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The $\beta \rightleftarrows \alpha'$ Transition in Sr_2SiO_4 (and Ca_2SiO_4, K_2SeO_4 *etc.*), involving a Modulated Structure

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Abstract

An analysis of the reported structures of β-Sr_2SiO_4 and α'-Sr_2SiO_4 and particularly of their bond lengths and derived strengths suggests that a controlling factor in the $\beta \rightleftarrows \alpha'$ transformation is the underbonding of Sr(1) and O(2), possibly as a result of excessive Sr · · Sr repulsion. The Sr(1)-O(2) bond-energy *vs* bond-length curve is a double-well potential, and therefore extremely anharmonic. This is probably the basis of the appearance of structural modulation at the ferroelastic ⇄ paraelastic transition. It seems likely that the same situation obtains with β-$Ca_2SiO_4 \rightleftarrows \alpha'$-$Ca_2SiO_4$, although the latter structure is probably not known with sufficient accuracy. Furthermore, the reported $a \times 3b \times c$ superstructure of α'-Ca_2SiO_4 probably corresponds to a modulated structure, with a periodicity close to (rather than exactly) $3 \times \mathbf{b}$. A similar approach throws light on the ferroelectric transition of K_2SeO_4, the ferroelastic transition of Cs_2CdBr_4 and the modulation in γ-Na_2CO_3.

Introduction

Modulated especially incommensurate structures have become rapidly more prominent in recent years, and a wide variety of compounds and structure types is involved. Among insulating materials those with structures related to the **β-K_2SO_4** type are particularly numerous and some have been studied very extensively, including K_2SeO_4, a prototype of many A_2BX_4 compounds (A = large cation, B = small cation, X = anion). Discussions of both experiment and theory are marked by a certain abstractedness owing to the absence of any simple, satisfying geometrical picture of the **β-K_2SO_4** structure and its close relatives. This omission can, we believe, be repaired.

In a quite different context, attention has recently been drawn to the regularity of the cation arrays in many structures (O'Keeffe & Hyde, 1981*a*,*b*, 1982; White & Hyde, 1982, 1983), and explanations of its significance proposed (O'Keeffe & Hyde, 1976, 1978*a*,*b*, 1979, 1982, 1984; O'Keeffe, Shavers & Hyde, 1981). More recently it has been shown (O'Keeffe & Hyde, 1985) that this approach leads logically and directly to simple geometrical descriptions of many common structure types (including **β-K_2SO_4**), for most of which no description was previously available, and some of which were considered to be very puzzling. [See, for example, Wyckoff (1968) on $BaSO_4$ and, directly relevant to the present problem, K_2SO_4.] These ideas have previously been used to relate the structures and unit-cell-axis orientations of the polymorphs of Ca_2SiO_4 and Sr_2SiO_4, which led to the suggestion that modulated structures might be expected to intervene in their phase transformations, at least in $\beta \rightleftarrows \alpha'$ (Barbier & Hyde, 1985), and a preliminary electron-microscope study of Sr_2SiO_4 has revealed that this was indeed the case (Stenberg & Hyde, 1986).

The transformation was achieved by 'beam-heating' in the microscope. The temperature for $\beta \rightleftarrows \alpha'$ is much lower for Sr_2SiO_4 than for Ca_2SiO_4: ~358 K compared with ~953 K. No hot-stage was available, and so the former was studied, its transformation being more readily accessible. But one presumes that the same sort of phenomenon will also be observed to occur in Ca_2SiO_4. Experiments are planned to check this point.

The present paper examines the slight differences between the reported structures of β- and α'-Sr_2SiO_4, in an attempt to interpret the occurrence of modulation in the $\beta \rightleftarrows \alpha'$ transition. It is based on the structural approach referred to above. Then it is extended to the transitions in other A_2BX_4 compounds, particularly K_2SeO_4 since this has been the subject of extensive research. The analysis is related to that used earlier in discussing transformations of crystal structures at high pressure (O'Keeffe & Hyde, 1981*b*, 1985) and the effect of cation-cation repulsions on the thermodynamic stability of compounds, particularly those that are 'cation-rich' (O'Keeffe & Hyde, 1984).

The structures of β-K_2SO_4, β-Sr_2SiO_4 and α'-Sr_2SiO_4

The **β-K_2SO_4** ($H1_6$) type is, of course, very widespread: it is the structure of many sulfates, selenates, vanadates, fluoborates *etc.* The (orthorhombic) structure of β-K_2SO_4 itself (McGinnety, 1972) is shown

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in Fig. 1 (unit-cell setting *Pmnb*). At the bottom of this figure we see the customary depiction of this structure as SO_4 tetrahedra and K atoms: the coordination of K by O is so ill-defined and irregular that no convincing K-centred polyhedron of anions can be identified. At the top, the anions are omitted for clarity, and the K_2S array is clearly seen to be regular and of the **$PbCl_2$** (C23) type, with S-centred trigonal prisms, K_6. In the centre, the structure is depicted as SO_4-'centred' trigonal prisms.

