The dehydration of brucite.

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Summary. This process has been reinvestigated, mainly with X-rays, using an FeO-containing, fibrous variety (nemalite), and also a nearly pure specimen. The results confirm that the transformation is oriented, the *c*- and *a*-directions of the brucite becoming the normals to (111) and ($1\bar{1}0$) in the periclase. There is an intermediate, spinel-like stage; the spinel *a*-axis is parallel to, and twice as long as, that of the periclase. This stage is especially prominent when nemalite is heated in air or nitrogen, but is shown also by the nearly pure material. The nemalite shows also a further intermediate stage under certain conditions. A new hypothesis is proposed for the dehydration mechanism, in which the number of oxygen atoms per unit volume is almost unchanged in those parts of the crystal that are converted into periclase. The process is essentially one of cation migration, and the occurrence of the spinel-like phase is readily explained. Similar mechanisms possibly apply to the dehydration of other lamellar hydroxides and oxy-hydroxides (e.g. gibbsite, kaolinite) and of certain carbonates and other oxy-salts.

MANY investigations on the dehydration of brucite ($Mg(OH)_2$) to periclase (MgO) have been reported. Among other approaches that have been followed are optics, X-ray crystallography, phase equilibria, thermodynamics and thermochemistry, chemical kinetics, and electron microscopy and diffraction. The earlier work was reviewed by Garrido (1951); among recent contributions may be mentioned those of Kennedy (1956), Roy and Roy (1957), Goodman (1958), Gregg and Razouk (1949), and Razouk and Mikhail (1959).

There are distinct indications of an intermediate stage in the process. Early signs of this were provided by optical studies (Rinne, 1891). Further evidence came from thermodynamic considerations (Roy and Roy, 1957) and from X-ray studies (Garrido, 1936*a*, 1951). Garrido showed that brucite crystals that had been dehydrated rapidly gave 'extra' X-ray reflections, which were not attributable to either brucite or periclase, though they could be indexed $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ on the periclase axes. He concluded that they were produced by a form of MgO in which some of the cations were not in their normal positions. Not all of the more recent investigators, however, have agreed that a recognizable intermediate stage exists.

The aim of the present work was to find whether there is a distinct, intermediate stage that can be isolated, and if there is to determine at least some features of its crystal structure. It was hoped that such a study might throw new light on the mechanism of the dehydration process.

Material.

Two specimens of brucite were used:

The impure, fibrous variety (nemalite) from Asbestos, Quebec, Canada. This has been fully described (Berman, 1932; West, 1932, 1934; Garrido, 1936*b*; Donnay, 1945), and our own optical, X-ray, and analytical (table I) observations in general confirmed the earlier reports.

TABLE I. Chemical analyses.

	1.	2.	3.
SiO_2	0·39	—	1·85
Fe_2O_3	—	1·95	1·55
FeO	—	9·57	9·30
MnO	0·89	—	—
MgO	67·34	60·33	59·87
H_2O	31·52	28·60	27·90
	100·14	100·45	100·47

1. Brucite: Wood's mine, Texas, Pennsylvania, U.S.A. (Kurnakov and Chernykh, 1926).
2. Nemalite: Asbestos, Quebec, Canada (Berman, 1932).
3. Ditto, this investigation.

The fibres are pale green and sometimes many inches long, and are elongated parallel to *a*. The crystallites are well aligned in this direction but are rotated at random around it, even in thin fibres. Long-exposure X-ray rotation photographs showed the presence of intergrown chrysotile, with its *c*-axis perpendicular to the fibre direction, but gave no indication of any other phases in the fibres selected for the present work. It was assumed that the SiO_2 occurred as chrysotile, and (following Donnay, 1945) that the small Fe_2O_3 content could be attributed to magnetite and the deficiency in water to periclase, the last two being in amounts too small for detection with X-rays. It was thus calculated that the fibres contained 92% of brucite of composition $Mg_{0\cdot92}Fe_{0\cdot08}(OH)_2$ together with 4% of serpentine, 2% of magnetite, and 2% of periclase.

