Oriented transformations in the system MnO–O–H₂O

By Lesley S. Dent Glasser and Ian B. Smith[1]

Department of Chemistry, University of Aberdeen

[Taken as read 7 November 1968]

Summary. Extensive studies on oriented reactions in the system MnO–O–H₂O have revealed surprising symmetry changes, which we have been unable to explain. Orientation relationships are often complicated, but where interpretation is possible, the results support the idea that orientations are controlled by the oxygen framework and that considerable migration of manganese occurs.

PREVIOUS studies on reactions in the system MnO–O–H₂O have shown that many of them proceed in an oriented fashion (Faulring, Zwicker, and Forgeng, 1960; Dasgupta, 1965; Dent Glasser and Smith, 1965; and many publications by Feitknecht and co-workers, summarized by Feitknecht, 1965); that is to say, a single crystal of the starting material reacts to form one or more single crystals of product. Such studies can yield valuable information about the mechanism of the reactions concerned. With this end in view, the present work extended the single-crystal studies to reactions not previously investigated by this method. The hope of formulating mechanisms was largely unrealized, but it seems nevertheless worthwhile to report the observations that were made. Fig. 1 summarizes some of the reactions that have been studied in this system. Results on the series groutite–ramsdellite–pyrolusite have been reported earlier (Dent Glasser and Smith, 1965). Results on the series manganite–pyrolusite–bixbyite reported by Dasgupta (1965) have been confirmed and extended in the present work.

The results can be conveniently considered under three main headings: pyrolusite–manganite–hausmannite, pyrolusite–bixbyite–hausmannite, and pyrolusite–manganosite.

Starting materials. We obtained specimens of naturally occurring manganese oxides and oxyhydroxides from many people, to all of whom we are very grateful. In the following list, where no other source is acknowledged, samples were supplied by the Department of Geology

[1] Present address: National Research Council, Atlantic Regional Laboratory, Halifax, Nova Scotia.

and Mineralogy, Aberdeen University, and sample numbers refer to their collections. Crystallographic data are given in table I.

Pyrolusite (β-MnO$_2$). Unless otherwise indicated, the studies used a sample from Ilmenau, Thuringia (G. 1544). Occasional runs were also made using a sample from Hungary, precise locality unknown (G. 1542),
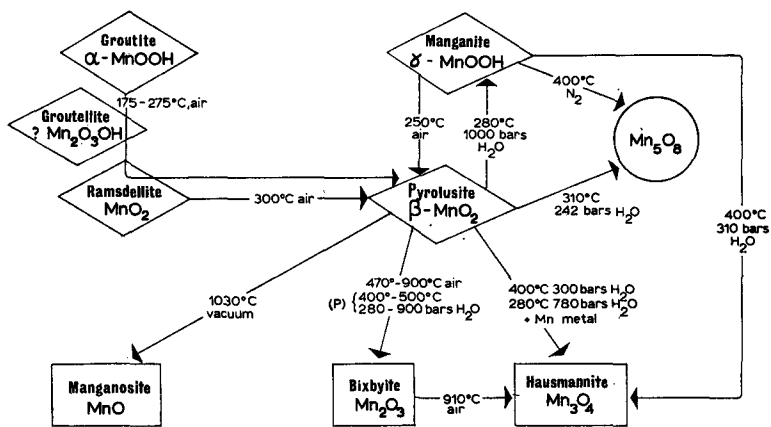

FIG. 1. Reactions in the systems MnO–O–H$_2$O. Rectangles indicate structures based on cubic close packing; diamonds those based on hexagonal close packing; circle, close packed in two dimensions only. P indicates reactions studied by X-ray powder methods only.

TABLE I

Mineral	Space group	a	b	c	β	Structure
Pyrolusite	P4$_2$/mnm	4·40 Å		2·88 Å		rutile
Manganite	B2$_1$d*	8·86	5·24 Å	5·70	90°	distorted rutile
Hausmannite	I4$_1$/amd	5·75		9·42		distorted spinel
Bixbyite	Ia3	9·37–9·40				c-type rare earth sesqui-oxide
Manganosite	Fm3m	4·44				sodium chloride

* Non-standard space group adopted by Buerger (Zeits. Krist., 1963, vol. 95, p. 163) to preserve pseudo-orthorhombic axes.

and using crystals of pyrolusite picked out from a bulk sample of ramsdellite from Lake Valley, Sierra Country, New Mexico, supplied by Dr. Howard T. Evans, Jr. of the United States Geological Survey.

