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Crystal structure of kristiansenite: a case of class IIB twinning by metric merohedry

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Abstract. The structure of the new disilicate kristiansenite, $Ca_2ScSn(Si_2O_7)(Si_2O_6OH)$, has been solved and refined from a crystal polysynthetically twinned by metric merohedry. The Bravais lattice is *mC*, with parameters $a = 10.028(1)$, $b = 8.408(1)$, $c = 13.339(2)$ Å, $\alpha = 90.01(1)$, $\beta = 109.10(1)$, $\gamma = 90.00(1)°$, but the space-group type is $C\bar{1}$ ($Z = 4$). The twin law is *m*', and the two components of the twin have nearly identical volumes: as a consequence, the Laue group of the twin is practically 2/*m*. By taking into account the twinning, an anisotropic refinement of the structure in $C\bar{1}$ converged to $R1 = 0.0242$ for 259 refined parameters and 4862 observed reflections. The effects of the twinning by metric merohedry and of the volume ratio of the components on the symmetry of the diffraction pattern are discussed. The triclinic structure approximates within about 0.1 Å the monoclinic symmetry, the lower symmetry resulting mainly from cation ordering. Kristiansenite represents a new type of silicate structure and the first known case with the presence of protonated and normal disilicate groups at the same time. The disilicate groups and the other polyhedra centred on cations lie on different alternating (101) planes.

Introduction

Buerger (1954) emphasised that "it is vital that one should not obtain experimental data for a crystal structure investigation from a twin under the supposition that he is using a single crystal. If one is so unfortunate as to make this error, sooner of later the investigation is bound to come against a barrier beyond which there is no proceeding until it is recognised that twinned material has been used". Nowadays, most structures can be solved and refined by using crystal X-ray diffraction data collected on twins (cf. Herbst-Irmer and Sheldrick, 1998). However, recognition of twins is still needed and recent papers have attracted the attention on new aspects of twinning which require particular care by the investigator: (i) *allotwinning*: oriented crystal association of polytypes (Nespolo *et al.*, 1999a); (ii) *plesiotwinning*: oriented crystal associations based on a large coincidence-site lattice (Nespolo *et al.*, 1999b); (iii) *twinning by selective merohedry*, in which the twin operation produces a violation of the non-space-group absences typical of OD structures (Nespolo *et al.*, 1999c); (iv) *twinning by metric merohedry* (Nespolo and Ferraris, 2000), which is the case appearing in the structure here reported, and is thus described in some details.

Twinning by merohedry

Twinning by merohedry is the oriented association of two or more merohedral[1] individuals (components) of the same crystalline compound, in which pairs of individuals are related by a *twin operation* belonging to the holohedral geometric crystal class of the individual (Friedel, 1904; 1926). In Table 1, twinning by merohedry has been subdivided on the basis of the point groups of the Bravais type of lattice, of the Bravais flock of the space-group, of the individual, and, for OD structures, of the family structure (terms according to the *International Tables for Crystallography*, vol. A, section 8; and Vol. C, section 9.2.2). The kind of merohedry that the French school implicitly dealt with is that in which the Bravais type of lattice and the Bravais flock of the space group correspond to the same point group, and it is now termed *syngonic merohedry* (see below; Nespolo and Ferraris, 2000). In some crystals, however, the point group of the Bravais type of lattice is accidentally higher than that of the Bravais flock of the space group. These crystals may undergo two kinds of twinning by merohedry: one is again a syngonic merohedry (the twin operations belong to the point group of the Bravais flock); the other is termed *metric merohedry* (the twin operations belong to the point group of the Bravais

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[1] The term "merohedral twin", sometimes appearing in the literature, is misleading. "Merohedral", in contrast to "holohedral", is an adjective identifying a crystal whose point group is a subgroup of the point group of its lattice (Friedel, 1926). A merohedral crystal may undergo twinning by merohedry, in which the twin operation belongs to the lattice of the individual; the corresponding adjective is "merohedric" (see also Catti and Ferraris, 1976).

