*Acta Cryst.* (1986). B42, 417–422

# A Preliminary Electron-Microscope Study of the $\beta \rightleftarrows \alpha'$ Transformation of Distrontium Silicate, $Sr_2SiO_4$

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(*Received 2 January 1986; accepted 23 May 1986*)


## Abstract

Some electron-microscope observations (mainly electron diffraction) confirm the suggestion [Barbier & Hyde (1985). *Acta Cryst.* B41, 383–390] that a modulated structure is likely to intervene in the $\beta$-$\rightleftarrows \alpha'$-$Sr_2SiO_4$ transformation. The diffraction patterns from beam-heated crystals indicate two apparently incommensurate modulations, $\mathbf{q}_1 = 0{\cdot}39\mathbf{b}^*$ and $\mathbf{q}_2 = 0{\cdot}30\mathbf{b}^*$. There are also variations in the monoclinic angle, $\beta$, of the unit cell, and changes in symmetry as indicated by systematic absences of Bragg reflections. While many questions remain unanswered, it is clear that previous understanding and explanations of the transformation must be augmented by the inclusion of periodic modulation of the structure(s) – for $Sr_2SiO_4$, and probably for $Ca_2SiO_4$ also.


## Introduction

Phase transformations between the $\beta$ and $\alpha'$ forms of $Ca_2SiO_4$ and of $Sr_2SiO_4$ are analogous. Both are interesting as representatives in the broad class of $\beta$-$K_2SO_4$-related types. A recent analysis of the crystal structures of the various polymorphs of $Ca_2SiO_4$ and $Sr_2SiO_4$ based on the geometries of their cation arrays (Barbier & Hyde, 1985) led to the suggestion that incommensurately modulated structures might be expected to intervene in the $\beta \rightleftarrows \alpha'$ transformations, and that electron-microscopy/diffraction studies were desirable.

In $Ca_2SiO_4$ the transformation temperature is ~953 K (Eysel & Hahn, 1970) but in $Sr_2SiO_4$ it is ~358 K (Catti, Gazzoni, Ivaldi & Zanini, 1983). The latter is more readily accessible by beam-heating in an electron microscope, and so we have carried out a preliminary examination of $Sr_2SiO_4$ by this method.

The lower-temperature polymorph, $\beta$-$Sr_2SiO_4$, is monoclinic ($P2_1/n$), with the structure (Catti, Gazzoni & Ivaldi, 1983) depicted in Fig. 1 as $SiO_4$-centred trigonal prisms of $Sr_6$. The higher-temperature polymorph, $\alpha'$-$Sr_2SiO_4$, is probably monoclinic ($P2_1/n$) also, similar to the $\beta$ form but with cell angle 90° compared with 92·67° for the $\beta$ form (Catti, Gazzoni, Ivaldi & Zanini, 1983). Its structure is shown in Fig. 2: the 'disordered' model of Catti, Gazzoni, Ivaldi & Zanini (1983) according to which there are two twin forms related by reflection in (100). [It has not proved possible to distinguish unequivocally this model from the 'average' structure with orthorhombic (*Pmnb*) symmetry (Catti, Gazzoni, Ivaldi & Zanini, 1983).]

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## Experimental

Following Catti, Gazzoni & Ivaldi (1983) $Sr_2SiO_4$ was synthesized by slow cooling (from ~1770 K) of a melt composed of a stoichiometric mixture of $SrCO_3$ and $SiO_2$ plus an $SrF_2$ flux. Single crystals were mechanically separated from the resulting solid, crushed, and dispersed in isobutanol. A drop of the dispersion was deposited on a holey carbon film (supported by a copper grid) and examined in a JEOL 100 CX or 200 CX microscope, mainly by electron diffraction. The $\beta \rightarrow \alpha'$ transformation was induced by focusing the electron beam on a crystal.

## Observations

### (i) *Electron diffraction*

The most commonly observed low-index diffraction patterns had zone axes [100] or [001] (settings $P12_1/n1$ for $\beta$ and *Pmnb* for $\alpha'$).‡ An example of each of these for the $\beta$ phase is shown in Fig. 3(*a*) and (*b*).