In Fig. 2(*a*) we show the corresponding (100) projection of the structure of β-Sr_2SiO_4 (Catti & Gazzoni, 1983; Catti, Gazzoni & Ivaldi, 1983). It is very similar to that of β-K_2SO_4, but not identical. The main differences are: (1) this structure is monoclinic, space group $P12_1/n1$; (2) the monoclinic angle $\beta = 92{\cdot}67°$; (3) the BO_4 tetrahedra are now tilted slightly, so that they no longer have a mirror plane parallel to (100) at $x = \pm\frac{1}{4}$; (4) as a result of (3) the tetrahedral edge parallel to **a** in β-K_2SO_4 is now slightly inclined to **a**.

Fig. 2(*b*) shows the corresponding projection of (one twin state of) the 'preferred' structure of α'-Sr_2SiO_4 – the 'disordered' model of Catti, Gazzoni, Ivaldi & Zanini (1983). It is similar to that of β-Sr_2SiO_4, still monoclinic ($P2_1/n$), but with $\beta = 90°$. The SiO_4 tetrahedra are tilted (from the mirror-symmetric orientation of β-K_2SO_4), although not quite as much as in β-Sr_2SiO_4. There is considerable discussion about this structure (Catti, Gazzoni, Ivaldi & Zanini, 1983; Catti, Gazzoni & Ivaldi, 1984) in an attempt to choose between two models: (1) the 'disordered' model, in which the SiO_4 tetrahedra are tilted, but, in any given crystal, in *both* positive and negative senses, so that it is really finely 'twinned' $P2_1/n$ [twin plane (100)]; or (2) the 'ordered' model, in which the tetrahedra are in the average (mirror-symmetric) position, and undergoing thermal libration [roughly between their orientations in Fig. 2(*b*) and the corresponding ones in the (100)-mirror-related twin]. The former is preferred but the choice is not straightforward. In Table 1 the problem is made explicit by listing the distances between the atom positions in the two, twin-related structures and comparing them with the published thermal parameters which are, in all cases, comparable. Later it will become clear that a third choice is more likely to be correct – a modulated structure which varies (in

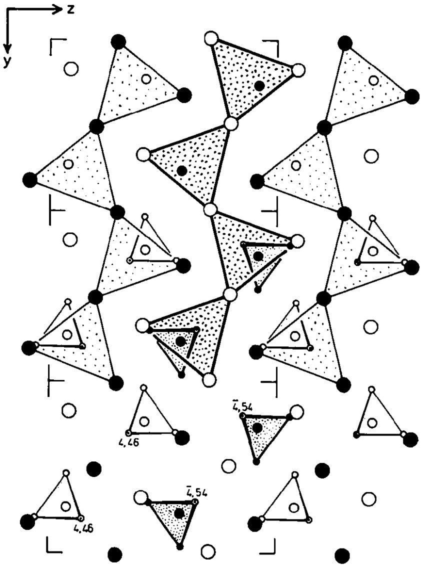
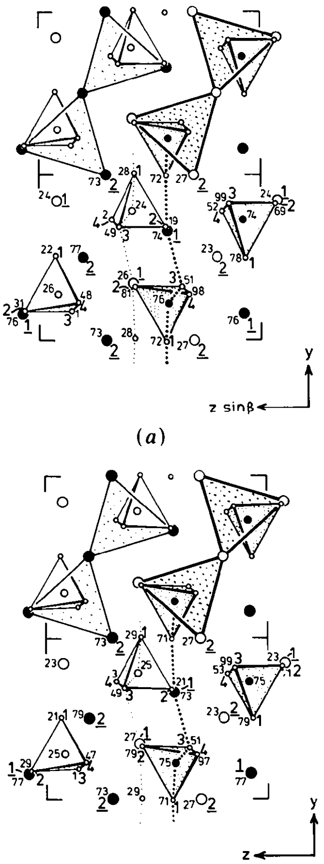


Fig. 1. The structure of β-K_2SO_4 projected on (100) when the unit-cell setting is *Pmnb*. Large, medium and small circles are K, S and O respectively: open/filled at $x = \frac{1}{4}/\frac{3}{4}$; dotted circles are two superimposed O atoms at heights given in units of $a/100$. The usual depiction, as K atoms and SO_4 groups, is shown at the bottom; only the cation array, **$PbCl_2$**-like K_2S, is shown at the top; and at the centre, the structure is shown as SO_4-'centred' K_6 trigonal prisms.



(*a*)

(*b*)

Fig. 2. (*a*) β-Sr_2SiO_4, and (*b*) α'-Sr_2SiO_4 ('disordered' model), both projected along [100]. Each diagram shows one of the two twin-related forms; the other is derived by reflection in (100). Large, medium and small circles are Sr, Si and O respectively; open/filled at $x = \frac{1}{4}/\frac{3}{4}$ (cations only); atom heights are in units of $a/100$ (small figures). Large digits indicate the crystallographically distinct atoms Sr(1) and Sr(2) (underlined) and O(1), O(2), O(3) and O(4) (not underlined). SiO_4 tetrahedra and some Sr trigonal prisms are drawn, and unit cells are indicated. *cf.* Fig. 1. The dotted lines are the chains of bonds roughly parallel to **b**, and referred to in the text. [There is very little difference between (*a*) and (*b*) apart from change in the monoclinic angle $\beta = 92{\cdot}67°$ in (*a*) to 90·00° in (*b*).]

