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## Low-Temperature Ordering of Hydrogen Atoms in CaHPO<sub>4</sub> (Monetite): X-ray and Neutron Diffraction Study at 145 K\*

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### Abstract

By structure refinement based on X-ray and neutron diffraction data collected on single crystals at 145 K (2370 and 1886 reflections, Mo  $K\alpha$  radiation and  $\lambda = 0.899$  Å, respectively) CaHPO<sub>4</sub> (monetite) is shown to undergo a reversible order/disorder phase transition involving H atoms only. The low-temperature (LT) phase is consistent with a  $P1$  structural model ( $R = 0.017$ , neutron data) where, however, only two H atoms are on non-centrosymmetrically related positions. The H atoms which were disordered in the high-temperature (HT) phase ( $P\bar{1}$  model) become ordered, so that the [101] chain of hydrogen bonds is now polar. In particular, the formally symmetric hydrogen bond of the HT phase becomes a quasi-symmetrical one with  $O\cdots O = 2.476$  (1),  $O-H = 1.222$  (7),  $H\cdots O = 1.259$  (7) Å and  $\angle O-H\cdots O = 172.6$  (5)°. Possible ferroelectricity in compounds  $MHXO_4$  and the appearance of a KKM (Kanters–Kroon–McAdam) effect due to constraints of pseudo-symmetry are discussed. [Crystal data: at 145 K  $a = 6.916$  (2),  $b = 6.619$  (2),  $c = 6.946$  (3) Å,  $\alpha = 96.18$  (3),  $\beta = 103.82$  (3),  $\gamma = 88.34$  (3)°.]

### Introduction

A refinement of neutron diffraction data (Catti, Ferraris & Filhol, 1977) showed that at room temperature (RT) CaHPO<sub>4</sub> has essentially an average  $P\bar{1}$  structure with H(1)† centred on a formally symmetric hydrogen bond  $O(7)\cdots O(7^I) = 2.459$  (1) Å across a centre of symmetry [symmetry-restricted (SR) (Catti & Ferraris, 1974) or type  $A$  hydrogen bond (Currie & Speakman, 1970)] and H(3) disordered over two centrosymmetrically related positions. The results of a tentative  $P1$  refinement and the presence of a heat-capacity anomaly between 270 and 290 K (Egan & Wakefield, 1964) supported also by a rough measurement of the dielectric constant, together with very weak effects of piezoelectricity and of generation of the second optical harmonic, suggested the existence of a high-temperature (HT) disordered  $P\bar{1}$  phase and a low-temperature (LT) ordered  $P1$  phase which, presumably, was in part present in the samples used for RT experiments. To check this hypothesis, a structural study at LT based on both neutron and X-ray measurements was undertaken.

† To simplify the notation in the tables and figures, O(5) and O(8) in this paper correspond to the same atoms translated by  $+b$  in Catti *et al.* (1977). Roman numerals represent the operations: (i)  $\bar{x}, \bar{y}, \bar{z}$ ; (ii)  $x, y, z - 1$ ; (iii)  $1 - x, \bar{y}, 1 - z$ ; (iv)  $x, 1 + y, 1 + z$ ; (v)  $x, 1 + y, z$ ; (vi)  $1 - x, 1 - y, 1 - z$ ; (vii)  $\bar{x}, 1 - y, 1 - z$ .

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### Experimental

A set of neutron powder spectra on commercial  $\text{CaHPO}_4$  (BDH) was recorded from 300 down to 5 K and *vice versa*, by the D1B diffractometer at ILL (Grenoble) with  $\lambda = 2.4 \text{ \AA}$ . Particularly around  $2\theta = 70^\circ$ , the spectra above 280 K and below 230 K (Fig. 1) are sufficiently different to show some definite and reversible alterations of the structure in this range of temperature.