A nearly pure brucite from Wood's mine, Texas, Lancaster County, Pennsylvania, U.S.A. (B.M. 33222). This also has been fully described, most recently by Brindley and Ogilvie (1952). The crystals were colourless, hexagonal flakes with (0001) cleavage and though, as Brindley and Ogilvie showed, they are not true single crystals, they could be regarded as such for the present purpose. X-ray and optical study gave no indications of phases other than brucite. Chemical analysis (table I) shows the latter to have the approximate composition $Mg_{0\cdot99}Mn_{0\cdot01}(OH)_2$.

Experimental procedure.

Fibres of nemalite, and single crystals of the Pennsylvania brucite, were heated under various conditions causing partial or complete dehydration. The products were pseudomorphs, not significantly changed in external dimensions. They were studied mainly by single-crystal X-ray methods, using filtered cobalt radiation. Some of the heated nemalite fibres were crushed and powder patterns also obtained, using an 11·46-cm. diameter camera. The following heating conditions were used:

Rapid heating in air. The crystal or fibre was put in a platinum foil microboat, which was then placed on a ceramic surface in a furnace already at the selected temperature, which was probably reached by the crystal within 2 seconds.

Slow heating in air or nitrogen. The crystal or fibre, in a platinum boat, was placed in a cold tube furnace, the temperature of which was then raised at 30° C. per minute.

Rapid heating in air, nitrogen, or hydrogen. The crystal or fibre was placed in a platinum foil boat of V-shaped cross-section, which was contained in a vacuum desiccator filled with the desired gas. An electric current was passed through the boat from end to end, thereby heating the crystal or fibre to red heat in a few seconds. When nitrogen or hydrogen was used, the desiccator was evacuated and filled with the gas several times before the crystal was heated. The nitrogen used in these experiments was a commercial product containing 99·9% N_2. For some runs, it was further purified by passage over red-hot copper.

A specimen of $MgFe_2O_4$ was prepared for comparison work by reaction of laboratory grade MgO and Fe_2O_3 in appropriate proportions at 1 320° C. for 5 hours, followed by regrinding and reheating under the same conditions. Its X-ray powder pattern, obtained using an 11·46-cm. diameter camera, agreed substantially with that reported by Posnjak (1930). The cubic cell was found to have a $8{\cdot}37 \pm 0{\cdot}01$ Å.

A quasi-static dehydration curve of nemalite (fig. 1) was obtained by heating a sample in a slow stream of 99·9% nitrogen at successively higher temperatures, each temperature being maintained until apparent constant weight was attained. An unweighed sample was heated under identical conditions, and fibres were removed at each temperature for X-ray examination, the results of which are included in fig. 1.