Table 1. Classification of twinning by merohedry. TLPG = Twin Lattice Point Group; SPGT = Shubnikov Point Group of the Twin; BFPG = Bravais Flock Point Group; LaPG = Laue Point Group of the individual; FSPG = Family Structure Point Group (modified after Nespolo *et al.*, 1999c; Nespolo and Ferraris, 2000).

TLPG = BFSG = SPGT = LaPG	TLPG = BFSG $\geq$ SPGT > LaPG		TLPG $\geq$ SPGT > BFSG $\geq$ LaPG	
Syngonic Merohedry Class I	Syngonic Merohedry class IIA		Metric Merohedry class IIB	
	SPGT $\leq$ FSPG	SPGT > FSPG	SPGT $\leq$ FSPG	SPGT > FSPG
	Syngonic Complete Merohedry	Syngonic Selective Merohedry	Metric Complete Merohedry	Metric Selective Merohedry

type of lattice but not to the point group of the Bravais flock) and corresponds to the degeneration to zero obliquity of the pseudo-merohedry, or to twin index 1 of the reticular merohedry (Nespolo and Ferraris, 2000)[2].

The symmetry of merohedric twins

The twin laws by merohedry and by reticular merohedry are usefully denoted by the symbols for black-and-white point groups after Shubnikov (Curien and Le Corre, 1958): the Hermann-Mauguin symbol for the point group of the individual is modified by adding the twin element(s) marked with primes. The symbol built in this way describes the twin law and represents the maximal diffractional symmetry. The real diffractional symmetry of a twin corresponds to the common symmetry of the individuals, augmented by the operation of the twin law only when the components have equal volume. The symmetry elements of the individuals are retained in the symmetry of the twin only if these elements are parallel; the symmetry of the twin can thus be lower than, equal to, or higher than the symmetry of the individual; when equal, the space orientation of the symmetry elements of the twin can be different from that of the symmetry elements of the individual (Buerger, 1954). Therefore, the Shubnikov symbols for the twin laws describe the diffractional symmetry of the whole twin edifice only when all the symmetry elements of the individuals are parallel and the components have (nearly) equal volume.

From the viewpoint of the diffractional behaviour, the twinning by merohedry was divided into classes I and II, depending on whether the twin operation does or does not belong to the Laue group of the individual (Catti and Ferraris, 1976). In class I merohedric twins the diffraction pattern does not differ from that of a single (untwinned) crystal, unless anomalous scattering is substantial. The inversion centre can always be chosen as twin operation and the set of intensities collected from a twin is indistinguishable from that collected from a single crystal. Instead, in class II merohedric twins, which correspond to the case in which the Laue symmetry of the crystal is lower than the symmetry of the twin, the twin operation overlaps reciprocal lattice nodes that are not equivalent under the Laue symmetry; consequently, the presence of twinning may hinder a correct derivation of the symmetry from the diffraction pattern.

Class II has been recently subdivided into class IIA (syngonic merohedry) and class IIB (metric merohedry) (Nespolo and Ferraris, 2000). In class IIA, the Laue point group of the twin at most coincides with the point group of the Bravais flock, which in its turn coincides with the point group of the Bravais class. In class IIB, the point group of the Bravais flock is a subgroup of the point group of the Bravais class, and the situation is thus more complicated. Assuming that Friedel's law is valid, the following cases can be realised. (1) The Shubnikov point group of the twin is lower than the acentric subgroup of the Bravais class: the Laue point group of the twin at most coincides with the point group of the Bravais flock, as for class IIA; (2) the Shubnikov point group of the twin is equal to or higher than the acentric subgroup of the Bravais class: the Laue point group of the twin coincides with the point group of the Bravais flock (2a) or with the point group of the Bravais class (2b) depending on whether the components do (2a) or do not (2b) significantly differ in volume. In the case (2b) the symmetry of the diffraction pattern coincides with the lattice metric symmetry (LMS): a wrong space-group type can thus be assumed. In the cases (1) and (2a) the symmetry of the diffraction pattern remains instead within the Bravais flock of the individual, resulting thus in a LMS higher than the Laue symmetry obtained from the intensity distribution (Catti and Ferraris, 1976; Nespolo and Ferraris, 2000). Particularly in the presence of polysynthetic twinning the case (2b) with components of (almost) identical volume is not rare.