X-ray data were collected at 145 K with a Syntex  $P2_1$  diffractometer on a tabular crystal (BDH commercial product) with dimensions  $0.08 \times 0.12 \times 0.20 \text{ mm}$ ;  $\text{Mo } K\alpha$  monochromatized radiation ( $\lambda = 0.71070 \text{ \AA}$ ) and  $\omega$  scan ( $\theta_{\text{max}} = 35^\circ$ ) were used. After rejection of 335 reflections with  $I \leq 2\sigma(I)$  a set of 2370 independent reflections remained for the crystal structure analysis. Least-squares refinement using the angular values of selected high- $\theta$  reflections gave the

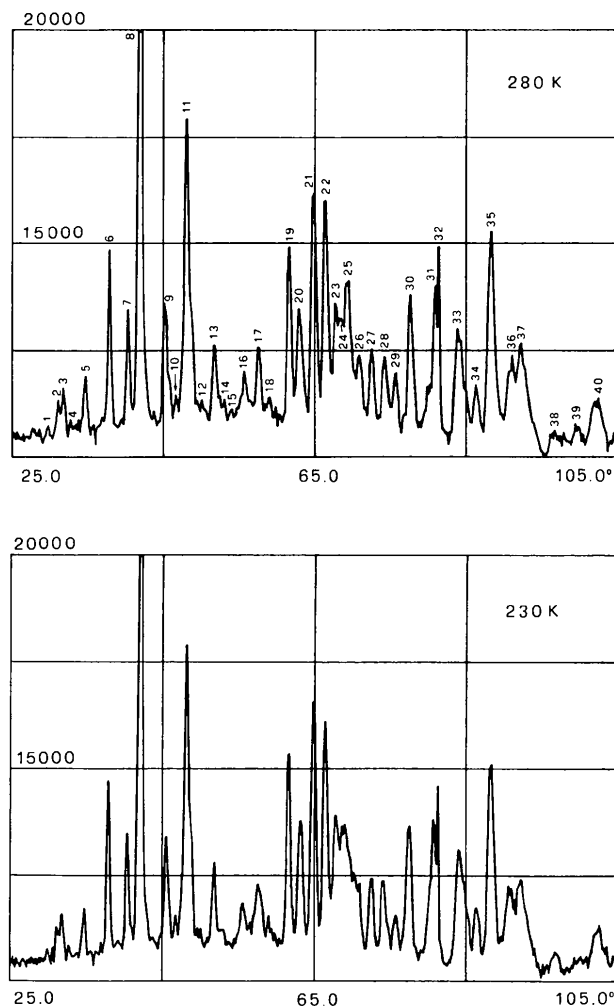


Fig. 1. Intensities (total counts) vs  $2\theta$  for the neutron diffraction powder spectra of  $\text{CaHPO}_4$  at 280 and 230 K;  $\lambda = 2.4 \text{ \AA}$ .

following unit-cell parameters which were used for all the calculations in this paper:  $a = 6.916(2)$ ,  $b = 6.619(2)$ ,  $c = 6.946(3) \text{ \AA}$ ,  $\alpha = 96.18(3)$ ,  $\beta = 103.82(3)$ ,  $\gamma = 88.34(3)^\circ$ . Only  $c$  shows a significant deviation from its RT value; accordingly, the major alteration in the crystal structure concerns the hydrogen bond donated by O(6), which has its largest component along the  $z$  axis (Fig. 2).

Single-crystal neutron diffraction data were collected at 145 K on the same instrument (D8, ILL Grenoble) and with the same crystal ( $11 \text{ mm}^3$ ) used for the RT work (Catti *et al.*, 1977). The previous experimental conditions were mainly kept, except for a shorter wavelength ( $\lambda = 0.8993 \text{ \AA}$ ). With  $\theta_{\text{max}} = 43^\circ$ , about 15% of the independent sphere of reflection was hindered by the prototype mount used for the Displex cryorefrigerator, and a set of 1886 independent reflections was obtained. The intensities were reduced to structure amplitudes by the method of Lehmann & Larsen (1974).