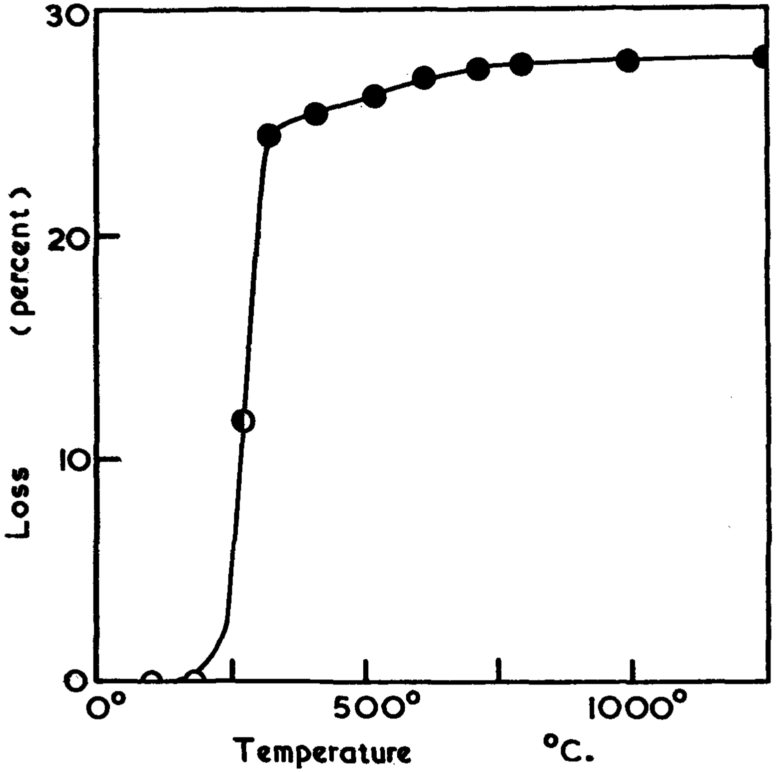

Fig. 1. Quasi-static dehydration curve for nemalite, showing results of X-ray examination of heated specimens. Phases detected: ○ brucite, ◐ brucite+MgO, ● MgO.

Results.

Phases detected in heated material. The X-ray patterns from heated crystals or fibres were found to depend on the heating rate and final temperature, and to a lesser extent on the period during which the latter was maintained. The reflections fell into the following five groups; all showed strongly preferred orientation: reflections of unchanged brucite (*B*); reflections of periclase (*P*); 'extra' reflections indexable on a spinel-type cell (*S*); additional 'extra' reflections not so indexable (*X*);

and reflections of metallic iron (Fe). Table II summarizes the types of reflections given by crystals or fibres heated under various conditions. Except with nemalite at 400° C., the time the final temperature was maintained was relatively unimportant. In general, the main effect of prolonging it was to give a sharper and clearer pattern in which weak reflections, including those of groups *S* and *X*, were more readily seen.

TABLE II. Groups of reflections detected in X-ray patterns of crystals or fibres heated under various conditions (summarized results). *B*, brucite; *P*, periclase; *S*, spinel-type extra reflections; *X*, further extra reflections; Fe, metallic iron.

Specimen and atmosphere.	Final temp. ° C.	Time final temp. was maintained.	Reflections detected in crystals after	
			Slow heating.	Rapid heating.
Nemalite in air	400°	⩽ 1½ hr.	*B*+weak *P*	*B*+weak *P*
	400°	3½–15 hr.	diffuse *P*	diffuse *P*
	500°	3½ min.–48 hr.	*P*	*P*+(sometimes) *S* & *X*
	600–700°	2–21 min.	*P*	*P*+weak *S*
	800–1 150°	2 min.–20 hr.	*P*+(sometimes) *S*	*P*+*S*
	1 350°	5 hr.	—	*P*+*S*
	c. 1 600°	1–5 min.	—	*P*
Nemalite in N_2	*c.* 800°	1–10 min.	*P*+weak *S*	*P*+*S*
Nemalite in H_2	*c.* 800°	1–10 min.	—	*P*+*S*+Fe
Pennsylvania brucite in air	400–750°	2–20 min.	*P*	*P*
	790–830°	2–60 min.	*P*	*P*+(sometimes) weak *S*
	800°	45 min.	—	*P*+stronger *S*

Crystallographic orientation of the periclase. The X-ray results for all samples where periclase was formed confirmed previous observations (Büssem and Köberich, 1932; West, 1932, 1934; Garrido, 1936*a*, 1951) on its orientation relative to that of the brucite. Fig. 2 shows the relationship; there are two principal orientations for the periclase; for both of them periclase (111) is perpendicular to brucite *c*, and periclase $(1\bar{1}0)$ to brucite *a*. With the Pennsylvania brucite, one orientation always predominated over the other. This confirms Garrido's result (1951). The nemalite gave only fibre rotation patterns, in which the two orientations are indistinguishable.

