Oriented transformation of manganite during heat treatment

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Summary. The transformation of manganite during heating has been studied by single crystal X-ray diffraction methods. It is observed that manganite transforms into pyrolusite keeping its original axial directions parallel to those of the transformed phase. Pyrolusite then transforms into Mn_2O_3 with its $[001] \parallel [110]$ or $[100]$ of Mn_2O_3; $[100] \parallel [\bar{1}10]$ or $[010]$ of Mn_2O_3 and $[010] \parallel [001]$ of Mn_2O_3. Evidence of an intermediate product in the pyrolusite $\rightarrow Mn_2O_3$ reaction has been found.

LIKE iron, manganese forms a series of oxides and oxyhydrides, of which manganite differs from its iron analogues in that during heat treatment it transforms into MnO_2 (pyrolusite). The structure of manganite is unlike those of any iron oxyhydroxides, and iron does not form a compound similar to MnO_2. Moreover MnO_2, when further heated, transforms into Mn_2O_3 (cubic), which in turn transforms into Mn_3O_4 (tetragonal); neither Mn_2O_3 nor Mn_3O_4 is structurally similar to cubic Fe_2O_3 or Fe_3O_4.

Manganite occurs in mineral veins, commonly associated with baryte, calcite, chalybite, braunite, hausmannite, &c. More commonly, it occurs as a replacement of other deposits formed by meteoric waters, associated with such minerals as pyrolusite, goethite, and psilomelane. The mineral reported as manganite from Indian ore deposits in Madhya Pradesh and Goa has physical properties very similar to those of manganite, but chemical analyses show it to be near pyrolusite, and Fermor (1909) preferred the name pseudomanganite.

Manganite alters very easily to pyrolusite, and perfect pseudomorphs after crystals of manganite are common. It was formerly supposed to be orthorhombic (Garrido, 1935), but Buerger (1936) showed that the diffraction symmetry was $2/m$ and the crystal system monoclinic with a 8·86 Å, b 5·24 Å, c 5·70 Å, β 90° with $8MnO.OH$ in the unit cell.

Pyrolusite (MnO_2), on the other hand, is one of the most commonly occurring manganese minerals and is formed under oxidizing conditions.

Strunz (1943) showed that, in nature, crystals of pyrolusite could occur as an intergrowth with manganite in parallel orientation. Pyrolusite is teragonal with a 4·44 Å and c 2·89 Å and $2MnO_2$ in the unit cell; the structure is similar to that of rutile. Note that the a and c dimensions of manganite are nearly double those of pyrolusite.

Mn_2O_3 is cubic (a 9·411 Å) and has $16Mn_2O_3$ in the unit cell. Pauling and Shappell (1930) determined the structure of bixbyite, $(Mn,Fe)_2O_3$, and found Mn_2O_3 to be isostructural with it.

Recently Faulring, Zwicker, and Forgang (1960) studied the transformation of cryptomelane and observed oriented transformations into cubic Mn_2O_3 at 600° C and then to Mn_3O_4 at 825° C. They also observed that when Mn_3O_4 was further heated to 1050° C, it transformed to a spinel phase.

Experimental

Manganite (Indian Museum Reg. No. P 57) from Ilfeld, Harz, Germany, was used in the present study. A portion of the sample was crushed to a fine powder and heated in a furnace at a specified temperature for ten hours. The sample was then cooled down to room temperature and weighed in a microbalance. In this manner, the same sample was heated at various temperatures and a weight-loss curve (fig. 1) obtained, showing a change in weight of about 1·3 % at 300° C, 10·3 % at 500° C and a total loss of weight of 13·5 % at 800° C.

The d.t.a. curve showed three endothermic peaks, at 375°, 565°, and 950° C, and resembled the curve found by Bahl (1963) and curve B published in 'The Differential Thermal Investigation of Clays' (1957). It differs from the more commonly accepted curve (curve A, *ibid.*) in showing an additional peak at 565° C; this peak has been attributed to impurities, but X-ray studies of the product after heating in the d.t.a. apparatus to the several peak temperatures show that the course of the transformation is in fact $MnOOH \overset{375°}{\rightarrow} MnO_2 \overset{565°}{\rightarrow} Mn_2O_3 \overset{950°}{\rightarrow} Mn_3O_4$, and the 565° peak is a real one; its absence from curve A is probably due to inadequate sensitivity of the apparatus.

