On the oriented conversion of $Ca(OH)_2$ to CaO

By S. CHATTERJI, M.Sc., D.Phil.

and J. W. JEFFERY, Ph.D., F.Inst.P.

Birkbeck College Crystallography Laboratory, University of London

Summary. In order to study the orientational relationship between $Ca(OH)_2$ and CaO, the transformation was carried out in stages inside an electron microscope by condensing the electron beam, and the process was monitored by electron diffraction. It has been found that at the initial stage all the hexagonal spots of $Ca(OH)_2$ split into two; on further heating one set of spots disappear. The remaining set of spots corresponds to the CaO structure, which has an orientational relationship to the hydroxide structure. To estimate the degree of orientation, a sample of brucite was treated in a similar way to the $Ca(OH)_2$; a comparison shows that a high degree of orientation is preserved in the conversion of $Ca(OH)_2$ to CaO. This observation is contrary to earlier reports.

IT has been reported that in the conversion of $Ca(OH)_2$ to CaO a poor degree of orientation is preserved with respect to the hydroxide structure (West, 1934), whereas in the conversion of $Mg(OH)_2$ to MgO a high degree of orientation is preserved, and a hypothesis has been put forward to explain this difference in the conversion of these structurally similar compounds (Ball and Taylor, 1961). In our study of the hydration of cements and cement compounds, electron-diffraction patterns of both unheated and heated hydration products are taken as a routine procedure. During evaluation of these diagrams it has been observed that some of the heated $Ca(OH)_2$ crystals gave electron diffraction patterns consisting of two sets of hexagonal spots, one inside the other. The inner set of spots, which are sharper, can be indexed on the basis of the $Ca(OH)_2$ unit cell (a_H 3·59 Å). The outer set of hexagonal spots can only be indexed if it is assumed that they are due to an oriented growth of CaO. A systematic study of this phenomenon was undertaken. $3CaO \cdot SiO_2$–$CaSO_4 \cdot 2H_2O$ pastes were used as the source of $Ca(OH)_2$ crystals. After about three hours hydration these pastes gave crystals of $Ca(OH)_2$ suitable for single-crystal electron-diffraction study, using previously described techniques (Chatterji and Jeffery, 1962). The crystals were heated by condensing the electron beam of the electron microscope (AE.

1–E.M. 6). Electron-diffraction diagrams were taken at different stages of conversion. Before taking an electron-diffraction pattern, the electron beam was decondensed to get the maximum resolution. To estimate the degree of orientation, a sample of brucite (Uist, Scotland) was treated in a similar way to the $Ca(OH)_2$.

Figs. 1 to 3 are the electron-diffraction diagrams at different stages of heating. After the first stage of heating the 110 spots of the hydroxide structure had decreased in intensity and an intense but slightly diffuse 220 reflection of the oxide structure appeared just outside it (fig. 2). Although not visible in the reproduction, weak diffuse spots also appeared just outside the 100 spots of the hydroxide. Further heating reduced the intensity and ultimately eliminated the reflections due to the hydroxide structure and the weak diffuse spots became incorporated into a very weak 111 powder ring of CaO. The 220 spots of the oxide became sharper, although slightly spread around the powder ring, and were the only remaining spots on the pattern (fig. 3).

Still further heating, after complete conversion to oxide, tended to spread the oxide spots and to bring out powder rings due to the oxide structure. It was observed that $Mg(OH)_2$ crystals were more difficult to heat up than $Ca(OH)_2$ crystals, probably due to the lower absorption of electrons. In a subsequent experiment, $Ca(OH)_2$ crystals were made by boiling CaO (from A.R. $CaCO_3$) in suspension. In this system the $Ca(OH)_2$ crystals were not big enough for single-crystal electron-diffraction study but they gave spotty ring diagrams. Splitting of the rings, corresponding to the single-crystal results, was observed on heating.

Our results on $Mg(OH)_2$ are consistent with the findings of Goodman (1964), except that he observed an outward movement of the spots but did not resolve the splitting and also he got diffused rings at the final stage, which we did not. These differences may be due to a larger electron-beam diameter and lower resolving power of his instrument. A comparison of $Mg(OH)_2$ and $Ca(OH)_2$ diagrams shows that a good degree of orientation is preserved in the conversion of $Ca(OH)_2$ to CaO. The splitting of the 100 spots of the hydroxide structures at the initial stage of heating indicates that the conversion goes through an inter-mediate stage.