Absorption corrections were neglected ( $\mu = 0.06 \text{ mm}^{-1}$  for neutrons, measured;  $\mu = 2.1 \text{ mm}^{-1}$  for X-rays). The main calculations were performed at the CSI-Piemonte Centre (Torino), with the XRAY set of programs (Stewart, Kundell & Baldwin, 1970) and with a modified version of ORFLS (Busing, Martin & Levy, 1962). The neutron scattering lengths were (Bacon, 1972): 5.10, 4.70, 5.80, and  $-3.74 \text{ fm}$  for P, Ca, O and H, respectively; the X-ray scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962).

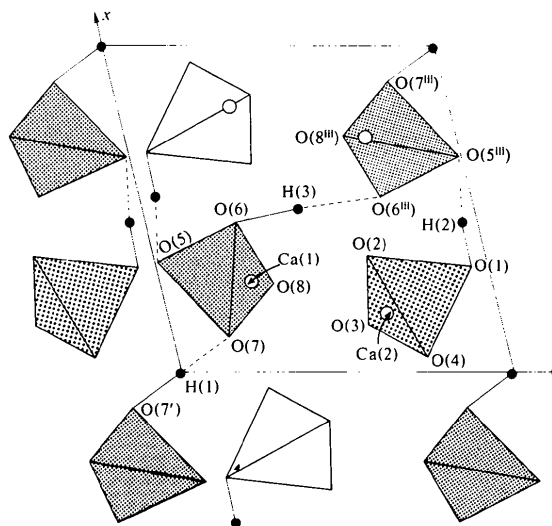


Fig. 2. Projection of the structure of the low-temperature phase of  $\text{CaHPO}_4$  onto the plane normal to  $b$ , emphasizing the hydrogen-bonding scheme and the tetrahedron pattern (P atoms are not shown).

## Refinement of the structure

At the last stage of the refinement the neutron data were corrected for secondary extinction by least-squares interpolation of the function  $I_c/I_o = k(1 + gI_c)$  with  $g = 6 \times 10^{-6} \text{ fm}^{-2}$  and  $k = 0.986$ ; weights =  $1/(100\sigma^2)$  were used. With the X-ray data unit weights were used and the secondary extinction was found to be negligible.

The following steps of refinement were performed (full-matrix least squares).

(1) Starting from the atomic parameters of Catti *et al.* (1977), a  $P\bar{1}$  model with H(1) on the origin and H(3) distributed over two centrosymmetrically related positions converged to  $R = 0.022$  ( $R = 0.028$  before correction for secondary extinction and with unit weights) and  $R = 0.032$  with neutron and X-ray data, respectively. The results of the X-ray refinement are reported in Table 1.\*

\* Lists of  $|F_o|$ ,  $F_c$  and of thermal parameters for the neutron and X-ray analyses have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34866 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates obtained from the neutron (first line) and the X-ray (second line) refinements of the low-temperature phase of CaHPO<sub>4</sub>

The values reported are for a centrosymmetric model except those of H(1) and H(3) in the neutron refinement; H(3) has an occupation factor of 0.5 in the X-ray refinement.

