Electron Diffraction Indications of Lattice Disorder in 3.15 Å C-S-H Phase

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Continuous streaks parallel to a* on electron diffraction patterns of 3.15 Å C—S—H phase reveal stacking disorder. The majority of crystals exhibit streaks only for $k + l = 2n$ ($k = 2n + 1$ and $l = 2n + 1$) corresponding to an Å-centered polytype. Streaks at both $k + l = 2n$ and $k + l = 2n + 1$ indicate an intergrowth of $A \infty 22$ and $P \infty 21$ in various proportions. Co-existing xonotlite predominantly has $P \infty 21$ stacking type.

In an earlier paper[1] we have described the general features of 3.15 Å C—S—H phase occuring in hidrothermally treated γ-dicalcium silicate-quarz mixtures. Sharp reflections on electron-diffraction patterns indicate a pseudo--cell, refined by X-ray powder data, with $a = 12.02$ Å, $b = 3.71$ Å, $c = 7.07$ Å,
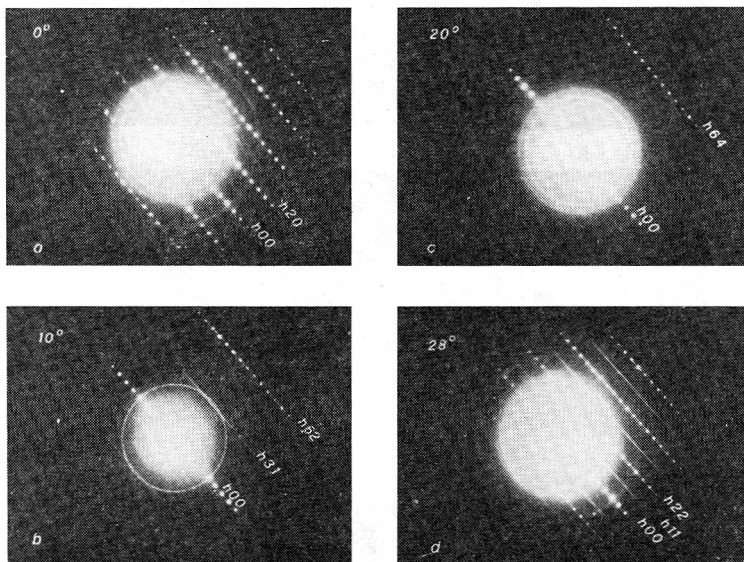

Figure 1. Characteristic ED patterns of the crystal showing streaks for $k + l = 2n + 1$ and $k + l = 2n$. The extra, weak spots along the rows with $k = 2n$ are probably due to twinning.
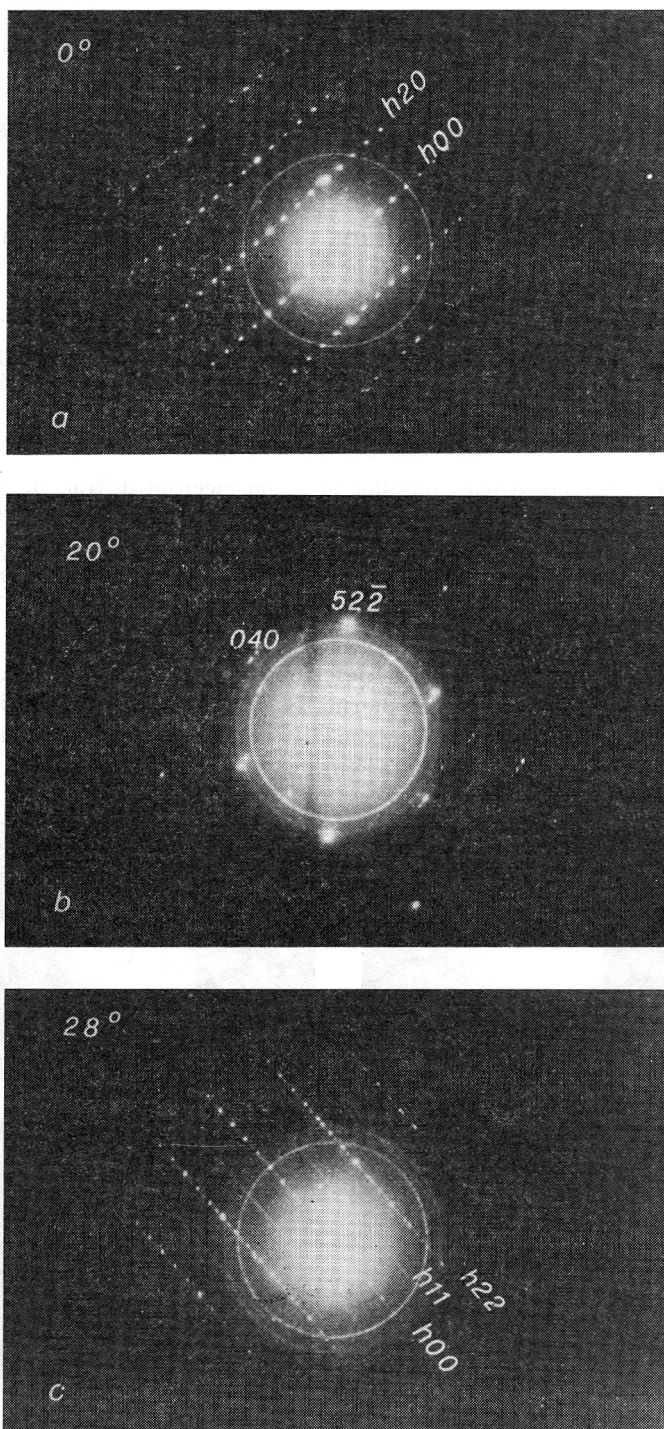
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Figure 2. Characteristic ED patterns of the crystal showing streaks for k + 1 = 2n a) hk0 reciprocal lattice section b) tilt axis — b*. c) tilt axis — a*.