Focusing the electron beam, to increase its intensity and 'heat' the crystal, often resulted in changes to these patterns, the most common of which were instantaneous and reversible, and are shown in Fig. 4. In Fig. 4(*a*) ([100] zone axis), in addition to the stronger Bragg reflections (as in Fig. 3*a*) weaker satellite reflections are visible – in pairs oriented along $\mathbf{b}^*$ and symmetrically disposed about the Bragg spots. When the beam was defocused the same crystal gave the diffraction pattern in Fig. 4(*b*), which is analogous

‡ We use throughout the same consistent set of unit-cell axial settings as before (Barbier & Hyde, 1985), $a < b < c$.

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to Fig. 3($a$), but no longer symmetrically oriented. Its **a** axis has tilted by approximately 2·6 to 2·8° about $\mathbf{b}^*$ (*i.e.* in the **c** direction): clearly the unit-cell angle of $\beta = 92·67°$ [for $\beta$-$Sr_2SiO_4$ at 298 K; very slightly less at higher temperatures (Catti & Gazzoni, 1983)] in Fig. 4($b$) changes to approximately 90° in Fig. 4($a$).

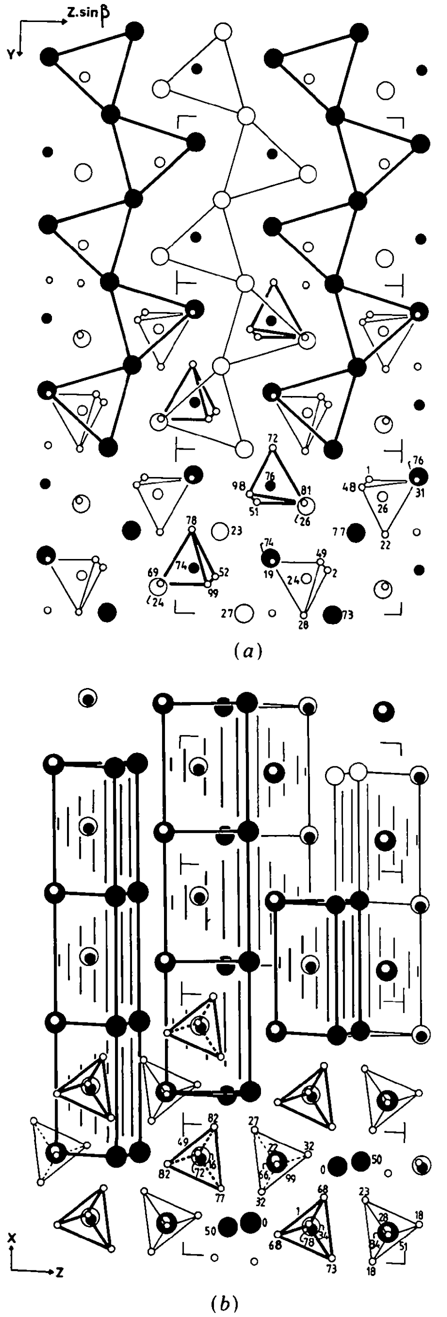


Fig. 1. The monoclinic structure of $\beta$-$Sr_2SiO_4$ projected ($a$) along [100] and ($b$) on (010). Large circles are Sr, medium circles are Si and small circles are O atoms: heights are in units of ($a$) $100x/a$, ($b$) $100y/b$. In each case the bottom of the figure shows Sr atoms and $SiO_4$ tetrahedra, the centre $SiO_4$-centred $Sr_6$ trigonal prisms, and the top the **$PbCl_2$**-like $Sr_2Si$ array.

Fig. 4($c$) shows both types of diffraction pattern in the same exposure, during which the transformation occurred. Fig. 5($a$) is similar to Fig. 4($c$); its satellites are very sharp. Measured from the nearest Bragg reflection and within the accuracy of measurement, all such satellites appear to have a spacing $\mathbf{q}_1 = \pm 0·39\mathbf{b}^*$.