The S- and X-reflections. The *S*- and *X*-reflections never occurred in the absence of *P*-reflections. They resembled these closely in diffuseness and angular spread, but were in general weaker. *S*-reflections were reproducibly developed and strongest in the patterns of nemalite fibres that had been heated rapidly in air or nitrogen to 800–1 150° C. (table II). With nemalite fibres that had been heated slowly or to other temperatures, and with crystals of Pennsylvania brucite under any conditions, they were weaker, fewer, and less reproducibly produced.

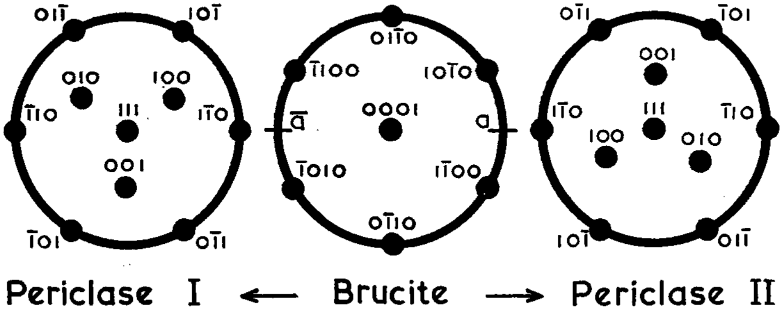

FIG. 2. Orientation relationships for the transformation of brucite into periclase, showing the brucite and the two orientations of the periclase in stereographic projection. Comparison of spacings: Brucite, c 4·75 Å., periclase d_{111} ($\frac{1}{2}\times 4{\cdot}86$) Å. Brucite, a 3·13 Å., periclase $d_{1\bar{1}0}$ 2·97 Å.

In the patterns from heated nemalite, some of the S-reflections occurred on the periclase layer lines, and others on additional layer lines corresponding to a doubling of the periclase repeat distance in the fibre direction. All could be indexed on a face-centred cubic lattice with its a-axis parallel to, and twice as long as, that of the periclase (i.e. a 8·42 Å.). This was also true of the S-reflections given by heated crystals of Pennsylvania brucite. This lattice is similar to that of a spinel and the relative intensities of the S-reflections given by heated nemalite were similar to those of the corresponding reflections of spinel itself ($MgAl_2O_4$). All of the P-reflections can necessarily also be indexed on the spinel-type lattice. The patterns as a whole, taking P- and S-reflections together, could thus be described as ones of periclase superimposed on ones of a spinel having an a-axis exactly twice that of the periclase. They might equally well be described as spinel-type patterns in which reflections with h, k, and l all even are anomalously strong.

West (1932, 1934) also noted the appearance of reflections attributable to a spinel in heated nemalite, and he concluded that $MgFe_2O_4$ had been formed through atmospheric oxidation of the FeO. The present work shows that this explanation is incorrect. Firstly, X-ray powder patterns showed a difference between the a-spacing of $MgFe_2O_4$ (8·37 Å.) and that of heated nemalite (8·42 Å.) several times greater than experimental error. Secondly, S-reflections were produced from nemalite on heating not only in air, but also in nitrogen or hydrogen. One sample, which had been heated rapidly in nitrogen to red heat, and which gave strong *S*-reflections, was analysed for FeO. The result (12·91%) differed insignificantly from that found for the original material (12·88% referred to the dry weight). Another sample, which had been heated in hydrogen, gave *S*- and *P*-reflections as well as ones from metallic iron. It seems most unlikely that oxidation could have occurred under these circumstances. Thirdly, the *S*-reflections were also given, though they were fewer and weaker, by heated crystals of the Pennsylvania brucite, which is almost pure $Mg(OH)_2$.

Although *S*-reflections were given by heated specimens of both nemalite and Pennsylvania brucite, there were some differences in the relative intensities in the two cases. With the heated nemalite, the three strongest *S*-reflections were 220, 311, and 511 (or 333) indexed on spinel-type axes. In the other case they were 111, 220, and 311.