Manganite (γ-MnOOH). The specimen used was from Laverock Braes, Grandholm, Aberdeen, Scotland (9041).

Hausmannite (Mn_3O_4). The specimen used was from Bigrigg, near Whitehaven, Cumberland, England (G. 1496).

Bixbyite (α-Mn_2O_3) from Catron City, New Mexico, supplied by Dr. Howard T. Evans, Jr., gave well-shaped cubes. Standard single-crystal X-ray photographs were taken about the [100] and [110] axes. Naturally occurring bixbyite contains iron, and its parameters therefore differ slightly from those of bixbyite prepared from pyrolusite.

Manganosite (MnO). A sample from Franklin Furnace, New Jersey, U.S.A., was supplied by Dr. Roy Philips, Geology Department, Durham University, England (sample number D. 52108).

Experimental methods

The principal method used for studying orientation relationships in single crystals was to try to adjust conditions so that the reaction studied did not proceed to completion. Photographs taken of the resultant pseudomorph (using oscillation, rotation, and Weissenberg techniques) show reflections from both starting material and products, and enable their relative orientations to be determined. Where this was not possible, relative orientations had to be determined from the outline of the pseudomorph, and it was not always possible to do this completely. For example, pyrolusite and manganite both occur as needles elongated parallel to *c*. Relative orientations along the needle axis could always be determined from morphology only, but in the plane perpendicular to the needle axis this was not usually possible.

The crystals were treated in various ways to produce reactions. For simple heat treatment standard furnaces were used. Heating experiments fell into two main categories: Rapid heating; the crystal was placed in a furnace, which was already at the required temperature. Slow heating; the crystal was placed in a cold furnace, which was then brought to the required temperature; the rates of heating varied between 3° and 8° C per minute. Crystals were also subjected to hydrothermal treatment. A single-crystal autoclave (Taylor, 1959), similar in principle to a Morey bomb, was used for some runs. When higher temperatures and pressures were needed, the crystals were wrapped in gold foil and placed in bombs of the 'cold-seal' type (Tuttle, 1949). When a reducing atmosphere was required, a little powdered manganese metal was placed in the bomb along with the foil-wrapped crystals.

Finally, runs were made heating crystals to temperatures in the range 850 to 1200° C under vacuum, pressures of 0·01–0·05 mm Hg being achieved.

Some supporting studies not using single crystals were also made, using standard techniques such as D.T.A. and T.G.A. The results of these served, in all cases, merely to confirm those in the literature.

The series pyrolusite–manganite–hausmannite

Single crystals of pyrolusite treated hydrothermally at 200 to 300° C and 1000 bars yielded mainly manganite. Addition of powdered manganese metal to runs at these temperatures and pressures produced hausmannite. At higher temperatures and somewhat lower pressures single crystals of pyrolusite could be converted directly to hausmannite without the presence of a reducing agent.

Transition temperatures and pressures determined in this way do not, of course, represent equilibrium values. In any case they should not be taken too seriously, for two reasons. Firstly, it is difficult to calculate water-vapour pressure accurately when using the single crystal autoclave, which has a very small volume. Secondly, the products from treatment of single crystals were found to be rather unpredictable and less reproducible than those from powders, so that the products from single crystals were sometimes different from those obtained by treating powdered samples under similar conditions.

In one run at 310° C and 242 bars for 26 hours a different product occurred along with hausmannite and some unchanged pyrolusite. This was identified with the phase Mn$_5$O$_8$ reported by Oswald, Feitknecht, and Wampetich (1965). The crystals were formed in oriented relationship to the original pyrolusite and were twinned. The axial lengths were similar to those reported for Mn$_5$O$_8$ (monoclinic, a, 10·347; b, 5·725; c, 4·852 Å; β, 109° 25'; $C2/m$ or $C2$) and the space group and intensities were also in agreement. The identity of the phase was confirmed by preparing Mn$_5$O$_8$ by topotactic decomposition of manganite at 400° C in nitrogen, a route mentioned by Oswald et $al.$, and comparing photographs of this preparation with those from the hydrothermal one.