Experimental

Kristiansenite, ideally $Ca_2ScSn(Si_2O_7)(Si_2O_6OH)$, is a new disilicate mineral occurring in an amazonite pegmatite at Heftetjern, Tørdal, Telemark (Norway). It has been approved by IMA (code 20000-51) and its full description

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[2] In the two-dimensional space, "point group of the Bravais flock" is tantamount to "point group of the syngony" (syngony = crystal system), since there is a 1 : 1 correspondence between crystal family, syngony and Bravais system: for this reason the term "syngonic merohedry" has been introduced. In the three-dimensional space this correspondence is lost; to the hexagonal crystal family two syngonies (trigonal and hexagonal) and two Bravais types of lattices (*hR* and *hP*) correspond. A trigonal crystal with lattice *hR* twinned within the same crystal family (*h*) may have two kinds of twinning: syngonic merohedry, with twin elements belonging to the *hR* lattice (only merohedral crystals) and reticular merohedry, with twin elements belonging to the *hP* sublattice of the *hR* lattice (twin index 3). Instead, a trigonal crystal with lattice *hP* twinned within the same crystal family (*h*) has only one kind of twinning and the twin elements belong to the *hP* lattice. This twinning corresponds to syngonic merohedry, because the Bravais flock of the trigonal syngony is 6/*mmmP*.

Table 2. Experimental data and results of the structure refinement for kristiansenite.

Diffractometer	Siemens P4
Radiation	MoK_α
Scan mode	$\theta - 2\theta$
Number of reflections for cell parameters	24
a (Å)	10.028(1)
b (Å)	8.408(1)
c (Å)	13.339(2)
α (°)	90.01(1)
β (°)	109.10(1)°
γ (°)	90.00(1)°
V (Å^3)	1062.7(3)
Space-group type	$C1$
Size of the prismatic crystal	0.03 × 0.02 × 0.01 mm
Absorption correction	Psi-scan
μ (mm^{-1})	4.51
Formula weight	552.49
Z	4
D_x (Mg mm^{-3})	3.64
Range for data collection	$1.62° < \vartheta < 35.00°$
Limiting indices	$-16 < h < 0$, $-13 < k < 13$, $-20 < l < 21$
Collected reflections	4921
Unique reflections	4915
Observed reflections [$I > 2\sigma(I)$]	4862
Standard reflections	2
Intensity monitoring interval	100 reflections
R_{int} (on F^2)	0.0051
Refinement method	Full-matrix least-squares on F^2
Refined parameters	259
GooF (S) (on F^2)	1.007
$R1$ [$I > 2\sigma(I)$]	0.0242
$wR2$ [$I > 2\sigma(I)$]	0.065
$R1$ (all data)	0.025
$wR2$ (all data)	0.066
Absolute structure parameter	0.03(2)
$\Delta\varrho_{\text{max}}$	0.93
$\Delta\varrho_{\text{min}}$	−1.26

shall be published elsewhere (Raade *et al.*, 2001). Single-crystal X-ray diffraction data have been collected on a Siemens P4 four-circle diffractometer (Table 2). Kristiansenite is structurally triclinic but revealed an mC Bravais lattice with parameters $a = 10.028(1)$, $b = 8.408(1)$, $c = 13.339(2)$ Å, $\alpha = 90.01(1)$, $\beta = 109.10(1)$, $\gamma = 90.00(1)°$, and is thus metrically monoclinic within experimental error ($Z = 4$). The Laue group $2/m$ was indicated within experimental error by the value of $R_{\text{merge}} = 0.023$ obtained by merging, according to monoclinic symmetry, the diffraction intensities collected for half reciprocal lattice (Table 2).