	x	y	z
P(1)	0.21149 (7)	0.38303 (7)	0.72509 (7)
	0.21053 (8)	0.38189 (7)	0.72423 (8)
P(2)	0.29128 (7)	-0.07032 (8)	0.20458 (7)
	0.29242 (9)	-0.06627 (8)	0.20569 (8)
Ca(1)	0.29053 (8)	0.41801 (9)	0.28088 (8)
	0.29194 (6)	0.42186 (7)	0.27807 (6)
Ca(2)	0.17828 (8)	0.83749 (9)	0.65969 (8)
	0.17737 (6)	0.83713 (6)	0.66068 (6)
O(1)	0.32276 (6)	0.33161 (7)	0.94331 (7)
	0.3232 (2)	0.3317 (2)	0.9420 (2)
O(2)	0.35911 (6)	0.49508 (7)	0.63958 (7)
	0.3570 (2)	0.4938 (2)	0.6369 (2)
O(3)	0.14291 (6)	0.18577 (7)	0.59581 (7)
	0.1413 (2)	0.1840 (2)	0.5955 (2)
O(4)	0.04484 (6)	0.53003 (7)	0.74827 (7)
	0.0431 (2)	0.5281 (2)	0.7477 (2)
O(5)	0.33626 (6)	-0.15869 (7)	0.00839 (7)
	0.3354 (2)	-0.1594 (3)	0.0102 (2)
O(6)	0.46149 (7)	0.07873 (7)	0.32141 (7)
	0.4615 (3)	0.0848 (3)	0.3172 (3)
O(7)	0.10346 (6)	0.06935 (7)	0.16364 (7)
	0.1020 (2)	0.0698 (2)	0.1637 (2)
O(8)	0.26774 (7)	-0.22972 (7)	0.33720 (7)
	0.2720 (3)	-0.2258 (3)	0.3401 (3)
H(1)	0.0058 (8)	-0.0106 (9)	-0.0026 (10)
	0	0	0
H(2)	0.4596 (1)	0.2588 (2)	0.9557 (2)
	0.428 (8)	0.274 (8)	0.939 (8)
H(3)	0.4991 (2)	0.0312 (3)	0.4647 (2)
	0.509 (20)	0.094 (20)	0.480 (20)

(2) A non-centrosymmetric model with H(1) and H(3) attached to only O(7<sup>1</sup>) and O(6), respectively, was refined by keeping constant the parameters of Ca, P, O and H(2) at the  $P\bar{1}$  values of model (1). With neutron data  $R = 0.017$  was thus obtained (Table 1);  $R$  was 0.022 before correction for secondary extinction and with unit weights. With X-ray data the positional shifts of H(1) and H(3) were unsatisfactory and the refinement was abandoned; in any case, the  $R$  value was 0.032 as for the  $P\bar{1}$  model.

(3) With neutron data, the atomic parameters obtained by Catti *et al.* (1977) for a  $P1$  model involving non-centrosymmetry for all the atoms converged practically to model (2), *i.e.* to a model which is not centrosymmetric for H(1) and H(3) only.

(4) Attempts to release heavy atoms and H(2) from centrosymmetry through shifts made on the hypothesis that P—OH should be longer than P—O bonds always converged to model (2).

(5) Model (2) was insensitive to the exchange of H(3), or alternatively of H(1), between centrosymmetrically related positions.

Refinements (3) and (4), which involve quasi-centrosymmetrically related positions, were performed by minimizing the quantity  $\sum_i w_i |F_o - F_c|_i^2$  instead of the usual  $\sum_i w_i (|F_o| - |F_c|)_i^2$  as suggested by Rae (1974), in order to avoid high covariance of pseudosymmetric parameters; the usual method was used in the other cases.

## Discussion

## The model

The  $R$  values leave no doubts that the  $P1$  model with H(3) ordered ( $R = 0.017$ ) is more realistic than the  $P\bar{1}$  structure ( $R = 0.022$ ). The former shows H(1) off the origin by several e.s.d.'s (Table 1) even if its displacement from the mid-point between O(7<sup>1</sup>) and O(7) is only  $5\sigma(\text{O—H})$  (Table 2). However, the non-hydrogen atoms and H(2) are left on centrosymmetrically related positions also in this model, and in principle this is only an approximation; it is then useless to discuss whether the O(7<sup>1</sup>)...O(7) hydrogen bond is symmetric or not. As already pointed out by Catti *et al.* (1977), at least the pseudo-centrosymmetric O atoms should have different P—O bond lengths according to whether O is an H carrier or not. For reasons which are not clear, but presumably connected with the pseudosymmetry of the real atomic positions, the best refinement has been obtained for a model which is not fully satisfactory in its crystal-chemical details. However, as in similar cases (Thomas, 1973; Thomas, Tellgren & Olovsson, 1974) it seems impossible to extract further information from the diffraction data: an excellent  $R$  value does not necessarily mean a wholly acceptable structure!