The fact that the *S*-reflections persist in heated nemalite up to at least 1 350° C. suggests, in view of the dehydration curve (fig. 1), that the phase yielding them can be anhydrous or nearly so. Specimens giving *S*-reflections that have been heated at lower temperatures appear still to contain some water. A nemalite fibre which had been heated rapidly to 800° C. so that it gave relatively strong *S*-reflections was weighed and ignited at 1 250° C. A loss of 1·9% occurred.

X-reflections were given irreproducibly by nemalite fibres heated rapidly to 500° C. They were very weak, and the only detectable ones appeared on additional layer lines corresponding to a quadrupling of the periclase repeat in the fibre direction. Such a quadrupling would be caused by a lattice that had a doubled *a*-axis, as in a spinel, but was primitive and not face-centred. However, the positions of the reflections on the layer lines did not agree with this hypothesis. Not enough *X*-reflections were present to allow a determination of the lattice giving rise to them. They can probably be attributed to some lattice related to that of periclase, but larger even than that of the spinel-like material.

The iron reflections. These were shown by a fibre of nemalite that had been heated to red heat in hydrogen; *P*- and *S*-reflections were also present. The iron reflections showed strong preferred orientation, comparable to that of the *S*- and *P*-reflections. The *a*-axis of the iron (body-centred cubic; *a* 2·86 Å.) was parallel to the fibre direction.

Discussion.

The present results confirm that distinct, intermediate stages in the formation of periclase can be recognized. These are most apparent with nemalite, but are detectable also with the nearly pure $Mg(OH)_2$ from Pennsylvania.

Homogeneous and inhomogeneous dehydration mechanisms. The orientation relationship in the brucite–periclase change is clearly determined primarily by a tendency for close-packed oxygen planes in the product to lie parallel to those in the starting material. Previous hypotheses, such as that of Goodman (1958), have been based on the assumption that the water is lost more or less uniformly from all parts of the crystal, i.e. that from every unit cell, containing one formula unit of $Mg(OH)_2$, one molecule of water is lost. The reaction has thus been visualized as a chemical condensation between the hydroxyl groups on the upper surface of each brucite layer and those on the lower surface of the next. Such a mechanism could be described as a homogeneous one.

A suitably elaborated homogeneous mechanism can explain the observed orientation relationship satisfactorily, but not the occurrence of a spinel-like intermediate stage. It is also difficult to see how one half of the oxygen ions could escape sideways, parallel to the plane of the layers, without completely disrupting the crystal structure. Tentatively, a different hypothesis can be considered in which the mechanism is assumed to be inhomogeneous. This implies that, in the brucite crystal, there develop donor and acceptor regions. The acceptor regions are the parts that are converted into periclase, which is produced, not by loss of hydroxyl ions, but by gain of cations and loss of protons. The donor regions are completely destroyed and become the pores that have been shown to exist in the pseudomorph (Goodman, 1958). Their cations migrate into the donor regions, and their hydroxyl ions provide all the oxygen for the water that is formed. These processes are represented diagramatically in fig. 3.

The spinel-like intermediate stage. The existence of such a stage follows reasonably from the assumption that the essential process is one of cation migration. If we consider an element of structure having four oxygen atoms per close-packed layer, there are, on the average, two cations per layer in brucite and four in periclase (fig. 4). The most obvious feature of the spinel structure is that it is an assemblage of close-packed oxygen ions with three cations per layer. In a general way, the formation of a spinel-like intermediate stage is readily explained as occurring naturally when the ratio of cations to oxygen passes through the value of 3:4.

