

## Structurally Related Dicalcium Silicate Phases

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### Abstract

From careful measurement and indexing of the powder diffraction patterns obtained for pure dicalcium silicate, unit-cell parameter *vs* temperature plots have been obtained covering the  $\beta$  and  $\alpha'$  dicalcium silicate phases. It is found that these phases are all closely related, the temperature variations, for example, being gradual from 293 K (the  $\beta$  phase) and more discontinuous between 993 and 1043 K corresponding to the  $\beta = \alpha'_L$  transition. Our conclusions lead to a simplified dicalcium silicate transformation scheme which requires that there is no phase differentiation within the  $\beta$ -phase regime.

### Introduction

There is still considerable uncertainty concerning the exact polymorphic scheme for pure dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ , or  $\text{C}_2\text{S}^*$  in shortened form). As part of a more generalized investigation into this topic, we have studied the variation with temperature of the  $\text{C}_2\text{S}$  unit-cell constants using a high-temperature powder

camera. While the  $\gamma$  phase is significantly different from the other  $\text{C}_2\text{S}$  structures, there is some evidence that all the remaining ( $\beta$ ,  $\alpha'_L$ ,  $\alpha'_H$  and  $\alpha$ )  $\text{C}_2\text{S}$  phases are structurally closely related, as shown by comparison with the low  $\text{K}_2\text{SO}_4$  structure (see Fig. 1*a* and *b*). The temperature plots obtained appear to support this view.

### Method

A high-temperature Guinier–Lenné powder camera was used, possessing a specimen temperature range from room temperature to 1543 K. This range covers all known  $\text{C}_2\text{S}$  transformations except the  $\alpha'_H = \alpha$  transformation. Using 120 h heating and cooling cycles, several pure  $\text{C}_2\text{S}$  samples were studied. The samples were prepared by standard methods (by heating ground stoichiometric mixtures of pure CaO and  $\text{SiO}_2$  to 1773 K, maintaining this temperature for one hour, cooling to 1673 K, maintaining this latter temperature for three hours, and then quenching) and selected on the basis of their known purity [emission spectroscopy tests and scanning electron microscope (SEM) energy-dispersive analysis of X-ray fluorescence (EDAX) confirmed that our samples were stoichiometric  $\text{Ca}_2\text{SiO}_4$ ] and the quality of their diffraction

\* In cement chemists' notation,  $\text{CaO} \equiv \text{C}$ ,  $\text{SiO}_2 \equiv \text{S}$ .

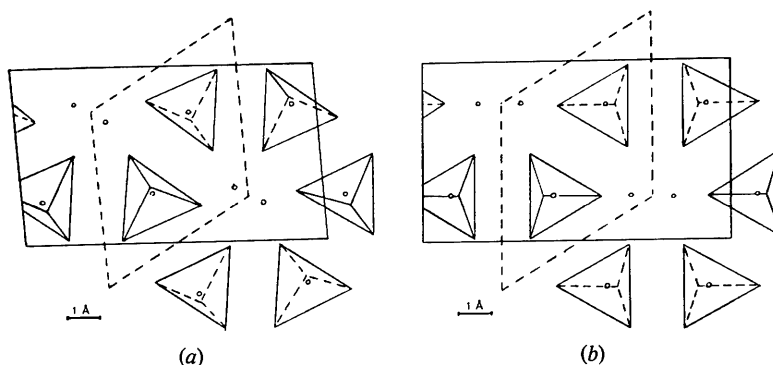


Fig. 1.  $\text{SiO}_4$  tetrahedra are as shown. Ca atoms are shown as small open circles. (a) Projection of the  $\beta$ - $\text{C}_2\text{S}$  structure, showing both the true unit cell (solid lines) and pseudohexagonal unit cell (dashed lines) (Eysel & Hahn, 1970; Midgley, 1952; Regourd & Guinier, 1974; Cruickshank, 1964). (b) Projection of the  $\alpha'$ - $\text{C}_2\text{S}$  structure based on the low  $\text{K}_2\text{SO}_4$  structure, showing both the true unit cell (solid lines) and the pseudohexagonal unit cell (dashed lines) (Eysel & Hahn, 1970; Suzuki & Yamaguchi, 1969; Regourd & Guinier, 1974).

patterns. Using repeated cycles (both heating and cooling cycles as the patterns obtained were reversible) for several samples and by careful measurement of the resulting diffraction patterns over 50 K intervals, we achieved the required accuracy in  $d$  spacing (about 0.002 at 2.5 Å spacings). The lines from the platinum sample grid were used as an internal standard for the  $C_2S$  diffraction patterns.