and $\beta = 98^0$, but continuous streaks parallel to a^* show that b and c are doubled in the true unit cell, while a has an indefinite value. From the transformation to β wollastonite at 700 °C it was concluded that the silicate part of the structure is built of »dreierketten«. However, $b = 7.42$ Å is rather larger than b for other calcium silicates containing dreierketten, and the difference may have some structural significance. From a sharp weight loss at 700 °C it follows that there are four OH groups per unit cell. However, taking into account also the continuous loss of weight between 300 and 650 °C, their amount is about three times higher. Considering these TG data and the Ca/Si ratio determined by the TEAM system the composition of the 3.15 Å C—S—H phase is either $Ca_8Si_{10}O_{27}(OH)_2$ or $Ca_8Si_{10}O_{25}(OH)_6$[2]. It is also possible that some water moleculs are present in addition to the OH ions that give water at 700 °C. Streaks on electron diffraction patterns revealed stacking disorder, and so the phase provides also an example of O—D structure[3] like wollastonite[4], foshagite[5], and xonotlite[6]. The streaks observed for $k + l = 2n$ indicated the suffix $A \infty 22$ (referring to pseudocell with $b = 3.71$ Å and $c = 7.07$ Å) for the reciprocal lattice of the 3.15 Å C—S—H phase (see Ref. 8). However, as streaks were also noticeable for $k + l = 2n + 1$, we presumed originally the true suffix to be $P \infty 22$.[1]

In order to define as precisely as possible the positions and relative intensities of streaky reflections associated with the positions of silicate anions[7], we registered series of ED-patterns corresponding to different reciprocal lattice sections using Philips EM 300 electron microscope supplied with a goniometer stage and rotation specimen holder. Investigations were carried out on a sample which was prepared by treating compacts of γ-dicalcium silicate--quartz mixtures (Ca/Si = 1 : 1) at 250 °C. Superheated steam conditions were maintained during the first period of reaction. The product contained both 3.15 Å C—S—H phase and xonotlite. TEM specimens were prepared by wet grinding of the sample in an agate ball mill and by disintegrating it in alcohol by ultrasonic treatment. Diluted suspension was sprayed on a carbon film, on which a thin layer of aluminium was evaporated to serve as internal standard. Series of ED patterns obtained by tilting one of the examined crystals around a^* are shown in Figure 1 a-d. Considering these patterns it seems that the suffix $P \infty 22$ corresponds to the reciprocal lattice of the 3.15 Å C—S—H phase. However, the majority of crystals exhibit streaks for $k + l = 2n$ ($k = 2n + 1$ and $l = 2n + 1$) only (Figure 2) corresponding to an A-cen-
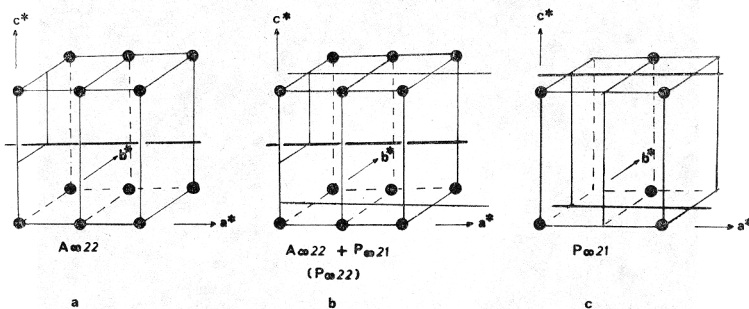