In brucite the oxygen atoms are hexagonal close packed; in spinel and in periclase they are cubic close packed. It is therefore necessary

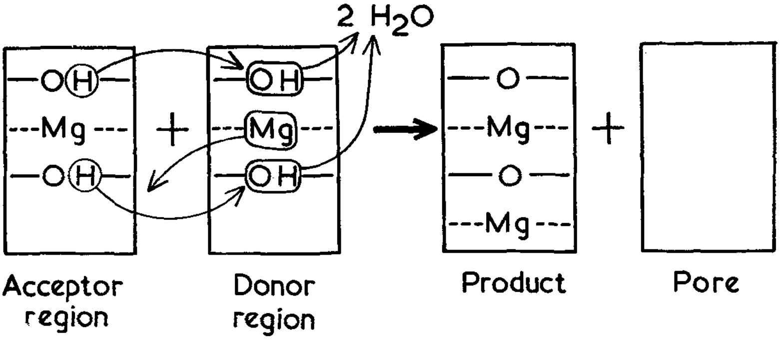

FIG. 3. Schematic representation of acceptor and donor regions, showing the migration of magnesium and hydrogen ions in opposite directions, and the expulsion of water from the donor regions.

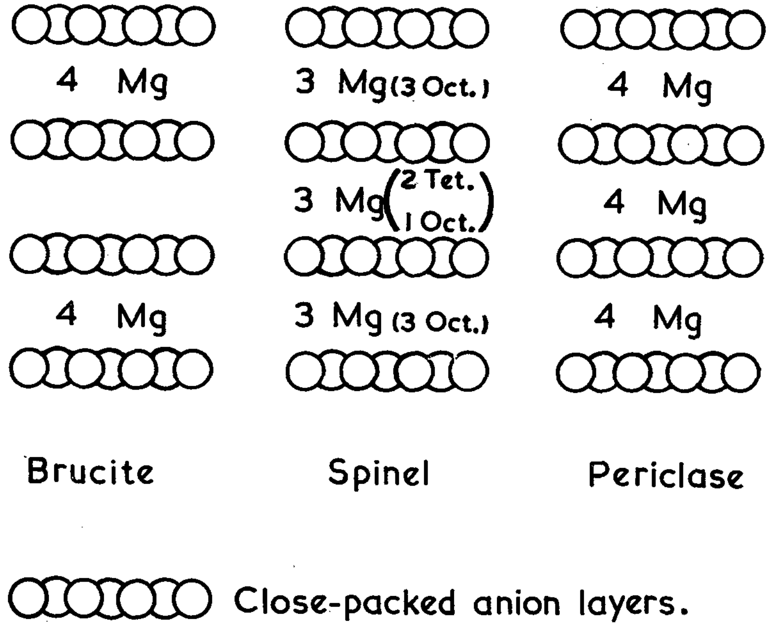

FIG. 4. Comparison of the structures of brucite, periclase, and the hypothetical spinel $Mg_3O_4H_2$. The numbers of magnesium ions in each case correspond to a unit of cross-section containing four O^{2-} or OH^- ions or both per close-packed layer.

to postulate that at some early stage in the transformation the oxygen layers slip over each other. Indirect evidence that such slip can occur is provided by the results of studies on the bending of MgO single crystals, which is known to involve movement of dislocations as in a metal (Mügge, 1919; May and Kronberg, 1960; Kelly and Williamson, 1960).

To balance the electrical charges, a true spinel intermediate stage would need to have the formula $Mg_3O_4H_2$. It may be supposed that the donor regions pass through this stage and that this is when the spinel-like structure begins to appear. However, the specimens in which *S*-reflections were actually observed were nearly or completely anhydrous and the structure therefore evidently retains spinel-like features after the cation: oxygen ratio has risen above the value of 3:4 characteristic of a true spinel. This can be explained by considering the different types of cation co-ordination, which can be tetrahedral or octahedral in the spinel (fig. 4). When more cations are added to the spinel structure, they must necessarily occupy vacant sites, which might also be either octahedral or tetrahedral. If it is assumed that the additional cations go entirely into octahedral sites, and that those already present in the spinel stay where they are, the result will be the periclase structure modified by the removal of one cation in eight to a tetrahedral site. This is assumed to be the situation approximated to in crystals giving *P*- and *S*-reflections; the two sets of reflections come from a single phase. Such crystals might equally well be described as ones of periclase containing a substantial proportion of Frenkel defects arranged in an ordered way. The present interpretation agrees with Garrido's view that some of the cations occupy anomalous positions in the intermediate material.