A few good single crystals, picked from the same sample, were examined by X-rays. Rotation photographs of one such crystal, taken around the [001] direction in a 3-cm radius camera using Fe-K radiation (Mn filtered), showed a very faint first layer line together with strong zero and second layer lines. All the diffraction spots were very sharp and the axial parameters (fig. 2), were a 8·942, b 5·278, c 5·743 Å, very near Nuffield's figures (1929) for samples from the same locality. The same

crystal was then heated to 300° C for three hours and a rotation photograph was again taken along the same direction in the same camera using the same radiation. Some of the spots in this photograph were found to be broad and diffuse (fig. 3) while the others were very sharp though weak. The sharp spots corresponded to the original manganite
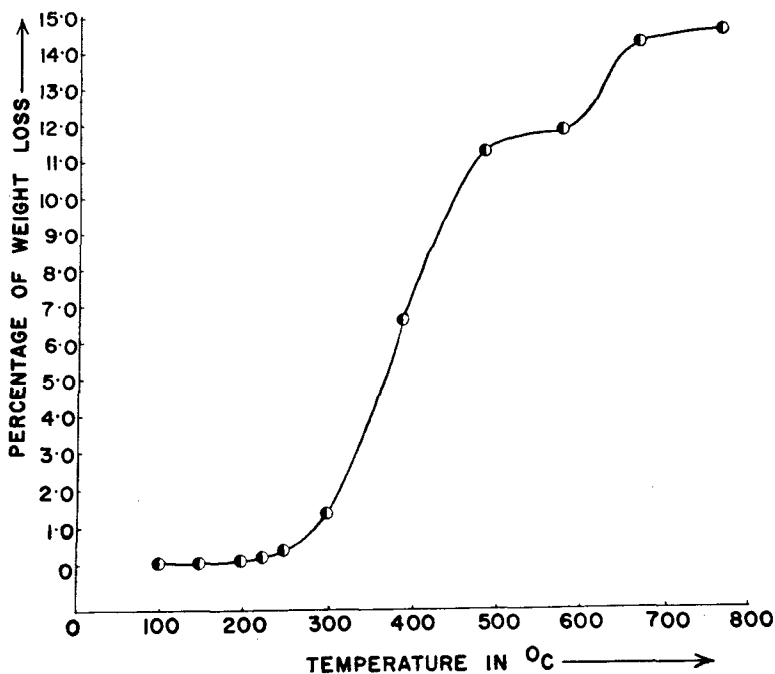

FIG. 1. Weight-loss curve for manganite.