Table 1. *Comparison of the atom parameters x in the two twin forms of 'disordered'* α'-Sr_2SiO_4 *and the thermal parameters,* $\sqrt{U}$

	x in twin 1	$\lvert\Delta x\rvert$ twin 1 → twin 2	$a.\Delta x$ (Å)	$\sqrt{U}$ (Å)	$a.\Delta x/\sqrt{U}$
Sr(1)	0·2651 (5)	0·0302	0·172	0·084	2·0
Sr(2)	0·2663 (4)	0·0326	0·185	0·061	3·0
Si	$\frac{1}{4}$	0	0	0·057	0
O(1)	0·292 (2)	0·084	0·477	0·089	5·4
O(2)	0·207 (2)	0·086	0·489	0·100	4·9
O(3)	0·488 (2)	0·024	0·136	0·089	1·5
O(4)	0·028 (2)	0·056	0·318	0·089	3·6

space) approximately between the twin-related, 'disordered' forms. Nevertheless, it is significant that the monoclinic angle β is not very different in β-Sr_2SiO_4 (92·67°) and α'-Sr_2SiO_4 (90°), and that the β-phase invariably occurs as crystals (macroscopically) twinned on (100). β is the ferroelastic form of α', which is the paraelastic form (Catti & Gazzoni, 1983).

Figs. 3(*a*) and 3(*b*) show the (010) projections of β- and α'-Sr_2SiO_4. Again, the close resemblance between the two is obvious.

The $\beta \rightleftarrows \alpha'$ transformation in Sr_2SiO_4

We now consider the specific differences between the reported structures of β- and α'-Sr_2SiO_4. These are too small to be apparent from a comparison of either *a* or *b* in Figs. 2 and 3, but are exposed by comparing corresponding individual bond lengths (l) or, better, the bond strengths (s) in the two structures. Those judged to be relevant to the subsequent discussion (having $s > 0{\cdot}05$ and $|\Delta s| > 0{\cdot}01$) are listed in Table 2. Values of s are calculated from bond lengths, l(Å), by the relations proposed by Brown (1981), *viz* $s(\text{Si–O}) = \exp[(1{\cdot}63 - l)/0{\cdot}36]$ and $s(\text{Sr–O}) = (l/2{\cdot}143)^{-7{\cdot}0}$.

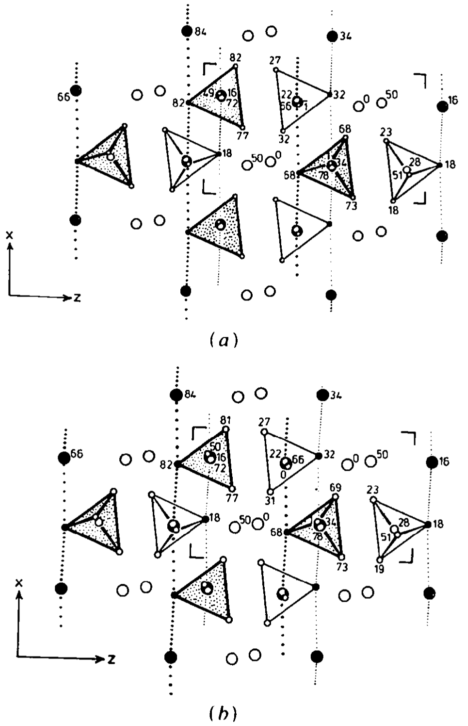


Fig. 3. The structures of (*a*) β-Sr_2SiO_4 and (*b*) the 'disordered' model of α'-Sr_2SiO_4 projected on (010). Large circles are Sr, medium circles are Si, and small circles are O atoms. SiO_4 tetrahedra are shown; and the dotted lines represent -Sr(1)-O(2)- chains, with the denser dots indicating the shorter bond. [The second twin of each is obtained by reflection in (100).]

Table 2. *Equivalent bonds with significant changes in strength between* α'- *and* β-Sr_2SiO_4

	$l_{\alpha'}$ (Å)	l_β (Å)	Δl $(\beta - \alpha')$	$s_{\alpha'}$	s_β	Δs $(\alpha' \to \beta)$	
Sr(1)–O(1)	2·384	2·373	−0·011	0·474	0·490	+0·016	
–O(2)	2·688	2·556	−0·132	0·205	0·283	+0·078	+0·058 net
	3·004	3·108	+0·104	0·094	0·074	−0·020	
–O(3)	2·841	2·764	−0·077	0·139	0·168	+0·029	
–O(4)	3·077	2·926	−0·151	0·079	0·113	+0·034	
–O(4)	2·743	2·779	+0·036	0·178	0·162	−0·016	
Sr(2)–O(3)	2·561	2·527	−0·034	0·287	0·315	+0·028	
–O(4)	2·479	2·519	+0·040	0·361	0·323	−0·038	
Si(1)–O(1)	1·627	1·646	+0·019	1·008	0·957	−0·051	
–O(2)	1·655	1·641	−0·014	0·933	0·970	+0·037	
–O(3)	1·621	1·642	+0·021	1·025	0·967	−0·058	
–O(4)	1·626	1·621	−0·005	1·011	1·025	+0·014	

Given the uncertainties in the determination of the α' structure (referred to above) it is clear that most of the changes in bond length and strength listed in Table 2 are on the verge of significance, the only exceptions being the second, third and fourth entries. But, within this proviso, we proceed as follows.