This seems to be the same phase as that prepared by Dasgupta (1965) and also by Davis (1967) in an impure form by heating manganite in air at 340° C. Dasgupta (private communication to Davis) prepared the phase in nearly pure form by heating manganite in a neutral atmosphere. Davis found that the product was twinned and appeared to be monoclinic, a, 9·9; b, 5·73; c, 4·89 Å; β, 98°, $I2$, Im, or $I2/m$, and suggested that it might be a polymorph of Mn$_2$O$_3$. The conditions of its formation suggest that it may in fact be Mn$_5$O$_8$; the cell dimensions confirm this. Davis's cell and lattice type correspond to those of Oswald,

Feitknecht, and Wampetich, but with a different choice of axes (fig. 2). The orientation relationships observed by Davis also agree reasonably well with our observations. Further confirmation was obtained by comparison of our photographs with the extra reflections noted by Dasgupta (shown in Fig. 3 of his 1965 paper).
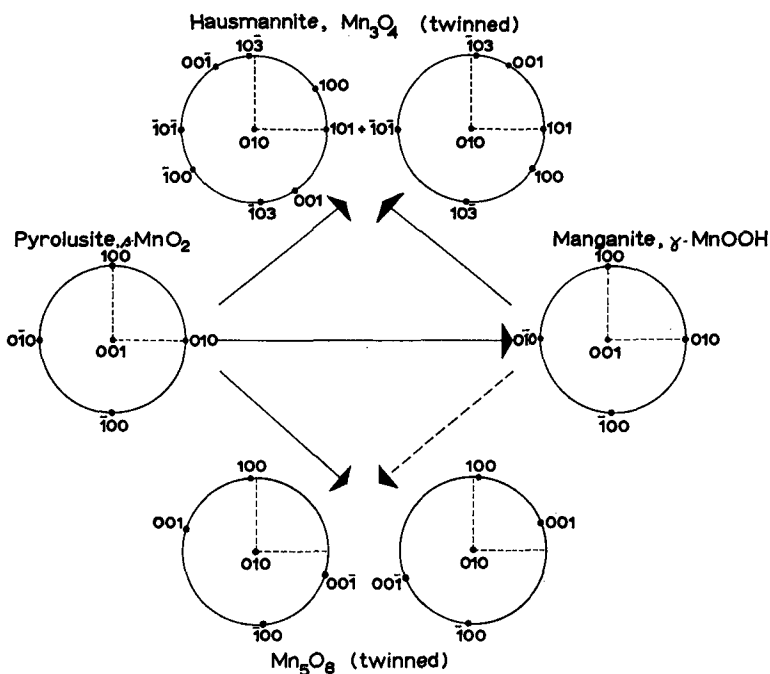

FIG. 2. Orientation relationships observed in the changes pyrolusite–manganite–hausmannite and pyrolusite–Mn_5O_8. The vertical and horizontal dotted lines provide reference directions on the stereograms. The dashed arrow represents a reaction for which the orientation relationships have not been fully determined.

Fig. 2 shows, as stereograms, the orientation relationships found for the changes pyrolusite–manganite–hausmannite and pyrolusite–Mn_5O_8. The relationship between pyrolusite and manganite is precisely the same as that found by Dasgupta (1965) for the conversion in the reverse direction. These changes are similar to the change groutite–ramsdellite discussed in an earlier paper (Dent Glasser and Smith, 1965). In the earlier paper, an extra phase was noted in the transformation and remained unexplained at that time. Subsequent studies showed that this phase corresponds both to the phase named groutellite by Klingsberg

and Roy (1959), which they believed to be intermediate in composition and structure between groutite and ramsdellite, and to the extra 'weak phase' noted by Fleischer, Richmond, and Evans (1962) in parallel orientation with ramsdellite. Table II shows data for groutellite from various sources, and compares the cell dimensions with those of groutite and ramsdellite. No corresponding intermediate phase was noted in the change pyrolusite–manganite.