phase, while the diffuse spots were due to the transformed phase. On further heating for some hours at this temperature (300° C), it was seen that in the rotation photograph of the heated crystal the spots due to the transformed phase became sharper and stronger. Measurements of d-values for all the spots of this transformed phase (fig. 3) showed the original crystal of manganite to have transformed into pyrolusite. The axial length 2·87 Å, as measured from the layer line distance, showed the direction of rotation of the transformed crystal to be [001] of pyrolusite. The $a (= b)$ dimension calculated from the spots on the zero layer line was found to be 4·44 Å (the measurements are not very accurate because of the larger dimensions of the spots of the transformed phase).
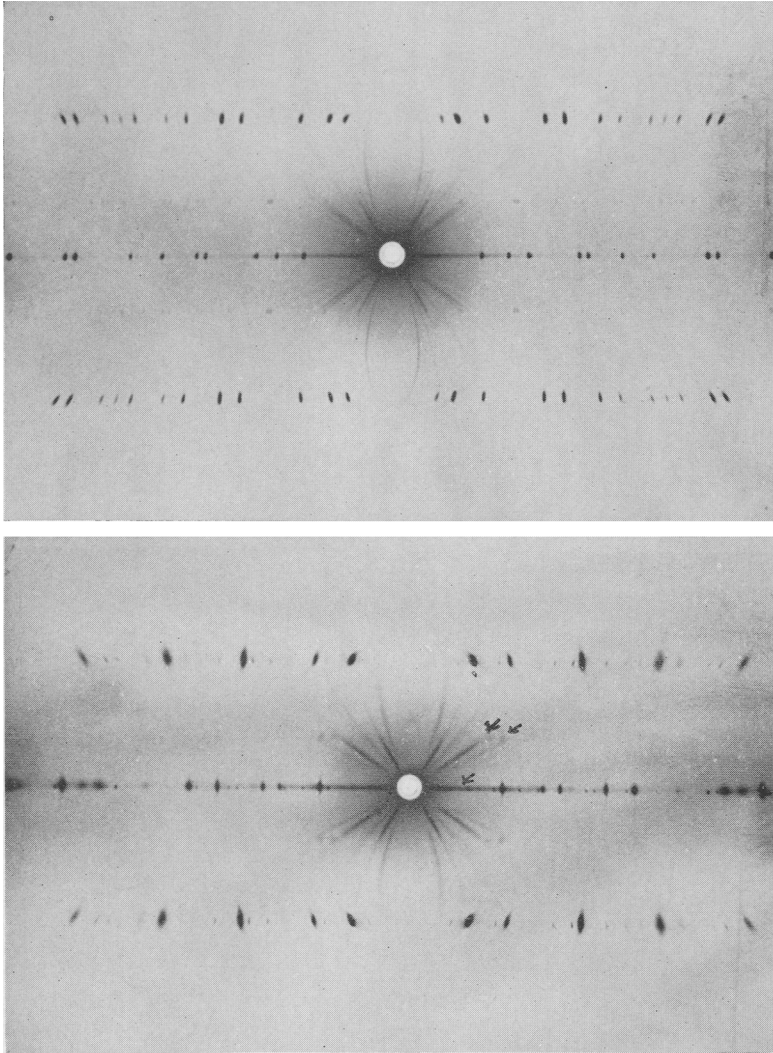
FIGS. 2 and 3. FIG. 2 (top): Rotation photograph of a single crystal of manganite taken along the [001] direction using Fe-$K\alpha$ radiation. FIG. 3 (bottom): Rotation photograph of the same crystal after heating to 300° C, taken along the original [001] direction using Fe-$K\alpha$ radiation. The extra diffractions mentioned in the text are marked.

Another interesting point noted in this photograph was the appearance of a weak spot ($d = 4 \cdot 95$ Å) on the zero layer line, and of two moderately weak spots ($d = 3 \cdot 09$ Å, and $d = 2 \cdot 77$ Å respectively) on a layer line corresponding to a periodicity of $5 \cdot 74$ Å, which is double that of pyrolusite along the [001] direction. None of these spots could be explained as due to either manganite or pyrolusite. To find out if those spots were due to another phase formed by heating pyrolusite, a single crystal of pyrolusite from Germany (Indian Museum Reg. No. P 27) was heated to 450° for a couple of hours. Rotation photographs of that heated crystal taken along the [001] direction of pyrolusite showed that the extra spots in fig. 3 were due to a phase produced by heating pyrolusite. Dr. L. D. Glasser of the University of Aberdeen, also confirmed this (priv. comm.). Further work is being carried out to isolate this transformed phase and to study it in detail. It is worth mentioning that if a crystal of manganite is heated at 220° C for 96 hours, a rotation photograph similar to that of fig. 3 is obtained, whereas if the crystal is powdered and heated at the same temperature for the same period complete conversion to pyrolusite takes place. This shows the effect of time of heating and grain size on the transformation temperature.

The same crystal of pyrolusite (obtained by heating manganite) was then heated to 500° C for three hours. When cooled down, there was no appreciable change in the outward appearance of the crystal, but the rotation photograph of the heated crystal, taken along the same direction as before (fig. 4) showed strong spots occurring along the arcs of the powder diffraction lines of the pattern of cubic Mn_2O_3. All these photographs indicate that when manganite transforms into pyrolusite and then into Mn_2O_3, one lattice can be transformed into another while retaining the same overall three-dimensional character. Considering the structures of the different phases formed, this can be explained in the following way.

Discussion

It has already been pointed out by Buerger (1936) that manganite is definitely monoclinic, with a structure similar to that of arsenopyrite. The most interesting feature of the structure of manganite is that to a first approximation it is similar to that of rutile, two unit cells being placed side by side along the a direction; by sharing edges, the manganese–oxygen octahedra form strings along the c-axis (fig. 5). The structure of pyrolusite (fig. 6) is similar to that of rutile, with Ti replaced by Mn.