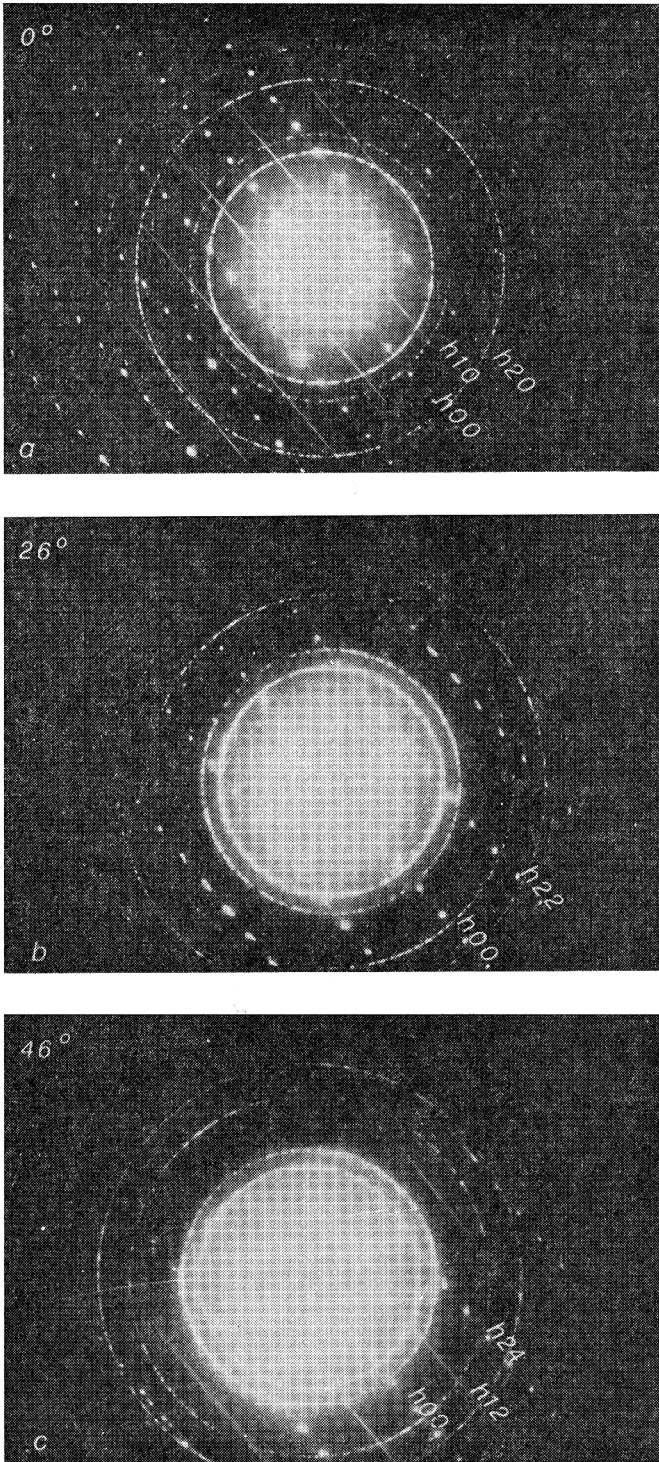Figure 3. Reciprocal lattices for 3.15 Å C—S—H phase (a and b) and xonotlite (c)

Figure 4. ED patterns of xonotlite, tilt axis — a^*.

tered polytype (Figure 3a). This polytype definitely prevails in the crystal structure of the 3.15 Å C—S—H phase; even in the case of crystals showing streaks both for k + l = 2n and k + l = 2n + 1 those for k + l = 2n are stronger (Figure 1). Most probably these crystals are intergrowts od A ∞ 22 and P ∞ 21 polytypes, and the suffix P ∞ 22 can appead as a result of the superposition of their reciprocal lattices (Figure 3b). Tentative structure of the 3.15 Å C—S—H phase[2] supports this view; the silicate part of the structure is condensation product of xonotlite ribbons and pyrosilicate groups. In the case od P ∞ 22 polytype the distance between silicate anions in c-direction should have been 2 × 7 Å; this is not possible for such a type of structure, which is according to the position of its CaO-sheets very similar to foshagite.

It is interesting to note that co-existing xonotlite predominantly has P ∞ 21 stacking type (Figure 3c) as seen from Figure. 4 which shows ED patterns of xonotlite obtained by tilting crystal around a^*. In case of xonotlite higher preparation temperatures ($>$ 185 °C) favour this polytype[8]. It can thus been concluded that the formation of an A-centered polytype in co-existing 3.15 Å C—S—H phase is favoured by steric reasons, though it has yet to be ascertained by the complete crystal structure determination.

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SAŽETAK

Elektronsko difrakcijski pokazatelji neuređenosti rešetke u 3.15 Å C—S—H fazi

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Neuređenost rešetke s obzirom na položaj silikatnih aniona u strukturi 3.15 Å C—S—H faze proučavana je metodom elektronske difrakcije. Uzimajući u obzir raspored i intenzitet difrakcijskih pruga na nizu difrakcijskih slika, koje odgovaraju različitim presjecima recipročne rešetke, ustanovljeno je da kristaliti 3.15 Å C—S—H faze odgovaraju uglavnom centriranom A ∞ 22 politipu, iako su na većem broju čestica istovremeno registrirani i oni efekti koji potječu od primitivnog P ∞ 21 motiva. Određeno je da je P ∞ 21 politip karakterističan za prateći ksonotlit.

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