A different type of diffraction pattern in Fig. 5($b$) was occasionally observed. The spacings of the Bragg reflections indicate that this also has a [100] zone

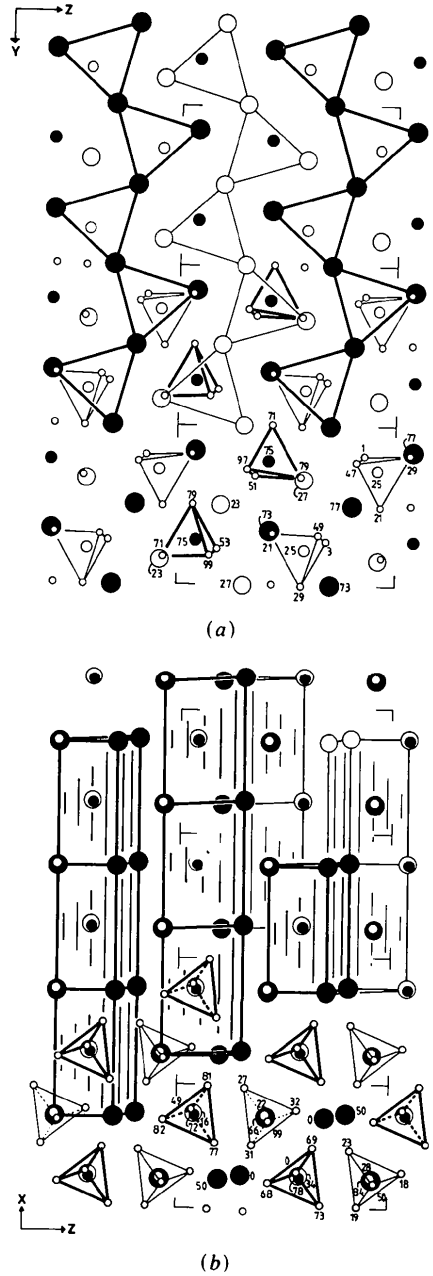


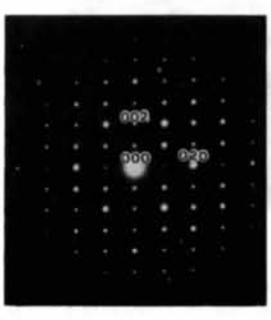
Fig. 2. The monoclinic (pseudo-orthorhombic) structure of $\alpha'$-$Sr_2SiO_4$. Compare Fig. 1. Twinning is by reflection in (100).

axis, but it differs from Fig. 5($a$) *etc.* in two ways: (1) the (major) satellite spacing is now $\mathbf{q}_2 = \pm 0{\cdot}30\mathbf{b}^*$, and (2) half the rows of Bragg reflections are now absent - the condition being $0kl$, $l = 2n$ (and probably also $0k0$, $k = 2n$), appropriate to space group $Pc2_1$- or $Pcn$- but *not* to $P2_1/n$ or $Pmnb$.

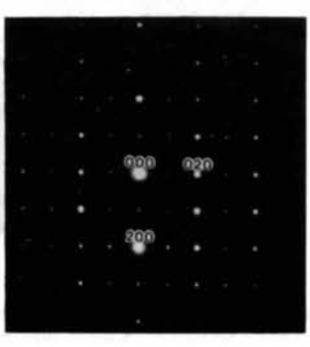
The diffraction pattern in Fig. 5($c$) consists of both those in Figs. 5($a$) and 5($b$), including both sets of satellites $\mathbf{q}_1$, and $\mathbf{q}_2$, although the former are weaker than the latter. But it is also clear that their zone axes are not coincident; they are offset by about 0·8° (and again, at least approximately, by tilting about $\mathbf{b}^*$ in the direction of $\mathbf{c}^*$), which suggests at least some unit-cell angles $\beta \neq 90{\cdot}0$ or 92·67°.