The mechanism of the transformation of manganite to pyrolusite is

very simple when the structures of the two are compared. If the pairs of (OH) ions in manganite are replaced by O ions throughout, the periodicities along the a and c directions of manganite will be halved and will become near to those of pyrolusite. If after that the Mn–O octahedra in manganite are twisted a little in a clockwise direction around
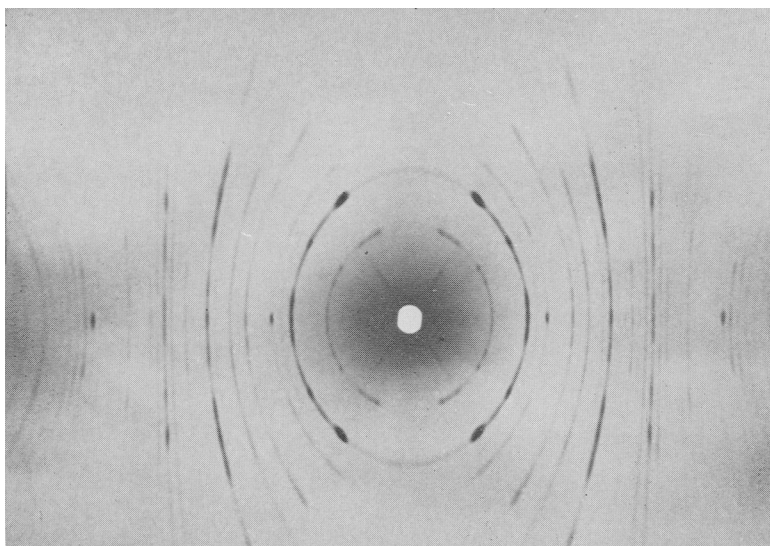

FIG. 4. Rotation photograph of the same crystal as figs. 2 and 3 after heating to 500° C, taken along the original [001] direction using Fe-$K\alpha$ radiation.

the c-axis, the structure of pyrolusite is obtained. During this replacement of (OH) by O there will be a slight contraction of a and an expansion of c. The period in the b direction is much affected by a contraction; this may be due to the difference between ionic radii of Mn^{3+} and Mn^{4+}. Thus the experimental observations correspond to the similarities between the structures of the two phases, and the oriented relationship between the two can be represented by the transformation matrix Man. → Pyro. [100/010/001].

The transformation of $MnO.OH$ to MnO_2 is not similar to those of the iron oxyhydroxides (Bernal, Dasgupta, and Mackay, 1957, 1959; Dasgupta, 1961), in which transformation takes place with the expulsion of H_2O, the resulting product being Fe_2O_3. In $MnO.OH$, if H_2O goes out during heating, the reaction should lead to an intermediate formation of Mn_2O_3.
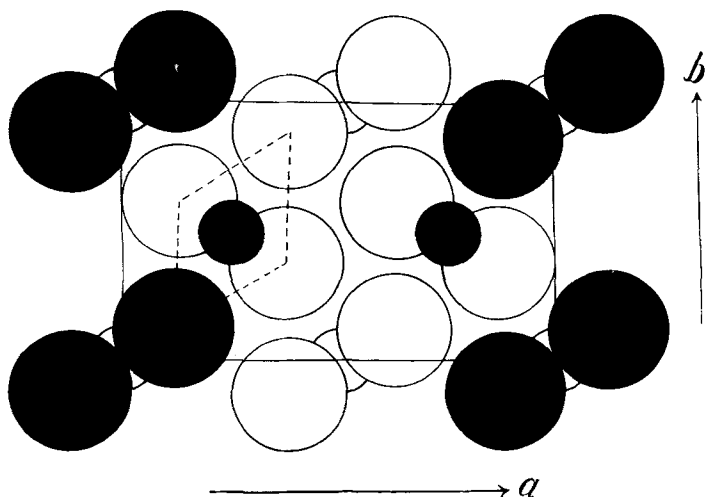
FIG. 5. Structure of manganite as proposed by Buerger (1936) and refined by Dachs (1963) projected along the [001] direction. Large black circles represent OH ions and large open circles O ions; small circles are Mn.
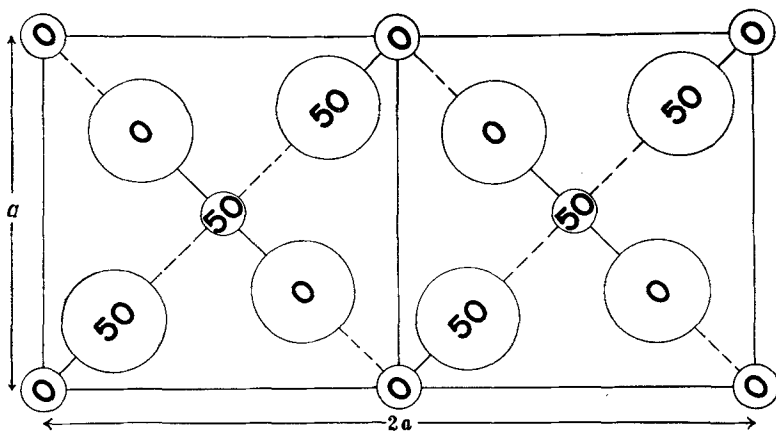