Transition to periclase: further considerations. The *X*-reflections apparently represent a more complex, though still ordered, arrangement of cations in tetrahedral sites with an equal number of octahedral vacancies. This structure is possibly derived from one formed before the cation:oxygen ratio is high enough to form a spinel.

The present results confirm Garrido's observation (1936*a*, 1951) that the periclase is formed in two principal orientations, one of which is better developed than the other. Garrido accounted for the latter fact by supposing that the cation–oxygen bonds were less disturbed in the formation of one of the two forms, but it seems that this cannot be correct, as the two are symmetrically related to the original brucite orientation (fig. 2). It appears more likely that, in any one crystal, transformation begins at more than one nucleus, and that at each nucleus there is an equal probability of each orientation developing; the number of nuclei must be so small that unequal proportions of the two orientations usually arise. On the present hypothesis for the mechanism, the orientation produced depends on the direction in which oxygen sheets move relative to each other in the change from hexagonal to cubic close packing.

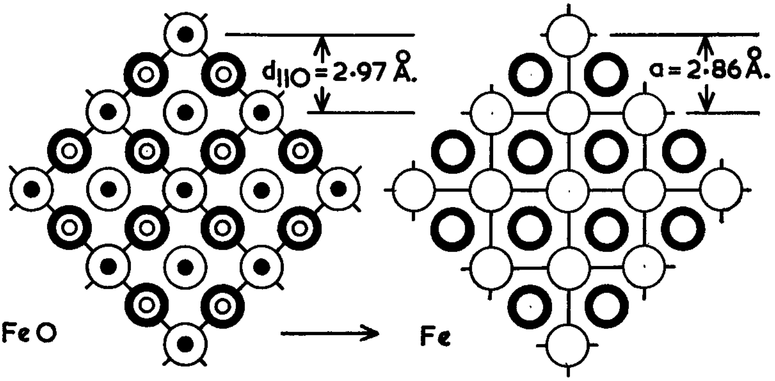

FIG. 5. The structures of FeO and metallic iron, drawn in the observed relative orientations; both structures are projected along *a*, which is 4·21 Å. long in FeO and 2·86 Å. in Fe. Large, open circles: Fe at height zero. Large, heavy circles: Fe at height *a*/2. Small, full circles: Oxygen at height zero. Small, open circles: Oxygen at height *a*/2.

The fact that the *S*- and *X*-reflections are given chiefly by crystals that have been heated rapidly can perhaps be explained by assuming that, under these conditions, a large proportion of the cations are migrating simultaneously. Movement of the cations probably becomes more difficult after all or most of the protons have been lost, and there will be a good chance that a cation in a tetrahedral site will not manage to escape from it before this has happened. Subsequent migration, in anhydrous material, is then very slow below about 1 600° C. With slowly heated crystals, the number of cations migrating simultaneously must be smaller, and there is a greater chance of the stable, periclase structure being formed before all the water has been lost. The persistence of the intermediate structures is stronger with nemalite than with the Pennsylvania brucite. This can possibly be attributed to the presence of the silicon, which by its ready adoption of fourfold co-ordination in some way stabilizes the spinel-like structure. Magnesium is not often found in tetrahedral co-ordination, though a well-established example is to be found in melilite (Warren, 1930; Smith, 1953).

The iron reflections. The occurrence of preferred orientation in these reflections can be attributed to a similarity between the positions of the iron atoms in the metal and those of the cations in periclase. If these cations were all Fe^{2+}, reduction to the metal could be effected by removal of the oxide ions followed by a small contraction in the lattice dimensions parallel to the fibre direction and a larger one perpendicular to it (fig. 5). The process can perhaps be visualized as involving cation migrations so as to cause segregation of regions of pure FeO in the oxide, followed by a migration of oxygen, possibly in atomic rather than ionic form, to combine with hydrogen on the surface of the crystallite.