Double diffraction makes it difficult to be sure of the extinction conditions for the satellite reflections (and, in some cases, for the Bragg reflections also), but it appears possible that the $\mathbf{q}_1$ satellites (along $\mathbf{b}^*$) occur either side of $0k0$ only when $k = 2n+1$, and $\mathbf{q}_2$ only when $k = 2n$: along $0k2$ possibly $k = 2n$ for $\mathbf{q}_1$ and $2n+1$ for $\mathbf{q}_2$. The uncertainty is too great to be confident of symmetries.

[001] zone-axis patterns were less frequently observed and, in this case, focusing the electron beam resulted in much slower changes. The resulting patterns were of two types, shown in Fig. 6. In Fig. 6($a$) the Bragg reflections probably obey the conditions $h00$, $h = 2n$, and certainly $hk0$, $k = 2n$ appropriate for $Pmnb$, and the satellites appear to be of the type $\mathbf{q}_2 = 0{\cdot}30\mathbf{b}^*$ *either side of the missing Bragg reflection* but not around the reflections observed (equivalent to $\mathbf{q}_3 = 0{\cdot}35\mathbf{b}^*$ either side of the Bragg reflections which are present). This is consistent with the surmised condition for $\mathbf{q}_1$ (above) - that they appear to occur about $0k0$ only for $k = 2n+1$ - *but not consistent with the condition deduced for* $\mathbf{q}_2$! Fig. 6($b$) is similar to Fig. 6($a$), although the reflections appear not to be perfectly aligned along $\mathbf{b}^*$. Ignoring this (the beam is very strongly focused) then this diffraction pattern appears to be that of Fig. 6($a$) but *with* additional $k = 2n+1$ Bragg reflections missing in that figure.




($a$)

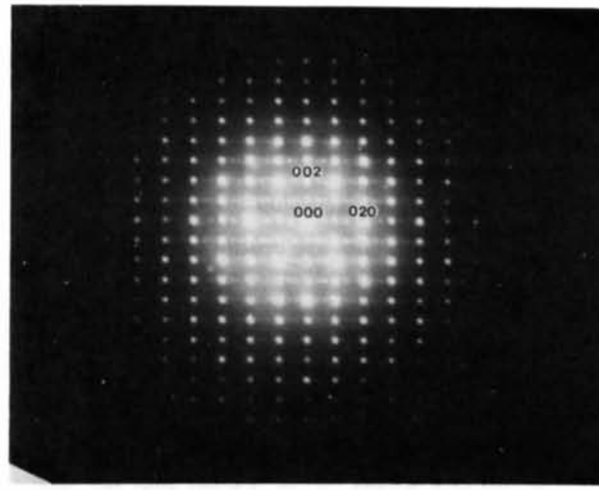



($b$)

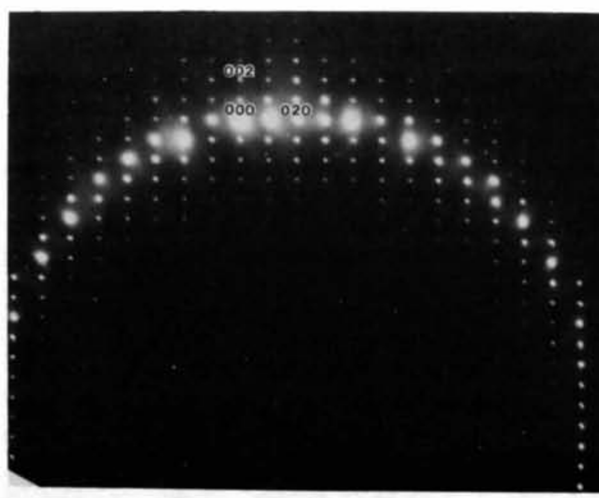
Fig. 3. ($a$) [100] and ($b$) [001] zone axis diffraction patterns from $\beta$-$Sr_2SiO_4$.