The broad picture is most immediately revealed by comparing bond-strength sums ($\sum s$) at the cations. At Si, $\sum s = 3{\cdot}9_{19}$ for β and $3{\cdot}9_{77}$ for α', both satisfactorily close to the ideal value $\sum s(\text{Si}) = 4{\cdot}0$. The situation is the same at Sr(2): $\sum s = 2{\cdot}0_{45}$ in β and α', the ideal value being $\sum s(\text{Sr}) = 2{\cdot}0$. But the Sr(1) atoms are distinctly underbonded especially – as previously pointed out by Catti, Gazzoni & Ivaldi (1983) – in the α' polymorph: $\sum s = 1{\cdot}8_{25}$ for β and $1{\cdot}7_{28}$ for α'.* Catti *et al.* attributed this to *over*bonding at Si in α', which was later seen to be an artefact (Catti, Gazzoni, Ivaldi & Zanini, 1983). On the other hand such underbonding has previously been identified in the alkali-metal oxides, where it was attributed to strong cation–cation repulsion stretching the bonds (*i.e.* preventing a closer approach of the cations to the anions) from those values appropriate to bond strengths (and bond-strength sums) of the expected (ideal) values (O'Keeffe & Hyde, 1984).

The bond-strength sums at the anions are less directly informative, but suggest the possibility of a similar situation in Sr_2SiO_4. The values are, for O(1) to O(4) respectively, $\sum s(\text{O}) = 1{\cdot}9_{29}$, $1{\cdot}9_{48}$, $1{\cdot}9_{44}$ and $1{\cdot}9_{68}$ for β and $1{\cdot}9_{63}$, $1{\cdot}8_{59}$, $1{\cdot}9_{63}$ and $1{\cdot}9_{49}$ for α'.

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* The exact values of $\sum s$ depend on the undefined point at which one cuts off the minimum s. Previously (Barbier & Hyde, 1985) we took $s < 0{\cdot}1$ as zero (no bond), and obtained $\sum s[\text{Sr}(1)] = 1{\cdot}61$ for β and 1·51 for α'. Here we have included all values of $s \geq 0{\cdot}01$.

With the exception of O(2) in α', these are rather uniform, suggesting that interactions between second-nearest-neighbour atoms may be responsible for the lower-than-ideal values of $\sum s$: a result not inconsistent with cation–cation repulsions being important. [Anion–anion distances of <4Å are plotted on the O···O interaction energy curve of Dashevsky (in Kitaigorodsky, 1973) in Fig. 4. Excluding the short edges of the SiO_4 tetrahedron, all but one of the distances in α'-Sr_2SiO_4 are on a rather flat part of the curve, suggesting that O···O interactions (or changes in them) are not very important.]

The exception to the uniform values of $\sum s(\mathrm{O})$ in the previous paragraph is the value $1\cdot8_{59}$ for O(2) in α'-Sr_2SiO_4. This immediately suggests that O(2) is important in the transformation $\beta \rightleftarrows \alpha'$; and we have already seen that Sr(1), being underbonded, is also likely to be important. These hints are confirmed by examining the individual values of s and Δs in Table 2: the largest Δs involves the Sr(1)-O(2) bonds. There are two of these, alternately long and short, producing a chain -M(1)-O(2)-M(1)-O(2)- along the x direction (Figs. 2 and 3). In the transition the shorter of the two (naturally) changes its strength more, $\Delta s(\beta-\alpha') = +0\cdot078$: it gets still shorter, and stronger, when $\alpha' \rightarrow \beta$. The longer of the two changes its length by almost the same amount ($\Delta l = +0\cdot104$ Å compared with $\Delta l = -0\cdot132$ Å for the shorter bond), and its $\Delta s(\beta-\alpha') = -0\cdot020$. The two changes are of course related, since the two bonds are almost collinear [and $a(\beta) \doteqdot a(\alpha')$]. The change $\alpha' \rightarrow \beta$ involves a shortening of the shorter M(1)-O(2) bond with a concomitant lengthening of the longer one; a shift of O(2) with respect to its two adjacent Sr(1) atoms, or *vice versa*. Clearly the relation between the energy and the length of the M(1)-O(2) bond is a double-well potential-energy curve.

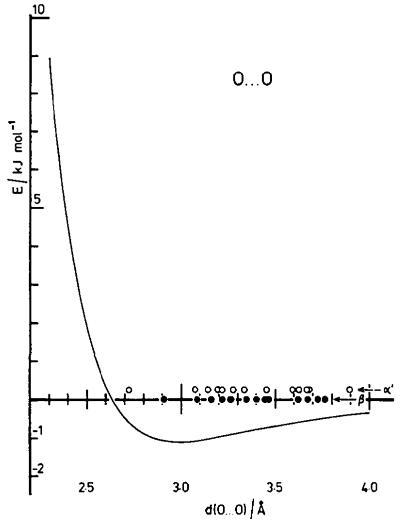

Fig. 4. Dashevsky's proposed relation between the potential energy of a pair of (non-bonded) oxygen atoms and their separation. The open and filled circles correspond to the calculated distances $d(\mathrm{O}\cdots\mathrm{O}) \leq 4$ Å in respectively α'-Sr_2SiO_4 and β-Sr_2SiO_4, and suggest that these interactions do not contribute significantly to the energy change in $\alpha' \rightleftarrows \beta$. [The much shorter edge lengths of the SiO_4 tetrahedra (~2·6 to 2·7 Å) are not shown.]