Results

Structure solution and refinement

The statistical analysis (SHELX97 package: Sheldrick, 1997) of the X-ray diffraction intensities showed contrasting results on the presence of the centre, giving $\langle|E^2 - 1|\rangle = 0.854$ [half-way between the values typical of centric (0.968) and acentric (0.736) structures (Viterbo, 1992)] and on the space-group type, being $C2$ slightly preferred to Cm. The structure has been solved by direct methods in the $C2$ space-group type, but the refinement was not satisfying, the final $R1$ value being 0.092; besides, the polarity (Flack, 1983) was uncertain (Table 2). Taking into account the uncertainties of the statistical analysis, the possibility of triclinic structural symmetry was considered. A triclinic structure is compatible with a $2/m$ Laue symmetry of the diffraction pattern only under two conditions (*i*) the crystal is metrically monoclinic and the triclinic structure is strongly pseudo-monoclinic; (*ii*) the monoclinic Laue symmetry is introduced by the twinning of components with nearly identical volumes.

According to hypothesis (*i*), a structure solution and refinement in the space-group type $C1$ (the unconventional C-centred cell was adopted for a triclinic space group in agreement with the metrically mC lattice) converged, without considering twinning, to $R1 = 0.07$ with still unsatisfactory Flack Factor. The next step was, according to hypothesis (*ii*), the consideration of the possible twin laws. Following the arguments reported above, for a triclinic merohedral (acentric) structure with monoclinic Bravais type of lattice, the following specific kinds of twinning can be expected: (1) Twinning by syngonic merohedry, class I, twin operation $\bar{1}$: the twin operation belongs to the Laue group of the structure, and overlaps equivalent diffractions; apart from the case of substantial anomalous scattering, the structure can be solved and refined even without taking twinning into account (Catti and Ferraris, 1976). (2) Twinning by metric merohedry, class IIB (the twin operation belongs to the metrically monoclinic Bravais type of lattice). Three cases can occur: (2a) Shubnikov point group $2'$ (the twin operation is 2); (2b) Shubnikov point group m' (the twin operation is m); (2c) Shubnikov point group $2'/m''$ (the twin operations are two of 2, m, and $\bar{1}$). The twin consists of two individuals in the cases (2a) and (2b), of four individuals in the case (2c). In the cases (2) the structure cannot be solved or at least satisfactorily refined, except when also the structure itself has a strong pseudo-symmetry consistent with the LMS.

The various hypotheses were tested following Herbst-Irmer and Sheldrick (1998). The case (1) is already excluded by the unsatisfactory refinement in $C1$ under hypothesis (*i*), which would also not account for the monoclinic symmetry of the intensities, but could occur as implicit component of the case (2c). The cases (2a) and (2b) gave close values of R, but consideration of the polarity (Flack Factor) shows (Table 2) that the correct twin operation is m, and the twin consists of two components of nearly equal volume. A test of case (2c) (Shubnikov point group $2'/m''$) resulted in zero volume for the two components which should be originated by the two-fold twin axis, confirming thus that the twin operation is m. Note that a distinction between (2a) and (2b) is possible only if a substantial contribution from the anomalous scattering is present, otherwise the polarity cannot be determined.

A first refinement test on the occupancy of the M sites was performed by using the Sn scattering curve. It clear resulted that the heavy cation Sn fills $M1$ and, subordinately, enters $M2$ and to a lesser degree $M3$ and $M4$; instead the lighter cations Sc and Fe are prevalently present in $M4$ and $M3$ and, subordinately, $M2$. Subsequently the following step consisted in the refinement of the electron