Table 2. *Interatomic distances (Å) and angles (°) in the hydrogen bonds for the refinements with neutron (first line, P1 model) and X-ray data (second line, P1 model); the third line shows the room-temperature results of Catti et al. (1977) for a P1 model [in the P1 model H(1) is fixed by symmetry]*

A	B	C	D	BC	CD	BD	∠ABC	∠BCD
P(1)—O(1)—H(2)···O(5 <sup>III</sup> )				1.039 (1)	1.519 (1)	2.556 (1)	116.0 (1)	175.4 (1)
				0.81 (7)	1.76 (7)	2.555 (2)	110 (5)	167 (5)
				1.042 (2)	1.521 (2)	2.560 (1)	117.0 (1)	175.6 (1)
P(2)—O(6)—H(3)···O(6 <sup>III</sup> )				1.047 (2)	1.685 (2)	2.724 (1)	103.8 (2)	170.9 (2)
				1.10 (12)	1.90 (13)	2.815 (3)	119 (7)	138 (10)
			O(8 <sup>III</sup> )	1.153 (6)	1.627 (6)	2.658 (1)	119.3 (3)	145.5 (5)
P(2)—O(7 <sup>I</sup> )—H(1)···O(7)				1.222 (7)	1.259 (7)	2.476 (1)	102.1 (4)	172.6 (5)
				1.237 (1)	1.237 (1)	2.474 (2)	106.0 (1)	180
				1.230 (1)	1.230 (1)	2.459 (1)	108.1 (1)	180

Table 3. *Interatomic distances in the Ca coordination polyhedra for neutrons (N) and X-rays (X)*

The e.s.d.'s are 0.001 and 0.002 Å for N and X respectively.

	N	X
Ca(1)—O(1 <sup>II</sup> )	2.414 Å	2.406 Å
Ca(1)—O(2)	2.423	2.421
Ca(1)—O(6)	2.519	2.501
Ca(1)—O(7)	2.632	2.658
Ca(1)—O(8 <sup>V</sup> )	2.330	2.331
Ca(1)—O(2 <sup>VI</sup> )	2.425	2.425
Ca(1)—O(4 <sup>IV</sup> )	2.299	2.298
Average	2.435	2.434
Ca(2)—O(2)	2.563	2.567
Ca(2)—O(3 <sup>V</sup> )	2.389	2.382
Ca(2)—O(4)	2.454	2.461
Ca(2)—O(5 <sup>IV</sup> )	2.405	2.410
Ca(2)—O(8 <sup>V</sup> )	2.456	2.458
Ca(2)—O(3 <sup>VI</sup> )	2.487	2.477
Ca(2)—O(6 <sup>VI</sup> )	2.538	2.530
Ca(2)—O(7 <sup>VII</sup> )	2.568	2.549
Average	2.483	2.479

The neutron and X-ray parameters are statistically, even if not substantially, different; this affects bond lengths in Ca (Table 3) more than in P polyhedra (Table 4). The largest discrepancies are observed for thermal parameters; in particular, for O(6) and O(8), which are involved in the area of major changes with respect to the disordered phase as discussed below, the discrepancies are large for the positional parameters too. This effect could be attributed to accumulation of errors which derive from the centrosymmetric constraint on heavy atoms and which, reasonably, are different for refinements based on electron or nuclear density. In this connection it is not surprising that the largest differences between neutron and X-ray thermal parameters are shown by the atoms of the P(2) tetrahedron, which would be expected to deviate from centrosymmetry most of all.