The indexing of the patterns was effected by a combination of the use of previously published data (Midgley, 1952; Regourd, Bigare, Forest & Guinier, 1969) and crystallographic package programs *LAPOD*\* and *DECAL*† (Langford & Marriner, 1973). At selected temperatures (293, 543, 993, 1293 and 1543 K), the larger  $d$  spacings could be fairly unambiguously indexed by comparison with the previously published data and an approximate unit cell determined. Further indexing was then achieved by comparing the remaining lines with the  $d$  spacings from the approximate unit cell. Incorrectly indexed lines were usually easily spotted by following the temperature variations of the  $d$  spacings and remaining lines of doubtful indexing were removed. The final refinements were carried out at 50 K intervals from 293 to 1543 K, using between 25 and 40 indexed lines at each temperature.

The axes for  $\beta$ - $C_2S$  were chosen in accordance with crystallographic convention for the monoclinic system and maintained through the orthorhombic  $\alpha'$  phases for the sake of continuity.

### Results and discussion

The unit-cell parameters for the  $\beta$  and  $\alpha$  phases are given in Table 1 for five particular temperatures, and also shown graphically in Fig. 2(a)–(e). Although there is some evidence that the  $\alpha'$  phases are superstructures, for the sake of graphical continuity Fig. 2(a)–(c) are all based on the simplest unit cells.

\* The program *LAPOD* refines given unit-cell parameters and indexed  $d$  spacings by Cohen's (1935) method of least squares and gives an estimate of the standard deviation in unit-cell constants.

† The program *DECAL* produces a listing of all possible  $d$  spacings along with indexes for any given unit cell and space group, down to a chosen minimum  $d$  spacing.

Table 1. Unit-cell parameters determined for  $\beta$  and  $\alpha'$   $C_2S$  phases (standard deviations in the last digit are given in parentheses) at various temperatures (see also Fig. 2a–e)

Temp. (K)	$C_2S$	Crystalline parameters			
		$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ angle (°)
293	$\beta$	5.515 (2)	6.752 (3)	9.294 (2)	94.34 (3)
993	$\beta$	5.544 (3)	6.802 (4)	9.419 (6)	93.28 (5)
1043	$\alpha'_L$	11.150 (6)	6.820 (4)	18.822 (7)	90.00
1293	$\alpha'_L$	11.207 (4)	6.849 (1)	18.952 (6)	90.00
1543	$\alpha'_H$	11.227 (4)	6.865 (3)	19.110 (12)	90.00