TABLE II. Data on identity of groutellite and the 'weak phase'

	Crystal data			
a	b	c (Å)		References
4·58	10·76	2·89	Groutite	Collins and Lipscomb (1949). Acta Cryst. vol. 2, p. 104.
4·61	9·54	2·88	'Weak phase'	Fleischer, Richmond, and Evans, 1962.
4·68	9·54	2·87		Observed data on phase occurring in parallel orientation with ramsdellite, Gavilan Mine; present work.
4·68	9·54	2·87		Observed data on phase occurring on X-ray photographs of heated groutite single crystals; present work.
4·71	9·52	—	Groutellite	Klingsberg and Roy, 1959.
4·533	9·27	2·866	Ramsdellite	Byström (1949). Acta Chem. Scand. vol. 3, p. 163.

Powder data

A			B		
I	d	hkl	I	d	hkl
100	4·219 Å	110	vs	4·228–4·209 Å	110
			vw	3·33	120
60	2·633	130	s	2·64–2·62	130
40	2·380	040	m	2·365–2·36	040
			w	2·12	140
			m	1·695–1·665	240

A. Groutellite: Klingsberg and Roy, 1959.
B. Present work: data calculated from extra lines appearing on X-ray photographs of heated powdered groutite.

The pyrolusite–manganite reaction shows a very interesting and rather surprising feature. Pyrolusite possesses a fourfold axis parallel to c; the a and b directions are therefore equivalent, and it would be expected that they would react in the same way, having equal chances of becoming a or b of manganite, which is monoclinic with $\beta = 90°$. Why then is manganite found in only one orientation and not in two?

The problem does not arise in the transition in the reverse direction studied by Dasgupta, in which the symmetry is increasing. Bown and Gay (1959), studying intergrowths in pyroxenes, found that if the exsolved phase had lower symmetry than the host, it was invariably

twinned so as to mimic the host symmetry. They called this the 'inter-growth symmetry principle' and stated that it was a general principle. It seems an eminently reasonable rule, but for reasons that are not clear it does not hold in many of the reactions of pyrolusite. Since pyrolusite is commonly found pseudomorphic after manganite it is possible that a 'memory effect' may be operating. Kitaigorodskiy
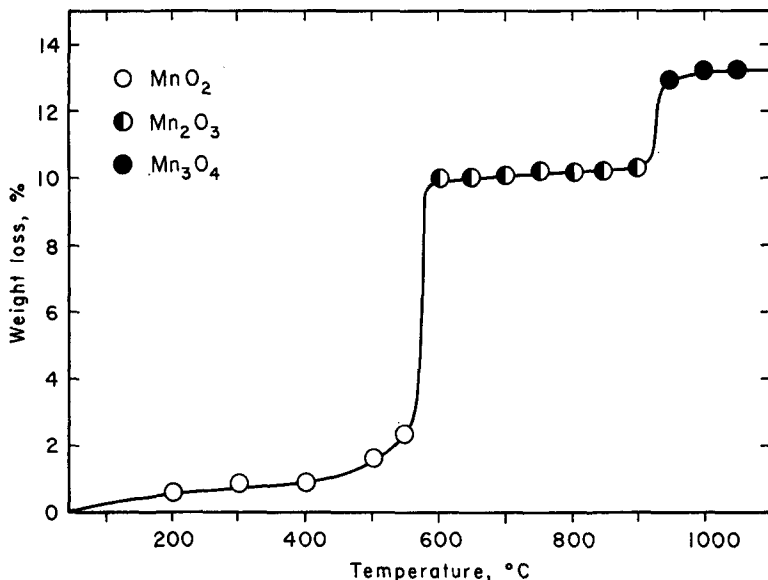

FIG. 3. Weight-loss curve for pyrolusite heated in air. Symbols represent the major constituent at each temperature identified from X-ray powder patterns.

et al. (1965) have observed such effects in non-structure-controlled reactions.

If the manganite formed in this way is subsequently converted to hausmannite the latter forms as twins (fig. 2). The orientation relation-ships are the same as those observed when pyrolusite is converted directly to hausmannite under hydrothermal reducing conditions but in the latter case the crystallinity of the product is greatly improved.

The series pyrolusite–bixbyite–hausmannite

Heating pyrolusite in air results in loss of oxygen. The weight-loss curve (fig. 3) shows two main steps. At about 550° C Mn_2O_3 (bixbyite) is formed and remains unchanged up to 900° C when further oxygen

loss occurs with the formation of Mn_3O_4 (hausmannite). These results agree well with those of numerous D.T.A. runs (see e.g. Mackenzie, 1957).