Table 3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for kristiansenite. $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
M1(Sn)	0.14016	0.5338	0.38844	0.0062(1)
M2	−0.3590(2)	0.5633(1)	−0.1118(2)	0.0072(1)
M3	0.3550(1)	0.5631(3)	0.10884(7)	0.0073(2)
M4	−0.1457(2)	0.5363(5)	−0.3911(1)	0.0094(3)
Ca1	0.3993(2)	0.1523(3)	0.1310(2)	0.0151(3)
Ca2	−0.3994(2)	0.1491(3)	−0.1386(2)	0.0159(3)
Ca3	0.1012(2)	0.9484(3)	0.3627(2)	0.0169(3)
Ca4	−0.0995(2)	0.9453(3)	−0.3660(2)	0.0162(4)
Si1	0.3735(2)	0.7670(4)	0.3197(2)	0.0078(4)
Si2	0.1653(2)	0.8759(4)	0.1162(2)	0.0068(4)
Si3	−0.3715(3)	0.7676(4)	−0.3209(2)	0.0087(4)
Si4	−0.1673(2)	0.8767(3)	−0.1181(2)	0.0070(3)
Si5	0.3320(2)	0.2209(4)	0.3811(2)	0.0070(3)
Si6	0.1285(3)	0.3321(4)	0.1774(2)	0.0069(4)
Si7	−0.3348(3)	0.2245(4)	−0.3848(2)	0.0069(4)
Si8	−0.1290(2)	0.3311(4)	−0.1815(2)	0.0077(4)
O1	0.4153(5)	0.6096(7)	0.2681(4)	0.010(1)
O2	0.5109(5)	0.8532(7)	0.4011(4)	0.005(1)
O3	0.2492(6)	0.7342(8)	0.3694(4)	0.010(1)
O4	0.3008(5)	0.8948(8)	0.2250(4)	0.011(1)
O5	0.1863(5)	1.022(1)	0.0449(4)	0.011(1)
O6	0.1724(6)	0.7036(8)	0.0651(4)	0.013(1)
O7	0.0256(5)	0.8987(7)	0.1531(4)	0.010(1)
O8	−0.2517(6)	0.7378(7)	−0.3723(4)	0.012(1)
O9	−0.4172(6)	0.6114(8)	−0.2702(4)	0.011(1)
O10	−0.3054(5)	0.8965(8)	−0.2261(4)	0.011(1)
O11	−0.5127(5)	0.8474(8)	−0.4071(4)	0.010(1)
O12	−0.1864(4)	1.025(1)	−0.0464(3)	0.010(1)
O13	−0.1757(6)	0.7016(9)	−0.0685(5)	0.011(1)
O14	−0.0264(6)	0.8947(8)	−0.1549(4)	0.010(1)
O15	−0.1888(5)	0.579(1)	−0.5466(4)	0.010(1)
O16	0.4760(6)	0.2049(8)	0.3512(4)	0.010(1)
O17	0.3224(6)	0.3961(9)	0.4316(4)	0.010(1)
O18	0.1963(5)	0.1992(8)	0.2701(4)	0.010(1)
O19	0.2403(5)	0.3700(6)	0.1169(4)	0.006(1)
O20	0.0892(6)	0.4928(8)	0.2305(4)	0.009(1)
O21	−0.0158(6)	0.2581(8)	0.0925(4)	0.013(1)
O22	0.1914(6)	0.5804(9)	0.5431(4)	0.008(1)
O23	−0.3297(6)	0.3974(8)	−0.4377(4)	0.010(1)
O24	−0.4796(5)	0.2063(6)	−0.3571(4)	0.007(1)
O25	−0.1983(5)	0.1983(8)	−0.2758(4)	0.010(1)
O26	−0.0871(5)	0.4885(7)	−0.2335(4)	0.010(1)
O27	−0.2429(6)	0.3684(8)	−0.1227(4)	0.010(1)
O28	0.0140(7)	0.2568(8)	−0.0960(5)	0.015(1)

contents for the three sites M where cations Sn^{4+}, Sc^{3+} and Fe^{3+} isomorphically substitute (Table 3). This refinement was performed by using mixed scattering curves calculated for the following approximate atomic compositions: 0.5 Sc + 0.2 Fe + 0.3 Sn for $M3$ and $M4$; 0.35 Sc + 0.65 Sn for $M2$. The resulting electron contents were: $M1 = 49.5$, $M2 = 38.6$, $M3 = 30.7$ and $M4 = 26.9$ for a total of 145.7 electrons to be compared with 149.3 electrons expected according to the M cation total from the chemical analysis (Raade *et al.*, 2001) normalised to 4 apfu (2.20 Sn + 1.40 Sc + 0.28 Fe + 0.08 Al + 0.04 Zr). Taking into account the chemical analysis (minor Al and Zr are ignored), the following compositions best match the refined electron contents of the M sites: $M1$ = 0.99 Sn + 0.01 Fe; $M2$ = 0.61 Sn + 0.39 Sc; $M3$ = 0.30 Sn + 0.50 Sc + 0.20 Fe; $M4$ = 0.17 Sn + 0.63 Sc + 0.20 Fe. Thus in the M sites a cation ordering is realised which could not be possible either in a triclinic holohedral or in a monoclinic structure. The positions of the hydrogen atoms belonging to the protonated oxoanions were not detected in the electron density difference map, but the presence of two OH groups per formula unit (pfu) is clearly individuated by crystal-chemical considerations discussed below. Information on the refinement procedures is given in Table 2.