Comparison with the decompositions of other minerals. Brucite is related structurally to a number of other lamellar hydroxides and oxy-hydroxides, such as gibbsite, kaolinite, and various compounds of iron, and one might expect similar mechanisms to apply to the dehydration reactions of all these substances. It is thus possible that the extensive published data relating to the dehydration processes of these other minerals may be better explained by inhomogeneous mechanisms than by the homogeneous ones that have generally been proposed. The same thing may be true of the decompositions of certain oxy-salts, such as chalybite ($FeCO_3$). Bernal, Dasgupta, and Mackay (1959) noted the occurrence of an oriented decarbonation in this case and drew attention to the difficulty of reconciling this with the fact that two-thirds of the oxygen is lost. This difficulty disappears if an inhomogeneous mechanism is accepted.

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References.

BERMAN (H.), 1932. Amer. Min., vol. 17, p. 313.

BERNAL (J. D.), DASGUPTA (D. R.), and MACKAY (A. L.), 1959. Clay Minerals Bull., vol. 4, p. 15.

BRINDLEY (G. W.) and OGILVIE (G. J.), 1952. Acta Cryst., vol. 5, p. 412.

BÜSSEM (W.) and KÖBERICH (F.), 1932. Zeits. physikal. Chem., ser. B, vol. 17, p. 310.

DONNAY (J. D. H.), 1945. Univ. Toronto Studies, Geol. Ser., No. 49, p. 5.

GARRIDO (J.), 1936*a*. Compt. Rend. Acad. Sci. Paris, vol. 203, p. 94.

—— 1936*b*. An. Soc. Españ. Fís. Quím., vol. 34, p. 853.

—— 1951. Ion. Rev. Españ. Quím. Aplic., vol. 11, pp. 206, 220, 453.

GOODMAN (J. F.), 1958. Proc. Roy. Soc., ser. A, vol. 247, p. 346.

GREGG (S. J.) and RAZOUK (R. I.), 1949. Journ. Chem. Soc., Suppl. vol., p. S 36.

Kelly (A.) and Williamson (G. K.), 1960. 5th Internat. Congr. Cryst., Abstracts of Communications, p. 33.
Kennedy (G. C.), 1956. Amer. Journ. Sci., vol. 254, p. 567.
[Kurnakov (N. S.) and Chernykh (V. V.)] Курнаков (Н. С.) и Черных (В. В.), 1926. [Зап. Росс. Мин. Общ. (Mém. Soc. Russe Min.), vol. 55, p. 74 (English with Russian summary)]; abstr. in Neues Jahrb. Min., 1927, Abt. A, vol. 1, p. 313.
May (J. E.) and Kronberg (M. L.), 1960. Journ. Amer. Ceram. Soc., vol. 43, p. 525.
Mügge (O.), 1919. Nachr. Gesell. Wiss. Göttingen, Math.-Phys. Kl., p. 47.
Posnjak (E.), 1930. Amer. Journ. Sci., ser. 5, vol. 19, p. 67.
Razouk (R. I.) and Mikhail (R. Sh.), 1959. Egypt. Journ. Chem., vol. 2, p. 207.
Rinne (F.), 1891. Zeits. deutsch. geol. Ges., vol. 43, p. 231.
Roy (D. M.) and Roy (R.), 1957. Amer. Journ. Sci., vol. 255, p. 573.
Smith (J. V.), 1953. Amer. Min., vol. 38, p. 643.
Warren (B. E.), 1930. Zeits. Krist., vol. 74, p. 131.
West (C. D.), 1932. Amer. Min., vol. 17, p. 316.
—— 1934. Ibid., vol. 19, p. 281.