(ii) *Electron microscope images*

Generally, it was difficult to get good images. The only exception was from the crystal which gave the electron diffraction pattern in Fig. 6($b$). Using a small $[\sim(3\text{Å})^{-1}]$ objective aperture we obtained the image in Fig. 7($a$) and, with larger aperture, that in Fig. 7($b$). The first shows very obvious diffuse fringes, with very sharp and more closely spaced fringes at right angles. The spacing of the latter is measured as ~5·6 Å, equivalent to $d(100) = 5{\cdot}663$ Å for $\beta$-$Sr_2SiO_4$ or 5·682 Å for $\alpha'$-$Sr_2SiO_4$. The diffuse fringe spacing is ~10·3 Å, equivalent to *approximately* $(3/2)d(010)$ or $3d(020) = 10{\cdot}630$ Å for $\beta$ and 10·635 Å for $\alpha'$. Careful measurement, using the sharp fringes (for




($a$)




($b$)

Fig. 4. ($a$) Oriented [100] zone axis diffraction pattern of beam-heated $Sr_2SiO_4$ showing satellite reflections. ($b$) Diffraction pattern of the same crystal as in ($a$) when the electron beam is defocused: note the tilt of the zone axis and the disappearance of the satellites.

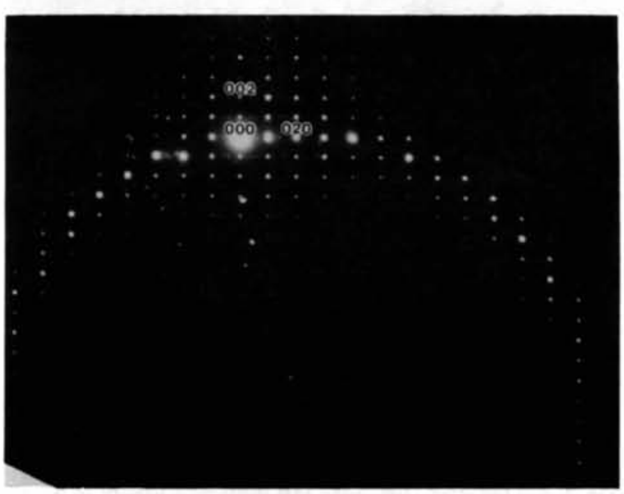
calibration) as 5·67 Å spacing [the average of $d(100)$ for $\beta$ and $\alpha'$], gives the broad fringe spacing as $10{\cdot}5 \pm 0{\cdot}1$ Å. (It is not entirely uniform, varying across the print by $\sim\pm1\%$.) If we assume the repeat corresponds to two fringes this gives $\mathbf{q} \approx 0{\cdot}34\mathbf{b}^*$ for both $\beta$ and $\alpha'$ - close to $3 \times \mathbf{b}$.

However, Fig. 7($b$) confirms that it is not exactly $3 \times \mathbf{b}$: we again see broad fringes similar to those in Fig. 7($a$) (as well as similar sharp fringes at right angles), and by the same method calculate $\mathbf{q} \approx 0{\cdot}35\mathbf{b}^*$ for both $\beta$ and $\alpha'$; but it is clear that their intensity and spacing are modulated. Our interpretation is that their true repeat distance is incommensurate with $3d(020)$, giving rise to the observed moiré effect (most obviously as a modulation of broad fringe intensity). This has a period (two maxima) of ~157 Å, from which we deduce a value of $\mathbf{q} \approx 0{\cdot}31\mathbf{b}^*$, which is to be compared with $\mathbf{q}_2 \approx 0{\cdot}30\mathbf{b}^*$ from the corresponding diffraction pattern: adequate agreement in view of the limited precision of measurement.