The differences between the X-ray and electron-diffraction work may be due to the highly ionizing character of the electron beam or the lower-ing of the decomposition temperature of $Ca(OH)_2$ under high vacuum or both (Meyers, 1942). It is hoped to test these possibilities by X-ray work on $Ca(OH)_2$ crystals decomposed under vacuum.
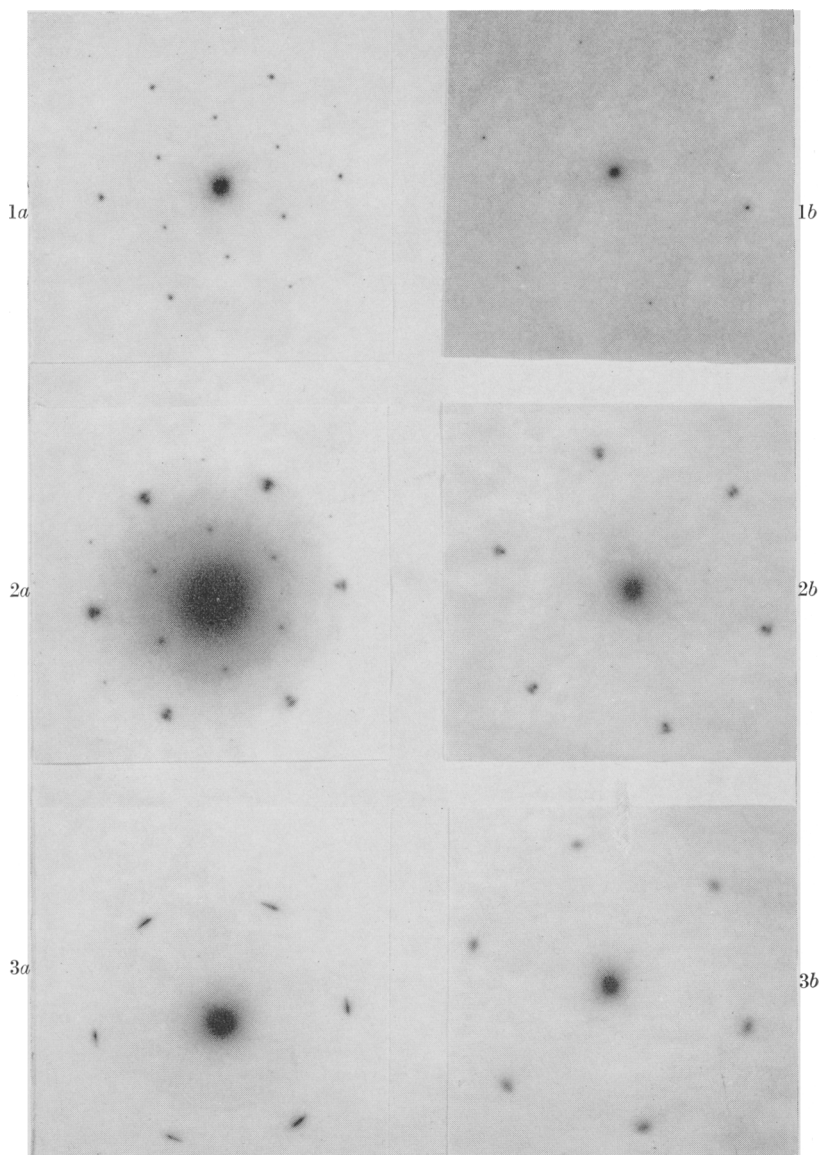
FIGS. 1 to 3. FIG. 1 (top). Electron-diffractograms of (a) Ca(OH)₂ and (b) Mg(OH)₂. FIG. 2 (middle). Electron diffractograms of the crystals of fig. 1, after partly decomposing hydroxides to oxides, showing splitting of 110 spots (splitting of 100 and 200 visible on original). (a) Ca(OH)₂ and (b) Mg(OH)₂. FIG. 3 (bottom). Electron-diffractogram of completely decomposed crystals. (a) CaO, (b) MgO.

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Postscript. Balmbra, Clunie, and Goodman (1966) have repeated the electron diffraction work of Goodman (1958), but used heating in an external vacuum furnace, instead of electron bombardment in the microscope, to produce the dehydration. They obtained similar electron diffraction diagrams, which suggests that the effects obtained by electron bombardment in the electron microscope are essentially due to heating rather than ionization. However, their evidence that an intermediate phase occurs without loss of water seems inconclusive, since the small crystals scraped from a cleavage face, which they used, would have lost a considerable amount of water after 15 min at 320° C (Anderson and Horlock, 1962).

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