi i(1 + r)\}|$$

is a minimum with respect to variations in *r*. Here again we neglect variations of continuous factors. Also the total number of layers is taken as infinite. To a good approximation the extreme values of the above expression correspond to the real values of *Q* given by

$$(1 - 2p) \sin r.2\pi - 2p \cos r. \frac{3}{2}\pi = 0.$$

The values of *p* thus calculated are shown in Table 2.

Even for pattern *D*, this result can be regarded as tolerably consistent with the condition  $p \ll 1$ , on which the validity of the simplified structure model depends.

In our case the line width of shifted lines theoretically depends only on *p*, provided that it is measured in reciprocal space and in the direction of the *k*-axis. The intensity falls to its half-maximum value at those points for which  $|1 - Q|$  is  $\sqrt{2}$  times its minimum value (again taking *r* as a variable). The ensuing value of the theoretical width at half height has been found graphically, and the results are stated in Table 2, together with those obtained from measured widths of four sufficiently isolated 'broad lines'. Considering that there is a substantial contribution to the observed broadening from the finite size of the crystallites (cf. section 2), especially for line No. 1, the agreement for *D* does not seem to be worse than could be expected. For patterns *E* and *F* the latter contribution is predominant, so that no significant comparison with theory can be made.

## 7. Discussion

It appears from sections 5 and 6 that the simplified structure model accounts fairly well for the observed diffraction effects, only one parameter (*p*) being adjusted to each pattern.

This agreement does not, of course, yield a rigorous proof of the adequacy of the model. The fact that it holds for three different patterns is a strong argument in favour of it. Even so, it is only the simplified model (randomly alternating translations *b* and *b'*) which is thus made plausible; the validity of the original model (with randomly alternating layers of double and single chains) depends merely on the fact that it seems difficult to arrive in a different way at the simplified model.

There is one argument which appears to prove that

the simplified model is indeed only an approximation. If it were exact, larger pyrolusite concentrations  $p$  than that of pattern  $D$  ( $p = 0.25$ ) would yield patterns converging to that of an  $ab'c$ -lattice (for which  $p = 0.50$ ), with the shifted lines gradually sharpening to normal powder lines. Now the continuous series of  $\gamma$ - $\text{MnO}_2$  patterns, which is generally supposed to exist, does nothing of the sort. Instead it shows an increasing deterioration, down to stages such as Fig. 1  $C$ . According to Delano (1950), a further continuous series exists between that stage and pyrolusite.

By heat treatment of  $\gamma$ - $\text{MnO}_2$ , Brenet *et al.* (1957) have indeed obtained a continuous transition from a pattern not unlike our Fig. 1  $D$ , to something close to the pyrolusite pattern. Comparison of the latter stages in this series with pure pyrolusite again shows anomalous shift and broadening of certain lines. Rather than attaching specific significance to one of those (as Brenet *et al.* (1957) do to (110),  $d = 3.11 \text{ \AA}$ ), we find that these phenomena are in qualitative agreement with another simplification of our model, valid for  $p$  near unity (viz., pyrolusite with  $b'$  stacking faults, corresponding to isolated ramsdellite layers).\*

Recently, an explanation in terms of atomic parameters has been given by Kedesdy *et al.* (1957) for the relation between  $\gamma$ - $\text{MnO}_2$  and ramsdellite. However, this hypothesis cannot possibly account for the anomalous diffraction phenomena shown by  $\gamma$ - $\text{MnO}_2$ .

\* In this connection a curious detail of many pyrolusite patterns may be mentioned. Fig. 1  $A$ , a pattern of a synthetic sample obtained by treating  $\gamma$ - $\text{MnO}_2$  at  $160^\circ$  with concentrated  $\text{HNO}_3$ , is shown here to represent a pure, well-crystallized  $\beta$ - $\text{MnO}_2$ . Fig. 1  $B$  is a pattern of a mineral sample with preferred orientation, the  $(hk0)$  reflections being enhanced on  $B'$  and suppressed on  $B''$ . Since  $B'$  was obtained by vertical, and  $B''$  by horizontal flow of the specimen paste, this sample obviously has the fibrous habitus mentioned by Vaux & Bennet (1937).

The broadening shown by several lines in Fig. 1  $B$  (notably (200), (210), (310) and (400)) cannot, however, be explained as particle-size broadening. The latter would make (400) hardly broader than (200), whereas it is actually twice as

Probably a similar argument holds for their interpretation of what they call  $\rho$ - $\text{MnO}_2$ , since neither the definition of that phase nor the reasons for distinguishing it from  $\gamma$ - $\text{MnO}_2$  have been made clear.

Finally, the author wishes to express his gratitude to Prof. Brenet (Institut de Chimie, Université de Strasbourg, France) for providing helpful samples and documentation; to Mrs van Damme-van Weele (Central Lab. T.N.O., Delft) for stimulating discussions; and to the Governing Board of the T.P.D. for their permission to publish.

### References

- BRENET, J. (1956). *Rev. Gen. de l'Electricité*, **65**, 61.  
 BRENET, J., GABANO, J. P. & SEIGNEURIN, M. (1957). *C. R. du 16<sup>e</sup> Congres Int. de Chimie Pure & Appl.*, **70**.  
 BYSTRÖM, A. M. (1949). *Acta Chem. Scand.* **3**, 163.  
 COLE, W. F., WADSLEY, A. D. & WALKLEY, A. (1947). *Trans. Electrochem. Soc.* **92**, 133.  
 DELANO, P. H. (1950). *Industr. Engng. Chem.* **42**, 523.  
 HENDRICKS, S. B. & TELLER, E. (1942). *J. Chem. Phys.* **10**, 147.  
 KEDESZY, H., KATZ, G. & LEVIN, S. B. (1957). *Acta Cryst.* **10**, 780.  
 KONDRASHEV, JU. D. & ZASLAVSKIJ, A. I. (1951). *Izv. Akad. Nauk SSSR., Ser. Fiz.*, **15**, 179.  
 MERING, J. (1949). *Acta Cryst.* **2**, 371.  
 STRUNZ, H. (1943). *Naturwiss.* **78**, 89.  
 VAUX, G. & BENNETT, H. (1937). *Min. Mag.* **24**, 521.  
*X-Ray Powder Data Card File* (1957). Card 7-222.

broad. It turns out that the line width is equal to the distance between doublet components which would be obtained from an orthorhombic lattice slightly departing from the alleged tetragonal lattice of pyrolusite. Indeed the broadened lines have the profile of a hardly resolved doublet.

Such patterns do not fit in the series found by Brenet *et al.* (1957), nor can they be interpreted in terms of the above model for  $\gamma$ - $\text{MnO}_2$ . On the other hand, they appear to shed new light on the much-debated existence of an orthorhombic, pseudo-tetragonal form of pyrolusite (Vaux & Bennett (1937); Strunz (1943)).

## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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**Group velocity and energy (or particle) flow density of waves in a periodic medium.** By E. H. WAGNER, *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin-Dahlem, Germany*

(Received 16 December 1958)

For the propagation of electromagnetic waves (X-rays or light) in crystals, the direction of the averaged Poynting vector is normal to the surface of dispersion in the

point representing the wave field. This has been pointed out by N. Kato (1958) recently, and the same relation holds for the current density vector of electron waves.