## Discussion

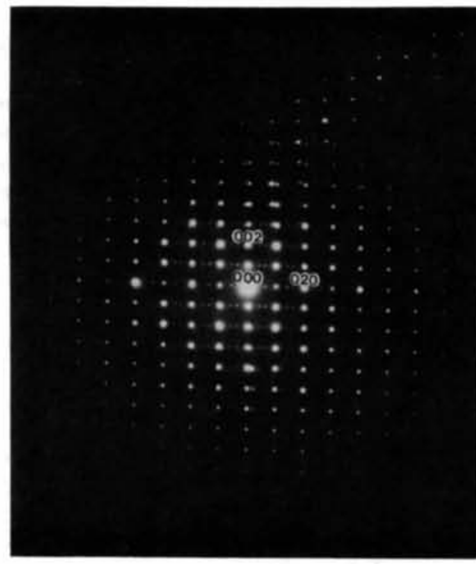
The present experiments are crude; in particular, the 'heating' of the specimen is uncontrolled, so that the temperatures involved are not known. But some of the results are quite precise: we observe two different sets of satellite reflections, with the different spacings apparently associated with different crystal symmetries: the value $\mathbf{q}_1 \approx 0{\cdot}39\mathbf{b}^*$ with $P2_1n$; the value $\mathbf{q}_2 \approx 0{\cdot}30\mathbf{b}^*$ with $Pc2_1$- or $Pcn$-. For the latter, more information is needed, but it is clear that the space group is neither that reported for $\beta$- nor that reported for $\alpha'$-$Sr_2SiO_4$.

These are new facts, consistent with our earlier suggestion that the $\beta \rightleftarrows \alpha'$ transition is likely to be associated with an incommensurate modulated structure (Barbier & Hyde, 1985). This result is not unexpected, in view of the large literature on the subject of modulated structures associated with phase transformations for other compounds with structures related to the $\beta$-$K_2SO_4$ type. Almost all of these are

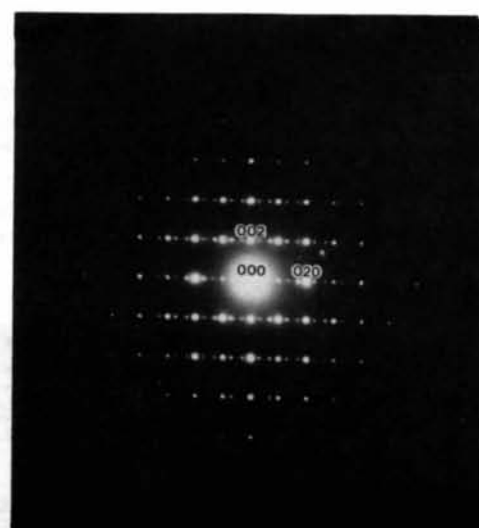



($c$)

Fig. 4 ($cont.$). ($c$) A combination of ($a$) and ($b$) owing to the transformation occurring during the exposure.




($a$)



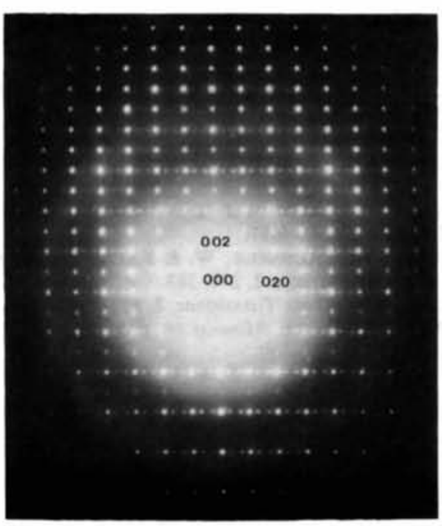

($b$)

Fig. 5. ($a$) Diffraction pattern similar to Fig. 4($c$), with very sharp satellite spots. ($b$) A quite different type of diffraction pattern, but with the same zone axis, [100], as in ($a$) and Fig. 4: half the $0kl^*$ rows are now absent, and the stronger satellites ($\mathbf{q}_2$) have a different spacing, $cf.$ especially Fig. 4($a$). (Note that both types of satellites are present, but $\mathbf{q}_1$ are very weak.)

modulated in the **b** direction, some with an approximately $2\times$ period [$(NH_4)_2BeF_4$ (Petzelt, 1981)] but most with an approximately $3\times$ period [$Rb_2ZnCl_4$ and $Rb_2ZnBr_4$ (Hogervorst & de Wolff, 1982); $K_2ZnCl_4$ (Kucharczyk, Paciorek & Kalicińska-Karut, 1981); $K_2SeO_4$ (Petzelt, 1981); *etc.*] - *cf.* our $\mathbf{q}_1$ which gives $\lambda_1 \approx 2{\cdot}6\times\mathbf{b}$ and $\mathbf{q}_2$ which gives $\lambda_2 \approx 3{\cdot}3\times\mathbf{b}^*$.