Table 4. *Interatomic distances and O—P—O angles for the P tetrahedra for neutrons (N) and X-rays (X)*

The e.s.d.'s are 0.001 Å, 0.05°, 0.002 Å and 0.1° for distances and angles for N and X respectively.

	N		X	
P(1)—O(1)	1.595 Å		1.592 Å	
P(1)—O(2)	1.541		1.542	
P(1)—O(3)	1.522		1.525	
P(1)—O(4)	1.514		1.515	
Average	1.543		1.544	
O(1)—O(2)	2.539 Å	108.11°	2.537 Å	108.0°
O(1)—O(3)	2.537	108.97	2.540	109.1
O(1)—O(4)	2.500	107.00	2.501	107.2
O(2)—O(3)	2.519	110.68	2.521	110.6
O(2)—O(4)	2.463	107.47	2.467	107.7
O(3)—O(4)	2.551	114.37	2.550	114.0
Average	2.518	109.43	2.519	109.4
P(2)—O(5)	1.522 Å		1.522 Å	
P(2)—O(6)	1.567		1.560	
P(2)—O(7)	1.560		1.560	
P(2)—O(8)	1.510		1.513	
Average	1.540		1.539	
O(5)—O(6)	2.528 Å	109.83°	2.525 Å	110.0°
O(5)—O(7)	2.524	109.98	2.525	110.0
O(5)—O(8)	2.534	113.44	2.519	112.2
O(6)—O(7)	2.456	103.54	2.460	104.1
O(6)—O(8)	2.501	108.70	2.509	109.4
O(7)—O(8)	2.528	110.89	2.531	110.9
Average	2.512	109.40	2.512	109.4

#### Comparison with the room-temperature phase

The overall aspect of the crystal structure is similar at room (Catti *et al.*, 1977) and low temperature (Fig. 2), since the shifts are never larger than 0.2 Å for a single coordinate and 0.4 Å for an atomic position and are practically confined to H(3), O(8), O(6) and Ca(1). The major shifts can be accounted for by a rotation of the P(2) tetrahedron around its edge O(7)—O(5), with O(6) coming closer to the *xz* plane and to O(6<sup>III</sup>); the opposite happens for O(8).

The main consequences of the ordering of H(3) and of the other shifts in the LT structure are the following.

(1)  $\text{O}(7^{\text{I}})\cdots\text{O}(7)$  becomes a quasi-symmetric hydrogen bond.

(2)  $\text{O}(6)\cdots\text{O}(8^{\text{III}})$  is no longer a hydrogen bond and edge of the  $\text{Ca}(2^{\text{I}})$  coordination polyhedron at the same time; the neutron results show unequivocally that the hydrogen bond involving H(3) is now established between O(6) and its pseudo-centrosymmetric atom  $\text{O}(6^{\text{III}})$  (Table 2). In fact, for comparison with values given in Table 2,  $\text{O}(6)\cdots\text{O}(8^{\text{III}})$  is 2.758 Å,  $\text{H}(3)\cdots\text{O}(8^{\text{III}})$  is 2.212 Å and  $\angle\text{O}(6)-\text{H}(3)\cdots\text{O}(8^{\text{III}})$  is  $110.4^\circ$ .

Since the refinement of RT data was relatively insensitive to ordering/disordering of H(3), in contrast to the present LT results, the hypothesis (Catti *et al.*, 1977) of a partial presence of a LT phase at RT would be supported.