At very low temperatures there are two possibilities, corresponding to the two twin orientations of the monoclinic β structure. At very high temperatures the system effectively has a single, mirror-symmetric potential well; and the two bonds, of different length in β, will now be of the same length: the situation in the **β-K_2SO_4** structure type, but not that in the 'disordered' α'-Sr_2SiO_4 structure type (monoclinic, with angle $\beta = 90°$) which is in a state corresponding to an intermediate temperature.

At these intermediate temperatures intermediate bond lengths l[Sr(1)-O(2)] are inevitable; the potential-energy curve is extremely anharmonic. The observed modulation(s) suggests a continuous, periodic variation in these lengths. But its direction is along **b**, not **a**; *i.e.* in a given (010) sheet of -Sr(1)-O(2)- chains the length(s) are fixed; but they vary from sheet to sheet in the **b** direction. This requires a strong, but not rigid (somewhat flexible), connection between adjacent sheets. Examination of Table 2 and Fig. 2 reveals that this exists. There is another recognizable chain, more or less in the **b** direction: *e.g.* Si is connected by a strong bond ($s \approx 1$) to O(1) which, in turn, is connected to Sr(1) by another strong bond ($s = 0\cdot4_{74}$ in α', $0\cdot4_{90}$ in β; $\Delta s = +0\cdot0_{16}$) which, in turn, is connected to O(3) by a fairly strong, but variable bond ($s = 0\cdot1_{39}$ in α', $0\cdot1_{68}$ in β; $\Delta s = 0\cdot0_{29}$, $\Delta l = -0\cdot077$ Å), which is finally connected to Si(1) by another strong bond ($s \approx 1$). This is the repeat unit in an infinite chain along **b**; and it is this chain which carries the modulation wave. It also links adjacent (001) sheets of $(SiO_4)Sr_6$ trigonal prisms. [There are weaker lateral connections also - roughly in the **c** direction - between these chains, from Sr(1) to O(4).]

To press this sort of analysis further is futile: the changes in the transformation $\beta \rightleftarrows \alpha'$ are very small, and neither the bond lengths (*i.e.* the structure determinations, especially that of α) nor the bond-length/bond-strength relations are sufficiently accurate to warrant closer scrutiny.

In reciprocal space, the two observed modulations in Sr_2SiO_4 are $\mathbf{q}_i = p_i.\mathbf{b}^*$ with $p_1 = 0\cdot39$ and $p_2 = 0\cdot30$ (Stenberg & Hyde, 1986). The wavelengths in real space are therefore $\lambda_i = \mathbf{b}/p_i$, with $\lambda_1 = 2\cdot56\mathbf{b} \simeq 18\cdot2$ Å and $\lambda_2 = 3\cdot33\mathbf{b} \simeq 23\cdot6$ Å [taking $b = 7\cdot087$ Å as the mean of the values for $\beta(b = 7\cdot084$ Å) and α' ($b = 7\cdot090$ Å)].

The major effect being the change in Sr(1)-O(2) bond lengths, O(2) moves towards *one* of its Sr(1) neighbours, roughly along **a**, and the SiO_4 tetrahedra therefore tilt, roughly around the **b** axis.† It is this

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† This is to some extent counteracted by the change in M(1)-O(4) which, alone, would produce a smaller tilt in the opposite sense.

tilt which is usually emphasized in discussions of transformations in **β-K_2SO_4**-related structures.

Ca_2SiO_4

In this case, the situation is not as clearcut as for β-$\rightleftarrows$ α'-Sr_2SiO_4, mainly because the α'-Ca_2SiO_4 structure is not as thoroughly studied as that of its strontium analogue. Hence we show in Fig. 5 only the β-Ca_2SiO_4 (larnite) structure. Nevertheless it appears likely that an analysis of the sort used above for Sr_2SiO_4 also applies here, and with a similar outcome.

First we can compare the lattice parameters of the two structures: β-Ca_2SiO_4 is $P2_1/n$ with $a = 5{\cdot}502$, $b = 6{\cdot}745$ and $c = 9{\cdot}297$ Å, $\beta = 94{\cdot}59°$ (Jost, Zeimer & Seydel, 1977) while (the corresponding subcell of) α'-Ca_2SiO_4 (said to be *Pmnb*) has $a = 5{\cdot}59$, $b = 6{\cdot}85$ and $c = 9{\cdot}49$ Å for a single-crystal sample 'stabilized' by the addition of 1 to 2 mol % of $Ca_3(PO_4)_2$ and at 1473 K (Saalfeld, 1975). The differences between β and α' are similar to those for Sr_2SiO_4 but larger, reflecting the larger spontaneous strain in the ferroelastic form β-Ca_2SiO_4 (monoclinic angle $\beta = 94{\cdot}59°$; *cf.* 92·67° for β-Sr_2SiO_4); which is why the $\beta \rightleftarrows \alpha'$ transformation temperature is so much higher for the Ca case (~953 K) than for the Sr case (~358 K).