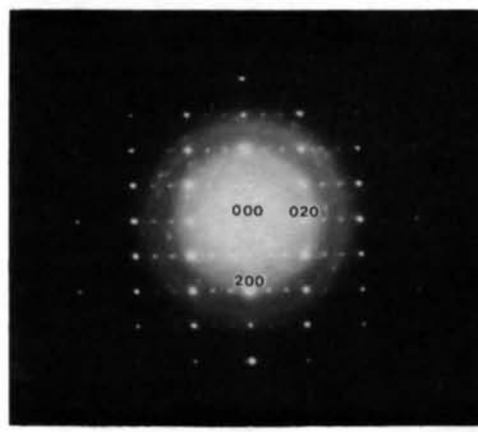
Strangely enough, previous recognition of this modulation phenomenon seems not to have carried over into the vast amount of research that has been published on $Ca_2SiO_4$ (or $Sr_2SiO_4$) or $Na_2SO_4$, $K_2SO_4$ *etc.*, all of which also have $\beta$-$K_2SO_4$-related structures. This is doubly strange in view of the discrepancies apparent in discussions of possible superstructures in the $\alpha'$-$Ca_2SiO_4$ phase (*Pmnb*). Particularly relevant in this context is the division of the $\alpha'$-$Ca_2SiO_4$ phase domain into two regions - at lower temperatures $\alpha'_L$ (973 K $\lesssim T \lesssim$ 1433 K) and at higher temperatures $\alpha'_H$ (1433 K $\leq T \leq$ 1723 K) (Eysel & Hahn, 1970). Of particular interest is the proposal that the *b* axis of $\alpha'_L$ is *tripled* (Saalfeld, 1975). The evidence is single-crystal oscillation photographs from which, as it appears to us, it would not be possible to assert that the diffraction pattern implies an *exactly* $3\times$ superlattice (rather than an approximately $3\times$ modulated structure). In view of our results, and the great similarity between $\beta$- and $\alpha'$-$Ca_2SiO_4$ and -$Sr_2SiO_4$, there is considerable doubt on this question. Indeed, this was exactly the situation for the low-temperature transition in $K_2SeO_4$: X-ray diffraction data suggested that a $3\times\mathbf{b}$ ($\mathbf{q}=\mathbf{b}^*/3$) superlattice developed when the *Pmnb* structure was cooled to 130 K; whereas subsequent neutron diffraction revealed that an incommensurate modulated structure, with **q** diffraction revealed that an incommensurate modulated structure, with $\mathbf{q}=(1-\delta)\mathbf{b}^*/3$ appeared at this temperature, with $\delta \approx 0{\cdot}07$ (*i.e.* $\mathbf{q}^{-1} = 3{\cdot}23\mathbf{b}$). As $T$ is reduced $\delta$ decreases to $\sim 0{\cdot}02$ at 93 K, at which temperature the structure 'locks in' to the $3\times\mathbf{b}$ superstructure, and $\delta$ jumps discontinuously to zero (Iizumi, Axe, Shirane & Shimaoka, 1977). [In $Sr_2SiO_4$ the analogue to this 'lock-in' would be the transition from the modulated structure(s) to the $\beta$ phase, with a $1\times\mathbf{b}$ structure.]

In their analysis of the observed behaviour of $K_2SeO_4$ Iizumi *et al.* (1977) identify the phonon mode whose softening is responsible for the structural

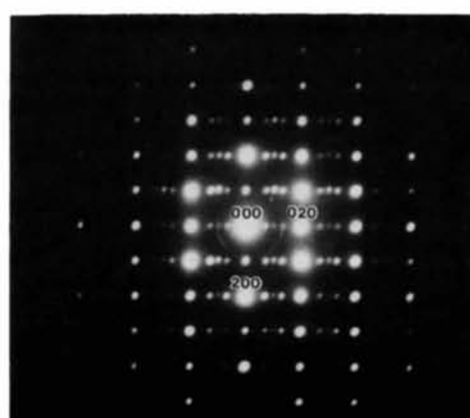



(*c*)

Fig. 5 (*cont.*). (*c*) Diffraction pattern equivalent to a combination of (*a*) and (*b*): both types of satellites, $\mathbf{q}_1$ and $\mathbf{q}_2$, are present, with comparable intensities; but notice that $\mathbf{q}_1$ predominates at the top of the figure (where *k* is odd and even), and $\mathbf{q}_2$ at the bottom (where *k* is only even), which means that there are two diffraction patterns with a small difference between the orientations of their zone axes.