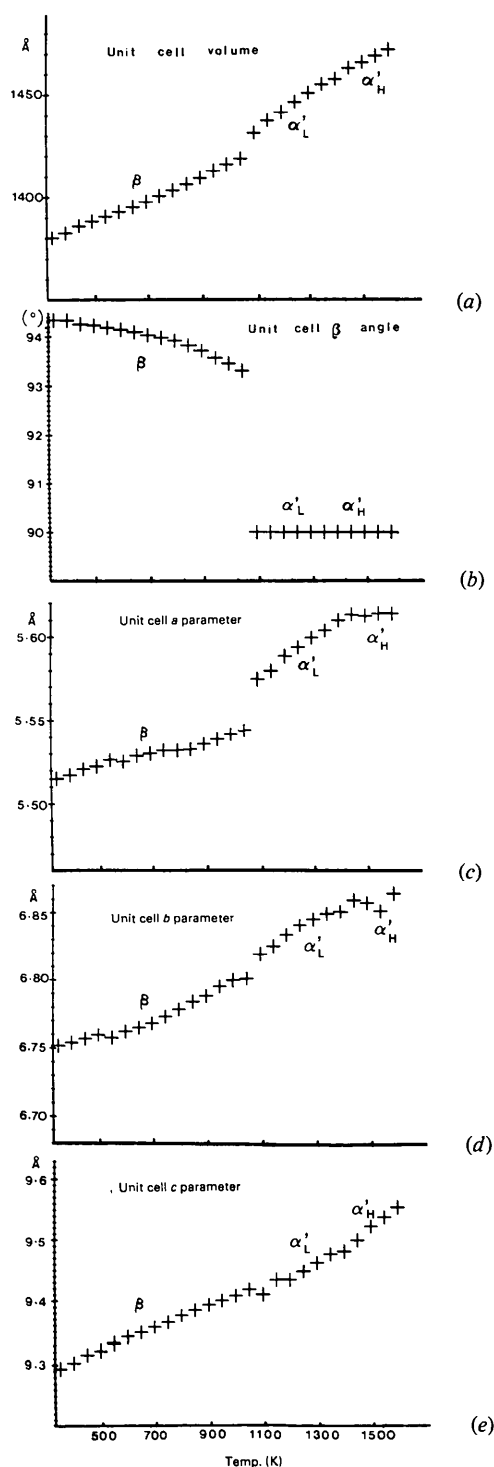


Fig. 2. Variations with temperature of the  $\beta$  and  $\alpha'$ - $C_2S$  unit-cell parameters. All parameters show a marked discontinuity between 993 and 1043 K corresponding to the  $\beta = \alpha'_L$  transformation and a change in slope (excluding the  $\beta$ -angle plot) at 1393 K corresponding to the  $\alpha'_L = \alpha'_H$  transformation. The accuracy of the plots at 1493 and 1543 K is diminished because of a fall-off in the intensity of the diffraction patterns.

Our work shows that the  $\alpha'$  phases are fairly complex superstructures with a doubling of at least the  $a$  and  $c$  parameters. This is in accordance with the work of Regourd *et al.* (1969) who found that they could only fully index their  $\alpha'_L-C_2S$  patterns on the basis of a superstructure involving a doubling up of their  $a$  and  $b$  cell parameters (our  $a$  and  $c$  parameters). The disappearance of their superstructure lines at 1433 K appears to support the case for the  $\alpha'_L = \alpha'_H$  transition suspected at this temperature. However, using a Guinier-Lenné camera we have found the superstructure lines to persist in the  $\alpha'_H$  phase up to at least 1543 K.

The unit cells for the  $\beta$  phase at 293 and 993 K appear to correspond to the  $\beta_L$  and  $\beta_H$  phases postulated by other workers (Niesel & Thormann, 1967; Niesel, 1972; Bredig, 1950) to be separate but structurally related phases. Our data, however, supports our contention that these phases are temperature-related extremes of the same  $\beta$  phase. The question of two separate or one continuous  $\beta$  phase is, however, compounded by grain-size effects (Niesel, 1972). The authors feel, however, that the continuous  $\beta$ -phase hypothesis can still accommodate these effects: if, for example, on cooling, the grain size permits a  $\beta \rightarrow \gamma$  transition (coarse grain), the  $\beta$ -phase unit cell just prior to the transformation should correspond to the unit cell for that particular temperature read off Fig. 2 (*e.g.* the so-called  $\beta_H$  if the temperature is close to 993 K), otherwise the low-temperature end member (the so-called  $\beta_L$ ) would be the room-temperature product.

Fig. 2(a)–(e) is particularly informative in that it illustrates three different situations with regard to the structurally related  $C_2S$  phases. Firstly, it is clear that there are no phase changes of any type in the range 293 to 993 K. As we have pointed out, this range is normally associated with the two so-called  $\beta_L$  and  $\beta_H$  phases, but we maintain that there is only one  $\beta$  phase and that  $\beta_L$  and  $\beta_H$  are just the temperature-related extremes of a single phase. At 993 K there is a small

but definite first-order transformation ( $\beta = \alpha'_L$ ) characterized in all the temperature plots (Fig. 2a–e) especially with regard to the discontinuous change of  $\beta$  angle to  $90^\circ$ . Between 993 and 1543 K there is a noticeable change in slope of the graphs of the cell dimensions at 1393 K indicating a second-order transformation, which would agree well with the known  $\alpha'_L = \alpha'_H$  transition at about 1430 K.

The  $\beta$  angle is continually changing up to 993 K (the  $\beta$  phase) implying that there must be some gradual relative rotation of the  $SiO_4$  tetrahedra. Fig. 1 illustrates this rotation and the discontinuous change of  $\beta$  angle to  $90^\circ$  at 993 K to the orthorhombic form.

On the basis of these variations and in keeping with the DTA transition peaks (Regourd & Guinier, 1974), we then propose that somewhat simplified transformation scheme for  $C_2S$  shown in Fig. 3, the  $\gamma$  phase being included for the sake of completeness.