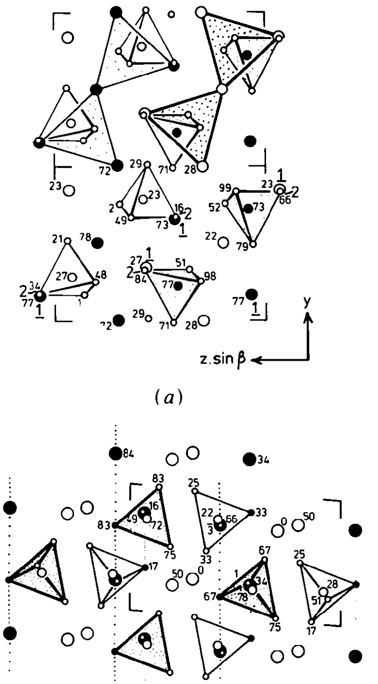

Fig. 5. β-Ca_2SiO_4 projected (*a*) along [100], (*b*) on (010): large, medium and small circles are respectively Ca, Si and O: heights (small figures) in units of $a/100$ or $b/100$. In (*a*) the cations (only) at $x \approx \frac{1}{4}$ and $\frac{3}{4}$ are represented by open and filled circles. The large figures indicate Ca(1) (underlined) and O(2). *Cf.* Figs. 1 and 2. In (*b*) the filled circles are the underbonded Ca(1) and O(2) atoms with short and long bonds in the -Ca(1)-O(2)-Ca(1)-O(2) chains indicated by respectively dense and less dense dotted lines.

Fig. 5 shows the presence of alternately long and short Ca(1)-O(2) bonds along the x direction: $3{\cdot}13_7$ and $2{\cdot}36_9$ Å, to be compared with $3{\cdot}10_8$ and $2{\cdot}56_6$ Å in β-Sr_2SiO_4.† Consistent with the larger spontaneous strain in the Ca case, its bond-length difference is proportionately larger, as is its bond-strength difference: for β-Ca, $s = 0{\cdot}0_{68}$ and $0{\cdot}3_{12}$, $\Delta s = 0{\cdot}2_{44}$; for β-Sr, $s = 0{\cdot}0_{74}$ and $0{\cdot}2_{83}$, $\Delta s = 0{\cdot}2_{09}$.

The broader picture, deduced from bond-strength sums at the cations, while again not as clear as for Sr_2SiO_4, nevertheless seems to be similar for Ca_2SiO_4. There is a problem with *absolute* values of bond strengths s - which appear to be too high for very long 'bonds' - using either of the equations for Ca-O given by Brown (1981): $s_1 = (l/1{\cdot}909)^{-5{\cdot}4}$ or $s_2 = \exp[(1{\cdot}896 - l)/0{\cdot}41]$. For long bonds the second equation appears to be more realistic than the first. Using it (and the equation used earlier for Si-O) one calculates $\sum s(\mathrm{Si}) = 3{\cdot}9_{97}$ (ideally 4·0) and, for $s_2 \geq 0{\cdot}01$, $\sum s_2[\mathrm{Ca(1)}] = 1{\cdot}8_{66}$, $\sum s_2[\mathrm{Ca(2)}] = 1{\cdot}9_{62}$. (The corresponding values using the other equation are $2{\cdot}0_{00}$ and $2{\cdot}0_{71}$ respectively.) To summarize: whatever the errors in the absolute values, the bond-strength sum at Ca(1) is significantly less than that at Ca(2).

The bond-strength sums at the oxygens also fit the pattern in Sr_2SiO_4, being $\sum s_2 = 1{\cdot}9_{90}$, $1{\cdot}9_{10}$, $1{\cdot}9_{49}$ and $1{\cdot}9_{69}$ for O(1) to O(4) respectively. And we note that, as in the case of β-Sr_2SiO_4, β-Ca_2SiO_4 is also invariably twinned.

Because of uncertainties in the α'-Ca_2SiO_4 structure, a similar analysis is not warranted for it. *If* (as reported) it is *Pmnb* then the 'long' and 'short' Ca(1)-O(2) bonds will be of equal length, and its structure will be that postulated above for α'-Sr_2SiO_4 at very high temperature. But there are several reports of the α' phase having a superstructure (or superstructures), at least for α'_L.‡ The nature of these is not agreed: $2\mathbf{a} \times \mathbf{b} \times 2\mathbf{c}$ (Regourd, Bigare, Forest & Guinier, 1968; Sarkar, 1980) and/or $\mathbf{a} \times 3\mathbf{b} \times \mathbf{c}$ (Saalfeld, 1975). But Saalfeld has cogently argued that the data of Regourd *et al.* are also consistent with $\mathbf{a} \times 3\mathbf{b} \times \mathbf{c}$. In view of our electron-diffraction evidence from Sr_2SiO_4 (Stenberg & Hyde, 1986) it seems likely that these earlier views may well be understandable misinterpretations of incommensurate ($\sim\mathbf{b}^*/3$) satellite reflections from a modulated α'-Ca_2SiO_4; *i.e.* that α'_L-Ca_2SiO_4 is modulated $P2_1/n$ (and, perhaps, α'_H is *Pmnb*?).

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† To keep the atom labels consistent with those used above for β-Sr_2SiO_4, we have interchanged the O(2) and O(4) atoms of Jost *et al.* (1977).

‡ The α' phase region is usually subdivided into low- and high-temperature domains, α'_L and α'_H.