The transformation pyrolusite–bixbyite resulted in a multiplicity of orientations of the product, shown as stereograms in fig. 4. Interpretation was further complicated by the fact that the orientations observed depended on whether the crystal was heated rapidly or slowly.

Four distinct transformation paths appear to be possible and these will be called A, B, C, and D (see fig. 4). In path A, the cubic bixbyite forms with a fourfold axis parallel to the c-axis of the original pyrolusite, thus preserving the symmetry of the starting material. By paths B, C, and D the bixbyite forms with only twofold symmetry at most parallel to the original fourfold axis, and it becomes of interest to consider whether the 'intergrowth symmetry principle' is obeyed. If it is, path B, for example, yields the two equivalent orientations designated by B_1 and B_2 in fig. 4; if it is not, only one of these orientations occurs. The two cases will be differentiated by referring to the former as 'twinned' and the latter as 'untwinned' even though the phenomenon is probably not true twinning.

Crystals heated rapidly were invariably 'untwinned'. Reaction followed paths D, B_1 together with C_1 and C_1' (which are closely related to B_1, but rotated $10°$ about [010]), and A. Crystals heated more slowly gave B_1 and B_2 in more or less equal amounts; C_1, C_1' and C_2, C_2' also appeared in the same ratio. The slower the rate of heating, the more nearly perfect the 'twinning' appeared. The amount of D present decreased, and where it was detectable at all, showed no 'twinning'. The proportion of A present was roughly the same as for rapidly heated crystals. A rough estimate of the proportions of the various orientations gave (as percentages):

Slow heating   A: $B_1 + B_2$: $C_1 + C_1'$ + $C_2 + C_2'$: D $\equiv$ 15:30:55–50: 0–5
Rapid heating A: B_1: $C_1 + C_1'$:D $\equiv$ 15:15:30:40.

Subsequent slow reheating of rapidly heated crystals produced no further change. Most of the experiments were made on the Ilmenau pyrolusite, but to eliminate the possibility that the phenomena were unique to material from this locality, the experiments were repeated using pyrolusite from Hungary and from Lake Valley; identical results were obtained.

On heating to higher temperatures to produce hausmannite, the orientations of the product surprisingly became very much simpler.
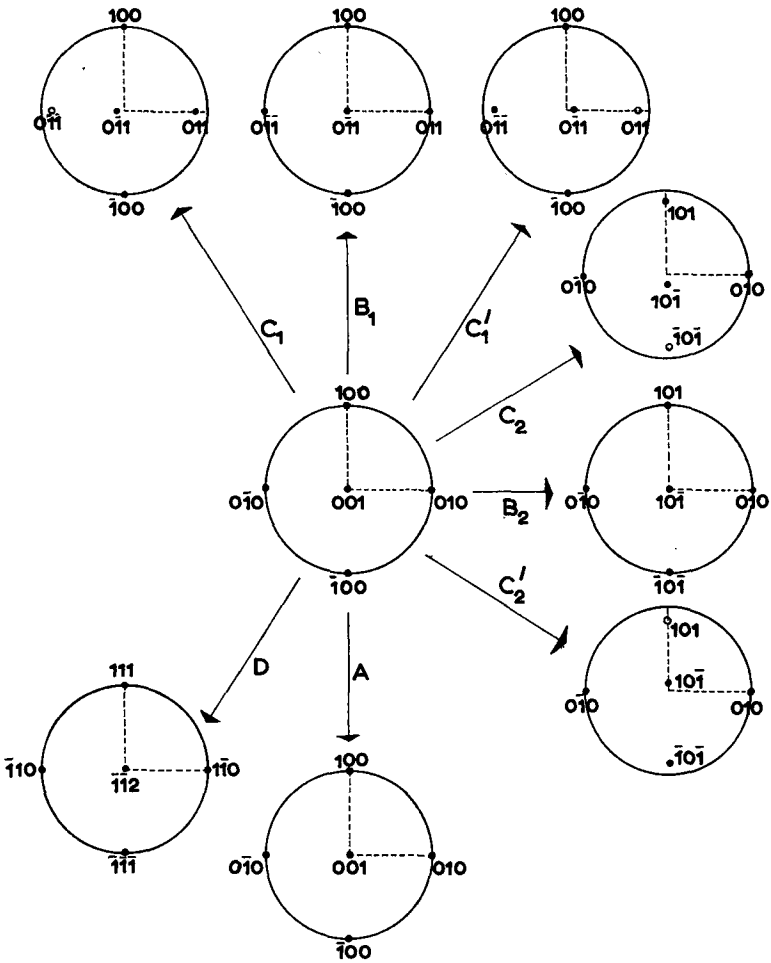
FIG. 4. Stereograms showing the orientations observed when pyrolusite is converted into bixbyite by heating in air. Open circles represent points on the lower hemisphere. The vertical and horizontal dotted lines provide reference directions.