### The phase transition

The reversible transition from the LT to the HT phase could be easily thought of as due to migration of 50% H(1) and H(3) from  $\text{O}(7^{\text{I}})$  and  $\text{O}(6)$  to  $\text{O}(7)$  and  $\text{O}(6^{\text{III}})$ , respectively, by the breaking of two O–H bonds. An alternative mechanism, which requires the break of three hydrogen bonds, can be put forward. Starting from their positions of Fig. 2, the  $\text{P}(2)$  and  $\text{P}(2^{\text{I}})$  tetrahedra rotate by  $180^\circ$  around their non-crystallographic twofold axes perpendicular to the  $\text{O}(6)-\text{O}(7)$  and  $\text{O}(6^{\text{I}})-\text{O}(7^{\text{I}})$  edges, carrying with them H(3) and H(1), respectively. After the rotation each H atom occupies a position which is pseudo-centrosymmetrically related to that formerly occupied by the other. If only 50% of these tetrahedra rotate in the structure, an average centre of symmetry will arise and the H(1) position will appear permanently occupied, because the two real positions are very close to the centre of symmetry; the occupation factor of the H(3) position, instead, will be 0.5. The disordered HT phase could be attained by such a means provided the energy barrier between the two positions of the  $\text{P}(2)$  and  $\text{P}(2^{\text{I}})$  tetrahedra is comparable with the thermal energy.

The best definition of the temperature of transition is that given by the heat capacity measurements of Egan & Wakefield (1964), which put it in the range 270–290 K, depending on the sample. This variability seems to be related to the presence of impurities and to the procedure of preparation which, presumably, affect the energy barrier for the proton migration or tetrahedra rotations and, therefore, the population of the two states *vs* temperature.

Since  $\text{CaHPO}_4$  is biologically and agriculturally important and the reversible phase transition occurs near room temperature, further investigations seem desirable.

### Is $\text{CaHPO}_4$ ferroelectric?

The chain of hydrogen bonds  $\text{O}(7^{\text{I}})-\text{H}(1)\cdots\text{O}(7)-\text{O}(6)-\text{H}(3)\cdots\text{O}(6^{\text{III}})-\text{O}(7^{\text{III}})-\text{H}(1^{\text{III}})\cdots$  causes the [101] direction to be highly polar; through a mechanism of rotation of P tetrahedra or of proton migration the polarization of the chain could be reversed by applying a suitable electric field. These structural features and the anomaly in the dielectric constant reported by Catti *et al.* (1977) (but more accurate measurements are wanted) show, therefore, that  $\text{CaHPO}_4$  is a candidate for ferroelectricity.

Several compounds with formula  $\text{MXO}_4$  ( $X = \text{P, S, As, Se}$ ;  $M = \text{Na, K, Rb, Cs, NH}_4^+$ ,  $\text{Ca, Sr, Ba, Sn, Pb}$ ) are known; in particular,  $\text{SrHAsO}_4$  (Nabor & Dalvi, 1977),  $\text{SrHPO}_4$  (Boudjada, Masse & Guitel, 1978) and  $\text{NaHSO}_4$  (Sonneveld & Visser, 1979) show a phase isostructural with HT  $\text{CaHPO}_4$ . The lengths of the  $\text{O}(7^{\text{I}})\cdots\text{O}(7)$  hydrogen bond are 2.482 and 2.497 Å in  $\text{SrHPO}_4$  and  $\text{NaHSO}_4$ , respectively, and these fairly large values should support a model with H(1) disordered rather than located on the centre of symmetry. At the moment, no studies on the electric behaviour of these isostructural phases are known, while other members of the family ( $\text{PbHPO}_4$ ,  $\text{PbHAsO}_4$ ,  $\text{BaHPO}_4$ ,  $\text{RbHSO}_4$ ,  $\text{NH}_4\text{HSO}_4$ ) are well known ferroelectrics (Schmidt, 1976).

### KKM effect due to false symmetry

The origin of the KKM effect (*i.e.* a double electron-density peak astride the special position expected for a H atom) has been discussed by Speakman and co-workers. In some cases it was clearly attributed to disorder (Currie, Speakman, Kanters & Kroon, 1975), and in others to polarization of the electron density (Thomas & Liminga, 1978); for a discussion see also Catti & Ferraris (1976).