K_2SeO_4

This has been very extensively studied and discussed, and a detailed analysis of its phase transitions at $T_i = 130$ K and $T_c = 93$ K given by Iizumi, Axe, Shirane & Shimaoka (1977). The room-temperature structure is β-K_2SO_4 type (*i.e.* isostructural with Catti *et al.*'s 'ordered' model for α'-Sr_2SiO_4 rather than their preferred 'disordered' model). The neutron diffraction observations of Iizumi *et al.*, and their analysis of lattice instability and mode-softening bears a striking resemblance to the case of $\alpha' \rightleftarrows \beta$-$Sr_2SiO_4$, but there are also important differences.

Below T_c, K_2SeO_4 has an $\mathbf{a}\times 3\mathbf{b}\times \mathbf{c}$ superlattice (using our unit-cell settings, to be consistent with the earlier part of this paper). Between T_c and T_i it has an incommensurate modulated structure, with $\mathbf{b}$ as the modulation direction and wavevector $\mathbf{q} = (1-\delta)\mathbf{b}^*/3$, with δ decreasing from $\sim 0{\cdot}07$ at T_i to $\sim 0{\cdot}04$ at T_c, at which temperature it suddenly drops to zero; *i.e.* $\mathbf{q} = p\,.\,\mathbf{b}^*$ with $\mathbf{q} = 0{\cdot}31$ to $0{\cdot}32$, compared with $0{\cdot}30$ and $0{\cdot}39$ in Sr_2SiO_4. But the low-temperature (super-) structure has space group $P2_1nb$ (*cf.* for Sr_2SiO_4, $P2_1/n$ and a cell $\mathbf{a}\times\mathbf{b}\times\mathbf{c}$); and the high → low transition is paraelectric to ferroelectric (not paraelastic to ferroelastic as for Sr_2SiO_4). Nevertheless, the atom shifts appear to be similar in the two cases - particularly shifts of K(1)[†] [$\equiv$ Sr(1)] parallel to x, and tilts of the SeO_4 ($\equiv SiO_4$) tetrahedra. Indeed, in their analysis Iizumi *et al.* suggest the possibility of both types of transformation, although no example was given for the ferroelastic case. The difference between them is simply the phase of the modulation wave: $\varphi = 0$ for the ferroelectric case and $\varphi = \pi/2$ for the ferroelastic case.

The low-temperature structure appears not to have been determined. That of the room-temperature form has been carefully analysed by Kálmán, Stephens & Cruickshank (1970) and, while some difficulty arises from the large thermal parameters of the oxygen atoms (*cf.* the analysis of the α'-Sr_2SiO_4 structure by Catti *et al.*), a bond-length/bond-strength analysis is again interesting. The atom chains analogous to -Sr(1)-O(2)-Sr(1)-O(2)- in Sr_2SiO_4 are now -K(1)-O(2)-K(1)-O(2)-, but they are symmetrical: the two bond lengths are the same, although the bonds are not very strong, $l(\text{K–O}) = 3{\cdot}016$ Å, $s_1 = 0{\cdot}0_{77}$ ($s_2 = 0{\cdot}0_{86}$);[‡] *cf.* $s(\text{Sr–O}) = 0{\cdot}2_{05}$ and $0{\cdot}0_{94}$ in α'-Sr_2SiO_4 and $s(\text{Sr–O}) = 0{\cdot}2_{83}$ and $0{\cdot}0_{74}$ in β-Sr_2SiO_4. The bond-strength sums are $\sum s_1 = 0{\cdot}8_{12}$ ($\sum s_2 = 0{\cdot}8_{55}$) for K(1), $\sum s_1 = 1{\cdot}1_{25}$ ($\sum s_2 = 1{\cdot}0_{40}$) for K(2), and $\sum s_1$ ($\sum s_2$) = $1{\cdot}9_{39}$ ($1{\cdot}9_{31}$), $1{\cdot}9_{75}$ ($1{\cdot}9_{74}$), $1{\cdot}8_{94}$ ($1{\cdot}8_{65}$) for O(1) to O(3) respectively. (There are only three crystallographically distinct oxygens in the *Pmnb* structures.) Using bond lengths uncorrected for thermal effects $\sum s(\text{Se}) = 6{\cdot}2_{06}$ and, corrected for thermal effects, $\sum s(\text{Se}) = 5{\cdot}8_{06}$. While, again, there are problems with absolute s values, it appears that K(1) is strongly underbonded, as was the analogous Sr(1) in Sr_2SiO_4 but that, of the oxygens, it is O(3) that is most heavily underbonded - in contrast with the situation in Sr_2SiO_4, where it is O(2). While the uncertainties in the values of $s(\text{K–O})$ must be emphasized, and may well be crucial, it is possible that herein lies the qualitative difference between the behaviour of K_2SeO_4 and Sr_2SiO_4. Iizumi *et al.* (1977) emphasize the 'interlayer forces' in the $\mathbf{b}$ direction ($\mathbf{a}$ in their setting of the unit cell), which depend heavily on the K(1)-O(3) bonds. But they also emphasize tilting of the SeO_4 tetrahedra (approximately about $\mathbf{b}$) and shifts of K(1) and O(2) in the x direction (their z) which correspond exactly to changes in K(1)-O(2) bond lengths analogous to those for Sr(1)-O(2) bonds in Sr_2SiO_4, which are clearly important in the $\beta \rightleftarrows \alpha'$ transformation of the latter compound.