Twinned hausmannite was obtained in precisely the same relationship to the original pyrolusite as had been obtained hydrothermally (fig. 2). This same relatively simple orientation was obtained even where the reaction had been stopped at the bixbyite stage and shown by photographs to contain a multiplicity of bixbyite orientations. Furthermore,

even when derived from 'twinned' bixbyite, the hausmannite showed no more than twofold symmetry about the original pyrolusite c-axis.

The series pyrolusite–manganosite

Single crystals of pyrolusite were heated in a vacuum, and were converted to MnO. The products gave poor photographs that were little better than fibre rotation photographs. In so far as any orientation relationships could be obtained, pyrolusite [001] became [011] of manganosite. It was not possible to determine any further relationships. This change is rather more drastic than the others studied, and seemed to cause the original pyrolusite crystal to disrupt.

Insufficient data were obtained for any mechanism to be postulated.

Structural relationships

Pyrolusite–manganite–Mn_5O_8. The structures of pyrolusite and manganite are related, and the transformation merely consists of adding protons to the pyrolusite structure in an ordered way together with slight movement of the Mn–O octahedra. The mechanism of this reaction seems therefore to be relatively simple.

Fig. 5 shows the structure of Mn_5O_8 (Oswald and Wampetich, 1967), together with that of MnO_2 in (approximately) the observed orientations. The oxygen framework of Mn_5O_8 is similar to that of MnO_2. The transformation preserves approximately close-packed oxygen planes, with some movement of adjacent planes relative to one another. Considerable migration of manganese atoms must occur.

Davis (1967), commenting on his observations on the extra phase (Mn_5O_8) formed on heating manganite, concludes that it must have been formed directly from manganite, because if it had been formed from pyrolusite it 'would have been present in two further orientations related to the present two by reflection across a pyrolusite (110) plane, in order to preserve the tetragonal symmetry of the parent lattice'. However, this was not found to be the case in the present experiments, and it seems that predictions can no longer safely be based on the 'intergrowth symmetry principle'.

Pyrolusite–hausmannite and manganite–hausmannite. These two transformations can conveniently be dealt with together because of the similarity between pyrolusite and manganite. Both these transformations are oriented and there is a strong correspondence between the oxygen packing in reactant and product. Fig. 5 shows the structures of pyrolusite and hausmannite drawn in the relative orientations

observed experimentally. The (100) plane of pyrolusite is parallel to the (101) plane of hausmannite, and this latter plane corresponds to close-packed oxygen planes parallel to (111) in a cubic spinel. Twinning across the (101) plane occurs because the hausmannite structure can
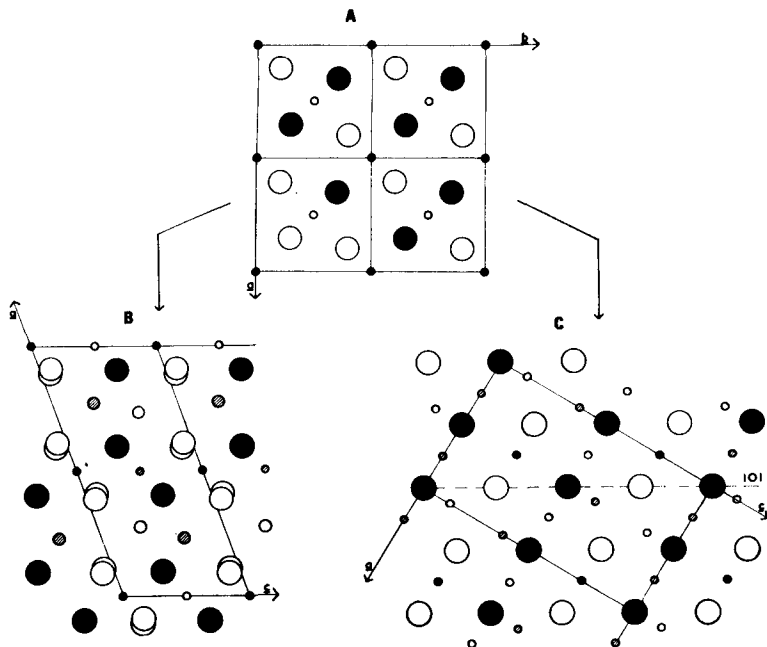