## Conclusions

The structural changes involving the  $\beta$  and  $\alpha'$  phases can be resolved in terms of differential thermal expansion (dilatational phase changes) and rotational transformations (Buerger, 1951). Both first-order ( $\beta = \alpha'_L$ ) and second-order ( $\alpha'_L = \alpha'_H$ ) transformations are shown by the temperature plots (Fig. 2a–e) but there is no evidence for any type of transformation within the  $\beta$  phase (293 to 993 K). Some previous workers (Niesel & Thormann, 1967; Niesel, 1972; Bredig, 1950), however, have subdivided the  $\beta$  phase into  $\beta_H$  and  $\beta_L$  (or  $\beta'$  and  $\beta$ ) phases but it is our contention that these are temperature extremes of a single  $\beta$  phase.

Finally, it is hoped that by using interactive computer graphics display facilities, these phase changes may be related more directly to structural changes occurring within the changing unit cell.

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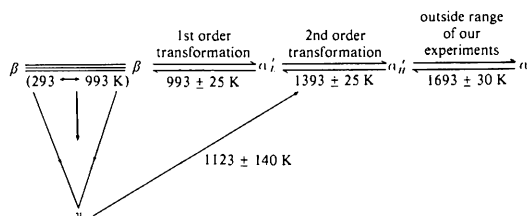


Fig. 3. The proposed transformation scheme for the known  $C_2S$  phases. The horizontal set are all structurally related and the treble line indicates a single  $\beta$  phase over the indicated temperature range, the  $\beta \rightarrow \gamma$  transformation being presumed to occur at any temperature within the range indicated.  $A \pm$  range is indicated for each transition temperature; these refer to the considerable range of values to be found in the literature for the  $\alpha = \alpha'_H$  and  $\gamma \rightarrow \alpha'_L$  transitions, and to the estimated probable error for the remaining transitions determined in this work.

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## Computer Simulation of Polytypes\*

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### Abstract

Polytypes have been simulated, treating them as analogues of a one-dimensional spin-half Ising chain with competing short-range and infinite-range interactions. Short-range interactions are treated as random variables to approximate conditions of growth from melt as well as from vapour. Besides ordered polytypes up to  $12R$ , short stretches of long-period polytypes (up to  $33R$ ) have been observed. Such long-period sequences could be of significance in the context of Frank's theory of polytypism. The form of short-range interactions employed in the study has been justified by carrying out model potential calculations.

### I. Introduction

In an earlier paper (Ramasesha & Rao, 1977, referred to as R & R from here on), we discussed our attempts at computer simulation of polytypes treating them as analogues of a one-dimensional spin-half Ising chain with competing short- and infinite-range interactions. The growth conditions simulated were akin to the conditions of growth of polytypes from melt, but the interaction parameters were considered as constant during any given simulation. However, during the growth of a polytype (whether it be from melt or vapour), it is reasonable to assume that the atoms in the layers are jostling about leading to fluctuations in interlayer interaction strength. A proper simulation of polytypes should take into account such fluctuations.

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This becomes possible if we treat the interaction parameters in the simulation as random variables (varying with time) during any given simulation. We have, therefore, carried out a computer simulation of polytype growth from vapour employing both constant and fluctuating short-range interaction parameters. Finally, we have carried out model potential calculations aimed at justifying the form of short-range interaction parameters employed in the present study.

### II. Model employed

Since any layer in a close-packed structure can either be in a hexagonal ( $h$ ) or a cubic ( $k$ ) configuration, each layer can be represented by any of the two spin states of an Ising spin with  $S = \frac{1}{2}$ . In this representation, a polytype corresponds to an ordered (equilibrium or metastable<sup>†</sup>) state of a chain of such spins. To obtain such an ordered state, it is necessary to invoke infinite-range interactions between the spins, the system of interest being essentially one-dimensional. As already discussed by R & R, such an interaction term can arise due to elastic interactions between the layers. This interaction favours a completely cubic or a completely hexagonal close-packed arrangement. In spin terminology, this is equivalent to the two possible states of magnetization of a ferromagnetic Ising chain. The elastic interaction, being infinite ranged, would in

<sup>†</sup> It is not possible to say definitely whether a given polytypic form is an equilibrium or a metastable phase under given temperature and pressure conditions because many polytypic forms exist with no discernible differences in stability at ordinary temperatures and pressures.