That the bond-strength sums $\sum s(\text{Se})$ are substantially different from the ideal value of $6{\cdot}0$ certainly clouds the issue. It suggests that the problem of thermal effects may not yet be satisfactorily resolved. Ignoring thermal effects yields bond lengths that are too short, of course, and consequently bond strengths that are too high: *cf.* $\sum s(\text{Se})_{\text{uncorr}} = 6{\cdot}2_{06}$ (instead of the ideal $6{\cdot}0$). But equally, correcting for thermal effects gives $\sum s(\text{Se})_{\text{corr}} = 5{\cdot}8_{06}$, which is too low. The s–l relation may be inaccurate but possibly the K_2SeO_4 structure is not exactly the **β-K_2SO_4** type. In this connection it is noteworthy that there are discrepancies between the observed Raman spectra of room-temperature K_2SeO_4 and the symmetry *Pmnb* of the β-K_2SO_4 structure type. These have recently been discussed by Massa, Ullmann & Hardy (1983).

In spite of the differences and uncertainties, the similarities between the K_2SeO_4 and Sr_2SiO_4 transformations are striking, and must be emphasized: (*a*) the $\pm\delta x$ shifts of K(1) and Sr(1), and (*b*) the alternation of bond lengths in the -M(1)-O(2)-M(1)-O(2)- chains in β-Sr_2SiO_4 and the incommensurate forms of K_2SeO_4 and, probably, α'-Sr_2SiO_4 also.

That the latter is important in Sr_2SiO_4 seems to us to be conclusively shown by the analysis we have given earlier. That it is also important in K_2SeO_4 is consistent with recent studies of the effect of hydrostatic pressure and, especially, uniaxial stress on the transition temperature T_i of K_2SeO_4. The double-well potential for the M(1)-O(2) bonds suggests that the energy peak (ΔE) between the two minima, and therefore the transition temperature, will be reduced as the difference between the two bond lengths decreases. This is consistent with the $\beta \rightleftarrows \alpha'$ transition temperature being lower for Sr_2SiO_4 than for

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[†] Iizumi *et al.* (1977) call these K_α.

[‡] The relations are again from Brown (1981): $s_1(\text{K–O}) = [l(\text{K–O})/2{\cdot}276]^{-9{\cdot}1}$, $s_2(\text{K–O}) = \exp\{[1{\cdot}84 - l(\text{K–O})]/0{\cdot}48\}$; $s(\text{Se–O}) = [l(\text{Se–O})/1{\cdot}775]^{-5{\cdot}0}$. All individual s values were summed: very few were small ($s < 0{\cdot}01$). Values of $l(\text{K–O})$ are from Kálmán *et al.* (1970), and are not corrected for thermal effects.

Ca_2SiO_4.* It is also consistent with the effect of hydrostatic pressure on the value of T_i for K_2SeO_4 - which is negative, approximately -70 K GPa^{-1}. Billesbach, Ullmann & Hardy (1985), following the birefringence of a single crystal of K_2SeO_4, have measured the dependence of T_i on uniaxial stress. They report $dT_i/d\sigma = -170(2)$, $+31(2)$ and $+77(2)$ K GPa^{-1} for **a**-, **b**- and **c**-axis stress, respectively. If, as we suggest, the important controlling factor is the change in $M(1)$-O(2) bond length the large, negative coefficient $dT_i/d\sigma$ for **a**-axis stress is exactly what one would expect, since the -$M(1)$-O(2)-$M(1)$- chain is almost linear and parallel to **a**, so that compression along **a** directly reduces ΔE, and therefore T_i. On the other hand, uniaxial compression along **b** or **c** will cause an expansion of **a**, an increase in ΔE, and a (smaller) *positive* coefficient $dT_i/d\sigma$ for **b**- and **c**-axis stress.

Conclusion

The approach we have used - with emphasis on '$M(1)$-O(2)' bonds - is believed to be generally applicable to A_2BX_4 structures related to the **β-K_2SO_4** type. Indeed, the preliminary step in a similar bond-strength analysis [examining only $\sum s(A)$] has recently been used to account for the high (*Pmnb*) to low ($P2_1/n$) temperature transition, *via* incommensurably modulated structures, in Cs_2CdBr_4 and Cs_2HgBr_4 (Altermatt, Arend, Gramlich, Niggli & Petter, 1984). But, whereas repulsive $A\cdots A$ (cation) interaction appears to be important in the cases of K_2SeO_4 and Sr_2SiO_4, in these halides it appears to be attractive Br···Br (anion) interactions.

A preliminary investigation of the γ-Na_2CO_3 modulated structure (van Aalst, den Hollander, Peterse & de Wolff, 1976) indicates that the same double-well potential for the -Na(3)-O(2)-Na(3)- chain in that structure [analogous to -$M(1)$-O(2)-$M(1)$ above] is a controlling factor, in spite of the difference in stoichiometry (but note that all these compounds are A_2BX_n) and a geometrically different, though topologically identical, cation array.

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* At first sight it appears to be *in*consistent with the positive (hydrostatic) pressure coefficient for the $\beta \rightleftarrows \alpha'$-$Ca_2SiO_4$ transition temperature, $dT/dp = 105(5)$ K GPa^{-1} (Klement & Cohen, 1974). But this is not necessarily the case, although it does demand that the sum of the two Ca(1)-O(2) bond lengths increases with increasing pressure.

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