The structure

Table 4 reports selected bond lengths and angles. The structure of kristiansenite (Fig. 1) represents a new type of silicate structure belonging to the disilicate class of minerals; to our knowledge, it is the first case where normal and protonated disilicate groups are present in the same structure. Independently from the refinement figures of merit, the structure is really triclinic because, as mentioned above, the resulting cation ordering is possible only in $C\bar{1}$. On the whole, however, the structure is pseudo-monoclinic, and the maximum difference in the positions of the atoms with respect to the average monoclinic structure is about 0.1 Å (Table 3). This pseudo-monoclinic symmetry and the cation order in the M sites explain why the average structure could be solved but not refined in the $C2$ space-group type.

O...O distances show that O11...O2 = 2.645(7) Å and O21...O28 = 2.627(9) Å must represent hydrogen bonds (Chiari and Ferraris, 1982) involving the two hydrogen atoms pfu. Bond valence sums (s; Brown and Altermatt, 1985) indicate O11 ($s = -1.40$) and O21 ($s = -1.42$) as donor oxygens while O2 ($s = -1.68$) and O28 ($s = -1.52$) are the acceptor oxygens. Each of these oxygens belong to one of the four independent disilicate groups (Tables 3, 4). Taking into account that (Ferraris and Ivaldi 1984) in protonated oxoanions Si—OH bonds are expected to be longer than Si—O bonds (apart from the bridging oxygens), the bond lengths Si3—O11 (1.647 Å) and Si6—O21 (1.640 Å) confirm the proposed hydrogen bonding scheme. In principle, apart from more exotic mechanisms, the Sn^{4+} → (Fe^{3+}, Sc^{3+}) substitution can be balanced either by an O^{2-} → (OH)$^-$ or a (monovalent cation) → Ca^{2+} substitution. However, the O^{2-} → (OH)$^-$ substitution must be excluded because the short O11...O2 and O21...O28 contacts cannot exist without hydrogen bonding. In the analysed sample (Raade *et al.*, 2001), instead, the Na$^+$ → Ca^{2+} substitution is surely active. The distribution of the tetravalent Sn^{4+} cations on all four M sites, instead of a concentration in practically two sites only, is a matter of bond valence balance. Note that both the very close M site sizes and the close octahedral cation radii (0.55, 0.69 and 0.74 Å for Fe^{3+}, Sn^{4+} and Sc^{3+} respectively) favour the pattern of cation distribution observed here.

Figure 1 shows that the disilicate groups and the other polyhedra centred on cations lie on different alternating (10$\bar{1}$) planes. The M octahedra are isolated from each other and aligned in [101] rows. The mentioned hydrogen bonds connect [101] rows of disilicate groups. In first approximation the four independent Ca cations are sevenfold coordinated (Table 4) and connect pairs of octahedral rows in the (10$\bar{1}$) plane. As discussed by Chiari and Fer-

Table 4. Selected bond lengths (Å) for kristiansenite.