A  $\Delta F_x$  map calculated in the plane of the  $\text{O}(7^{\text{I}})-\text{H}(1)\cdots\text{O}(7)$  hydrogen bond, with the LT X-ray data of this work, showed the electron distribution with a double maximum (0.80 Å separation) across the centre of symmetry which is typical of the KKM effect. The corresponding  $\Delta F_N$  map shows a single ellipsoidal peak at the H(1) position with its major axis along the  $\text{O}(7^{\text{I}})\cdots\text{O}(7)$  direction, in agreement with a value of  $173^\circ$  for the angle between the direction of maximum thermal motion and the  $\text{O}(7^{\text{I}})-\text{H}(1)$  bond. The double maximum in the  $\Delta F_x$  map is clearly due, in this case, to the artificial disorder introduced by the constraints of the false  $\text{P}\bar{1}$  symmetry and is favoured by the electron density polarization of the  $\text{O}(7^{\text{I}})-\text{H}(1)$  bond; in contrast, the vicinity of the proton to the false centre of symmetry does not allow the split of the maximum in the  $\Delta F_N$  map.

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## Verfeinerung der Struktur von Tinaksit, $\text{Ca}_2\text{K}_2\text{NaTiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$

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### Abstract

$\text{Ca}_2\text{K}_2\text{NaTiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$  is triclinic, with  $a = 10.377$  (3),  $b = 12.166$  (3),  $c = 7.059$  (1) Å,  $\alpha = 90.91$  (1),  $\beta = 99.3$  (1),  $\gamma = 92.76$  (3)°,  $V = 878.8$  Å<sup>3</sup>,  $D_x = 2.321$  Mg m<sup>-3</sup>,  $Z = 2$ , space group  $P\bar{1}$ . The crystal structure of tinaxite, reported by Petrunina, Ilyukhin & Belov [*Sov. Phys. Dokl.* (1971). 16, 338–340], has been refined to  $R = 0.033$ . There are two hybrid *Dreierdoppelketten* in the unit cell with Si–O bond lengths varying from 1.566 to 1.657 Å according to the different linkages of the  $[\text{SiO}_4]$  tetrahedra.

### Einleitung

Vor einigen Jahren bestimmten Petrunina, Ilyukhin & Belov (1971) die Struktur des Tinaksits. Mit über 1500 Reflexdaten erreichten sie einen  $R$ -Wert von 0,15 und in einer späteren Arbeit (Kuz'min, Petrunina, Ilyukhin & Belov, 1973) einen  $R$ -Wert von 0,10. Tinaksit ist das

einzig bisher bekannte Silikat mit eindeutig hybridem Anion, d.h. mit einem Silikatanion, das durch Verknüpfung eines unverzweigten mit einem verzweigten Anion aufgebaut ist (Liebau, 1978). Insbesondere aus diesem Grunde ist die Kenntnis genauerer Bindungslängen und -winkel dieser Struktur von kristallchemischem Interesse. Da sie jedoch grosse Schwankungsbreiten aufwies, schien es wünschenswert, eine Strukturverfeinerung durchzuführen.

Dazu standen hellbraune, nadlige Einkristalle, die zusammen mit Aegirinnadeln in Charoit eingebettet waren, zur Verfügung. Die Gesteinsprobe stammte aus der UdSSR (Baikalsee, nach mündlicher Mitteilung). Die chemische Zusammensetzung  $\text{Ca}_2\text{K}_2\text{NaTiO}[\text{Si}_7\text{O}_{18}(\text{OH})]$  der Tinaksitkristalle wurde aus der Arbeit von Petrunina *et al.* (1971) übernommen und auf analytischem Wege nicht überprüft. Der geringe Eisengehalt, der von Rogov, Rogova, Vorongov & Moleva (1965) in Tinaksit nachgewiesen wurde und auf den die hellbraune Farbe der Kristalle hinweist, wurde bei der Verfeinerung der Atomparameter ebenso wie in der