FIG. 5. The structures (somewhat idealized) of (A) pyrolusite, (B) Mn_5O_8, and (C) hausmannite in the orientations observed. Large circles represent oxygen atoms, smaller ones manganese atoms. Oxygen atoms shaded similarly are at similar heights in all three structures: plain are at 0,1 in (A), $0,b/2,1$ in (B) and (C); stippled ones at $\frac{1}{2}$ in (A), $\frac{1}{4}$, $\frac{3}{4}$ in (B) and (C). Stippled manganese atoms are at the same heights as stippled oxygen atoms, and plain ones are at 0,1 in all cases; lightly shaded ones in (B) and (C) are at $b/2$. The slightly larger Mn atoms in (B) represent Mn^{2+}.

grow in either of two ways from the close-packed oxygen planes. Nevertheless, this twinning does not preserve the original fourfold symmetry of pyrolusite, so once again the 'intergrowth symmetry principle' is not obeyed.

Pyrolusite–bixbyite–hausmannite. When hausmannite forms after passing through bixbyite the same simple relationship to the original pyrolusite is found (fig. 2). It is therefore all the more surprising that

such a multiplicity of orientations intervenes. There is only very short-range correspondence between the structures of pyrolusite and bixbyite or between bixbyite and hausmannite in the orientations observed. No suggestions are therefore put forward as to the mechanism. Nor can any explanation be given as to why the four or more orientations of bixbyite finally yield only two of hausmannite. The behaviour may be similar to that of pyrolusite itself yielding fewer orientations than expected. This too may be a 'memory effect', or just possibly may depend on the mosaic structure of the crystals.

References

BOWN (M. G.) and GAY (P.), 1959. Amer. Min., vol. 44. p. 592.

DASGUPTA (D. R.), 1965. Min. Mag., vol. 35, p. 131.

DAVIS (R. J.), 1967. *Ibid.*, vol. 36, p. 274.

DENT GLASSER (L. S.) and SMITH (I. B.), 1965. *Ibid.*, vol. 35, p. 327.

FAULRING (G. M.), ZWICKER (W. K.), and FORGENG (W. D.), 1960. Amer. Min., vol. 45, p. 946.

FEITKNECHT (W.), 1965. The Reactivity of Solids: Plenary lectures I.U.P.A.C. 5th Int. Symposium on the Reactivity of Solids, Munich, 1964, p. 423.

FLEISCHER (M.), RICHMOND (W. E.), and EVANS (H. T., *Jr.*), 1962. Amer. Min., vol. 47, p. 47.

KITAIGORODSKIY (A. I.), MNYUKH (Yu. V.), and ASADOV (Yu. G.), 1965. Journ. Phys. Chem. Solids, vol. 26, p. 463.

KLINGSBERG (C.) and ROY (R.), 1959. Amer. Min., vol. 44, p. 819.

MACKENZIE (R. C.), 1957. The differential thermal investigation of clays, p. 299. Min. Soc., London.

OSWALD (H. R.), FEITKNECHT (W.), and WAMPETICH (M. J.), 1965. Nature, vol. 207, p. 72.

—— and WAMPETICH (M. J.), 1967. Helv. Chim. Acta, vol. 50, p. 2023.

TAYLOR (H. F. W.), 1959. Min. Mag., vol. 32, p. 110.

TUTTLE (O. F.), 1949. Geol. Soc. Amer. Bull., vol. 60, p. 1727.