Cation	Anion	Bond	Cation	Anion	Bond	Cation	Anion	Bond
M1	O22	1.994(5)	M2	O5	2.018(5)	M3	O12	1.999(4)
	O20	2.029(6)		O9	2.040(5)		O19	2.013(5)
	O2	2.040(5)		O27	2.042(6)		O1	2.048(5)
	O3	2.069(6)		O13	2.091(7)		O6	2.095(6)
	O17	2.079(6)		O28	2.119(7)		O7	2.127(6)
	O16	2.119(6)		O14	2.128(6)		O21	2.145(6)
⟨M1–O⟩		2.055(6)	⟨M2–O⟩		2.073(6)	⟨M3–O⟩		2.071(5)
M4	O15	2.008(5)	Ca1	O5	2.339(7)	Ca2	O26	2.326(6)
	O26	2.028(5)		O20	2.352(6)		O12	2.331(7)
	O8	2.059(6)		O19	2.394(6)		O27	2.385(6)
	O23	2.098(6)		O7	2.396(6)		O14	2.398(6)
	O24	2.128(6)		O13	2.552(6)		O6	2.613(6)
	O11	2.130(6)		O16	2.817(6)		O10	2.735(7)
⟨M4–O⟩		2.075(6)		O4	2.836(7)		O24	2.800(6)
			⟨Ca1–O⟩		2.527(6)	⟨Ca2–O⟩		2.513(6)
				O6	3.166(6)		O25	3.164(6)
				O18	3.196(6)		O13	3.223(7)
Ca3	O1	2.316(5)	Ca4	O8	2.302(6)			
	O3	2.317(6)		O9	2.323(6)			
	O15	2.331(6)		O24	2.325(6)			
	O16	2.380(7)		O22	2.343(7)			
	O23	2.558(5)		O17	2.586(6)			
	O7	2.679(5)		O14	2.701(5)			
	O18	2.766(6)		O25	2.780(7)			
⟨Ca3–O⟩		2.478(6)	⟨Ca4–O⟩		2.480(6)			
	O4	3.161(6)		O23	3.178(7)			
	O17	3.246(7)			3.229(7)			
Si1	O1	1.609(6)	Si2	O5	1.610(9)	Si3	O8	1.586(6)
	O3	1.615(6)		O6	1.612(7)		O9	1.611(7)
	O2	1.620(6)		O4	1.639(5)		O10	1.632(6)
	O4	1.637(6)		O7	1.642(5)		O11	1.647(6)
⟨Si1–O⟩		1.620(6)	⟨Si2–O⟩		1.626(6)	⟨Si3–O⟩		1.619(6)
Si4	O12	1.624(9)	Si5	O15	1.592(7)	Si6	O19	1.613(6)
	O13	1.626(8)		O16	1.625(6)		O20	1.632(7)
	O14	1.647(6)		O17	1.636(8)		O18	1.640(6)
	O10	1.648(5)		O18	1.660(5)		O21	1.640(6)
⟨Si4–O⟩		1.636(7)	⟨Si5–O⟩		1.628(6)	⟨Si6–O⟩		1.631(6)
Si7	O24	1.619(6)	Si8	O26	1.613(6)			
	O22	1.621(8)		O27	1.614(6)			
	O23	1.624(7)		O28	1.637(6)			
	O25	1.653(5)		O25	1.655(6)			
⟨Si7–O⟩		1.629(6)	⟨Si8–O⟩		1.630(6)			

raris (1990) and Chiari (1990), the coordination environment of Ca is usually very distorted; in particular the separation between first and second coordination spheres can be smooth and not sharp as normally occurs for well-behaved coordination polyhedra. In kristiansenite a 7 + 2 coordination is more appropriate for the four Ca cations (Table 4), the tenth neighbour having a distance of 3.502 (O21), 3.505 (O28), 3.601 (O2) and 3.577 Å (O11) for Ca1, Ca2, Ca3 and Ca4 respectively. The strong distortion of the Ca polyhedra in kristiansenite is reflected by their low (~5.6) ECoN (Effective Coordination Number, Hoppe *et al.*, 1989).

Discussion

Conditions for twinning are, in order of priority, metric and structural. The higher the degree of pseudo-symmetry of the structure, the higher is the probability of getting an 'acceptable' structure solution even with a model corresponding only to the average structure. However, effects like (*i*) presence of non-space-group absences, (*ii*) ambiguous intensity statistics, (*iii*) R values higher than those obtained for similar cases, (*iv*) structural disorder, (*v*) not-positively-defined anisotropic atomic displacements, (*vi*) uncertain polarity (Flack Factor) and (*vii*) high residues of electron density (particularly on special positions) are strong signals which can indicate a lower symmetry possibly (but not necessarily) masked by twinning.