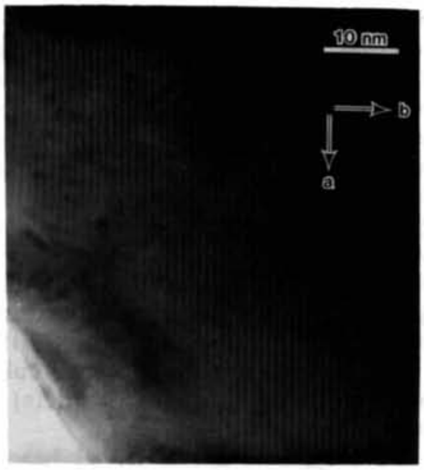



(*a*)

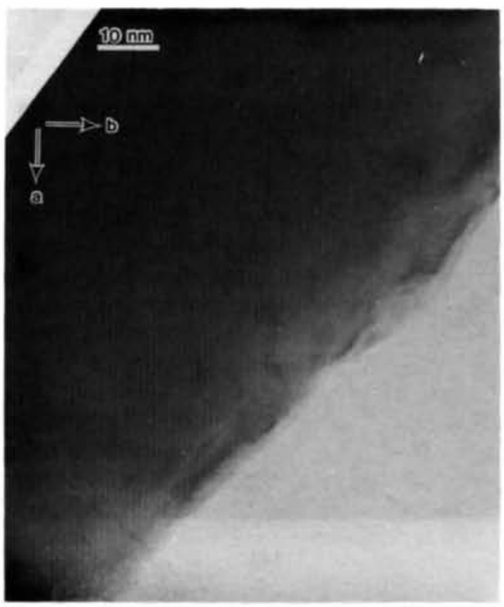



(*b*)

Fig. 6. [001] zone axis diffraction patterns with $\mathbf{q}_2$ satellites: (*b*) is similar to (*a*), but with additional Bragg reflections, $k = 2n+1$.




(*a*)




(*b*)

Fig. 7. Electron-microscope bright-field images corresponding to the Fig. 6(*b*) diffraction pattern: (*a*) small objective aperture, (*b*) large objective aperture. (10nm ≡ 100Å.)

changes. They point out that two distinct possibilities exist, differing only in the phase of the atom displacement wave. One (appropriate to $K_2SeO_4$) has $\varphi = 0$, and the *Pmnb* structure transforms (at the 'lock-in') to $P2_1nb$, the transition being paraelectric (high $T$) to ferroelectric (low $T$). The other, clearly appropriate to $Sr_2SiO_4$, has $\varphi = \pi/2$ and the high-temperature *Pmnb* transforming to the low-temperature $P2_1/n$; a transformation from paraelastic ($\alpha'$) to ferroelastic ($\beta$). [*cf.* Catti & Gazzoni (1983) who studied the ferroelasticity of $\beta$-$Sr_2SiO_4$.]

## Conclusion

More, and more careful, experiments in the electron microscope are clearly necessary (and are proceeding). But it is already apparent that solution of the phase equilibrium and structure problems, endemic for the systems $Ca_2SiO_4$ and $Sr_2SiO_4$ (and related ones), requires the broader considerations appropriate to $K_2SeO_4$ *etc.*, *i.e.* the introduction of the possibility of modulation and incommensurability. The confusion that has developed, particularly about the $\alpha'$ structure, appears to be a direct consequence of ignoring this.

We are grateful to Mr Peter Barlow for technical assistance, with the microscopy and photography.

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