FIG. 6. Structure of pyrolusite projected along the [001] direction. Large circles represent O ions and small Mn.

It seems unlikely that Mn_2O_3, once formed by the dehydration of manganite, will be oxidized to MnO_2 and again converted into Mn_2O_3 on heating, and the weight-loss curve does not throw any light on this point; Bernal (1960), in his article on topotaxy, stated that hydrogen

ions can enter or leave a system where there is a corresponding valency change of one of the other positive ions. One striking example that he mentioned was the manganese oxyhydroxide system where the change from $Mn(OH)_2$, through manganese oxyhydroxide $MnO.OH$, to MnO_2 occurs without gross change in the lattice dimensions, but he could not verify this by use of single crystals. The present study gives positive support to his statement. Recently, Feitknecht and his co-workers (1960) have shown that the reverse reaction, reduction of MnO_2 by hydrazine, is a topochemical reaction taking place by the migration of electrons and protons through the lattice.

Fig. 4 shows that when a pyrolusite crystal (obtained by heating a crystal of manganite) is further heated, it transforms into Mn_2O_3 through an intermediate phase. There are definite evidences that this second transformation is also a topochemical one. Examination of fig. 4 shows that along the zero layer line of that photograph sharp spots occur corresponding to the spacings 4·73 Å (vw), 2·25 Å (s), 1·56 Å (vw), 1·49 Å (vvw), 1·31 Å (vw), and 1·175 Å (m) respectively, due to reflections from 200, 400, 600, 640, and 800 planes of Mn_2O_3 respectively (the axis of rotation was [001] of the pyrolusite); there are also elongated spots corresponding to reflections from (hh0) and (hhl) planes along the zero layer line. There are also indications of layer-line periodicities corresponding to the [100] and [110] spacings of Mn_2O_3. Thus it is seen that, like the cryptomelane to Mn_2O_3 transformation, the oriented relationship between pyrolusite to Mn_2O_3 is: $[001]_{pyro} \parallel [110]$ and $[100]_{Mn_2O_3}$; $[100]_{pyro} \parallel [1\bar{1}0]$ and $[010]_{Mn_2O_3}$; and $[010]_{pyro} \parallel [001]_{Mn_2O_3}$. The orientations of the MnO_6 octahedra in the structure of Mn_2O_3 are not as simple as in manganite and pyrolusite, and so the mechanism of the transformation could not be explained. The orientations of the intermediate phase with respect to pyrolusite have not yet been established though it is evident that one of its zone axes is parallel to [001] of pyrolusite.

The Mn_2O_3 crystal (heated MnO_2 crystal) when further heated to 900° C gave a powder diffraction pattern of Mn_3O_4 and no oriented relationship could be observed between Mn_2O_3 and Mn_3O_4, in agreement with Faulring and his co-workers. The reason for this may be that the strain developed in the Mn_2O_3 crystal (as evident from the photograph, fig. 4) completely broke down the structure at that high temperature.

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