Several cases of structures solved in a space-group type different from the correct one, also without concurrence of twinning, are reported in the literature; even if at first sight it might appear surprising, unnecessarily low symmetry have been sometimes assigned to structures (see the systematic analysis by Marsh, 1995). The presence of twinning makes the situation more complex. The diffrac-

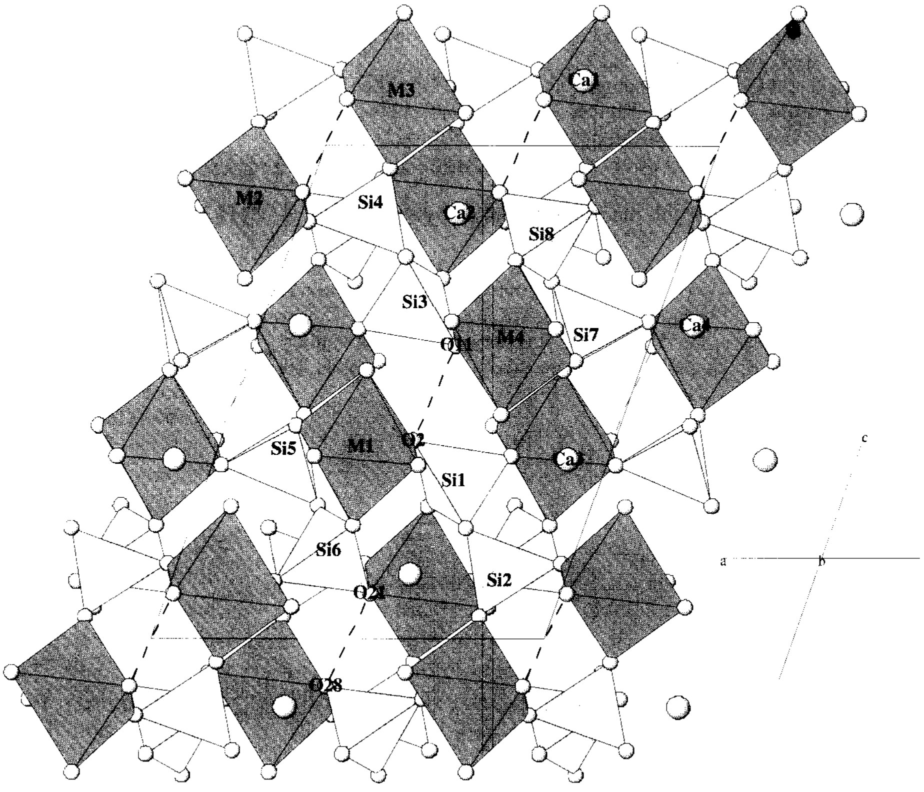

Fig. 1. Perspective view of the structure of kristiansenite along [010]. The independent cation sites are labelled and the directions of the two independent O...O hydrogen bonds are shown by broken lines.

tion symmetry of a twin can differ significantly from that of the individual, with both reduction (a typical case is that of quartz twins with inclined axes, of which the most famous is the Japan law) and augmentation of symmetry elements, even simultaneously. In fact, symmetry elements for each individual that are not parallel in the twin are not retained as symmetry elements for the twin. Besides, when the components of a twin have nearly identical volumes (a rather common case), the twin operation tends to be retained as diffraction symmetry operation of the twin. In this case, a symmetry higher than the structural symmetry could be adopted in the process of structure solution: the resulting symmetry constraints may permit to obtain an average structure, but not the correct one.

When the components have a relevant difference in volume, the twin operation clearly does not appear in the diffractional symmetry of the twin. In this case the diffracted intensities tend to be close to those of the individual and a solution of the structure may be obtained, but the refinement should not reach satisfying convergence. An instructive case has been recently met in refining the structure of the twinned monoclinic new mineral hydroxyclinohumite, $Mg_9[SiO_4]_4(OH,F)_2$ (Ferraris *et al.*, 2000), in which one component represented 96% of the volume. Because of the presence of a metrically orthorhombic sublattice, twinning by reticular pseudo-merohedry occurred and not all the reflections were overlapped. In particular, weak reflections coming from the smaller component doubled the *c* parameter of the monoclinic cell and non-space-group absences occurred. The latter aspect and the high value of *R* (0.12) obtained for an average structure in the twin cell, prompted to investigate the presence of twinning. The final refinement, performed taking into account the twin law {001}, improved to $R = 0.026$.

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