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Hydrogen Bonding in the Crystalline State. CaHPO_4 (Monetite), $P\bar{1}$ or $P1$? A Novel Neutron Diffraction Study*

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1749 independent reflexions, measured on a single-crystal neutron diffractometer ($\lambda = 1.217 \text{ \AA}$), were used for refining the crystal structure of CaHPO_4 in both space groups $P\bar{1}$ ($R = 0.0283$) and $P1$ ($R = 0.0286$). In the $P\bar{1}$ model a proton lies on a symmetry centre forming a symmetric hydrogen bond (2.459 \AA) and another is statistically distributed between two centrosymmetric positions; in the $P1$ models the first proton is slightly off the centre and the second is either ordered or disordered. By crystal–chemical considerations on the refinements, and taking into account a heat capacity anomaly at about 280 K together with very weak effects of piezoelectricity and of generation of the second optical harmonic at room temperature, the existence of a low-temperature ordered ($P1$) phase and a high-temperature disordered ($P\bar{1}$) phase is suggested; diffraction data would come from a crystal in the disordered phase with a small fraction of the ordered one. A peculiar version of the KKM effect is shown by the difference maps. X-ray and neutron diffraction refinements are compared statistically.

Introduction

CaHPO_4 (monetite) has been the subject of several crystallographic (MacLennan & Beevers, 1955; Jones & Cruickshank, 1961; Curry, Denne & Jones, 1968; Denne & Jones, 1971; Dickens, Bowen & Brown, 1972), spectroscopic (Blinic & Hadži, 1960; Petrov, Šoptrajanov, Fuson & Lawson, 1967) and other physicochemical studies (Egan & Wakefield, 1964).

The structural model refined in space group $P\bar{1}$ ($Z = 4$) by Dickens *et al.* (1972), with X-ray data ($R = 0.031$), implies that H(1)† is on an inversion centre, forming a symmetric hydrogen bond $\text{O}(7) \cdots \text{O}(7') =$

$2.458(2) \text{ \AA}$ [type *A* (Currie & Speakman, 1970) or symmetry-restricted (SR) hydrogen bond (Catti & Ferraris, 1974)]; H(2) forms the hydrogen bond $\text{O}(1) \cdots \text{O}(5')^{\ddagger} = 2.565(1) \text{ \AA}$, and the third independent hydrogen atom, H(3), is disordered over two centrosymmetric positions and is involved in the hydrogen bond $\text{O}(6) \cdots \text{O}(8')^{\ddagger} = 2.669(1) \text{ \AA}$ which is also an edge of the coordination polyhedron of $\text{Ca}(2')$ (Fig. 1). [101] chains of P(2) coordination tetrahedra, linked *via* the hydrogen bonds involving H(1) and H(3) are present in the structure; the P(1) tetrahedra are connected to these chains by the third hydrogen bond.

However, according to Denne & Jones (1971) 'Professor W. G. Perdok found that monetite gave the weakest positive piezoelectric effect yet detected with his Giebe & Scheibe apparatus'; such an effect was also reported by the same authors for the isostructural (Ferraris & Chiari, 1970) CaHAsO_4 (weilite). At that time, they proposed a $P1$ model with H(3) ordered and H(1) in an asymmetric position; however, the quality and quantity of their neutron diffraction data did not allow

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† Atoms are numbered according to Denne & Jones (1971); Dickens *et al.* (1972) interchanged H(1) and H(2). A prime denotes an atom in a centrosymmetric (or quasi-centrosymmetric) position for the $P\bar{1}$ (or $P1$) model. Roman numerals represent the translations: (i) $-c$; (ii) $+a + b + c$; (iii) $+b + c$; (iv) $+b$; (v) $+c$; (vi) $-b$; (vii) $+a + c$.

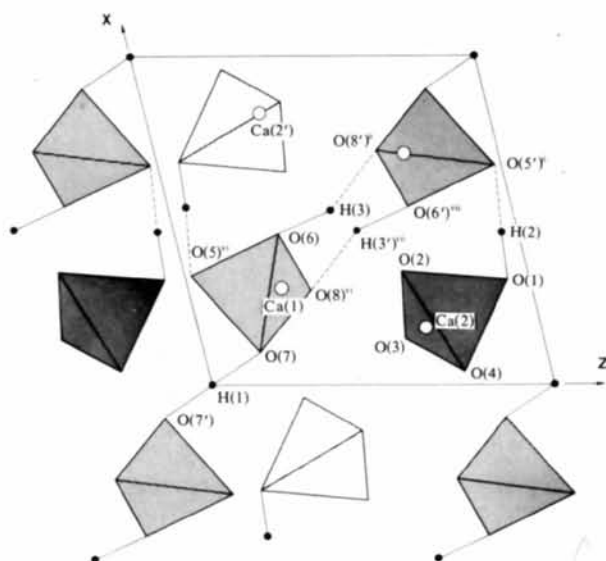


Fig. 1. Projection of the $P1$ structure of CaHPO_4 onto the plane normal to b , emphasizing the hydrogen-bonding scheme and the PO_4 tetrahedra pattern (P atoms are not shown).

them to choose a definite ordered model (presence of HPO_4 groups alone or together with PO_4 and H_2PO_4 groups) and to remove the heavy atoms from centrosymmetric positions. The last point is clearly a serious crystal-chemical drawback, particularly as far as the O atoms bonded to H(1) and H(3) are concerned.

Experimental

A sample of synthetic CaHPO_4 prepared by Dr V. R. Lehr (TVA, Alabama) was supplied by Dr D. W. Jones (Bradford University); a single crystal was ground to a rough cylinder 11 mm^3 (diameter 1.7–1.9 mm, length 4.3 mm), [010] elongated within a few degrees.

Neutron diffraction intensities were collected on the D8 four-circle diffractometer at the HFR of the Institute Laue-Langevin (Grenoble). The following measurement conditions were used: room temperature; $\lambda = 1.217 \text{ \AA}$ with Cu(200) monochromator; neutron beam divergence $60'$; beam flux onto the crystal $10^7 \text{ n cm}^{-2} \text{ s}^{-1}$; step-scan technique ($\omega-2\theta$) with 31 steps for every reflexion; $2\theta \leq 120^\circ$; scan width and pre-set monitor counting increasing with 2θ (2.50 to 6.15° in 2θ and up to 50% counting increase); the 341 and 501 reflexions were measured as references every 40 reflexions. Probably because of a fracture on the surface of the monochromator, the peak profiles looked asymmetric with an inflexion on the low- θ side. For each reflexion, the counts for the first three and last three steps were averaged to obtain the background, with a program written by one of us (AF); after removal of 140 reflexions with $I \leq 3\sigma(I)$, a set of 1749 independent observations was left.

The cell parameters of Dickens *et al.* (1972) were used: $a = 6.910(1)$, $b = 6.627(2)$, $c = 6.998(2) \text{ \AA}$, $\alpha = 96.34(2)$, $\beta = 103.82(2)$, $\gamma = 88.33(2)^\circ$. The scattering lengths were (Bacon, 1972): P, 5.10; Ca, 4.70; O, 5.80 and H, $-3.74 \times 10^{-13} \text{ cm}$.

The absorption correction was neglected (measured absorption coefficient: $\mu = 1.2 \text{ cm}^{-1}$). All the main calculations were performed at the Computing Centre of the University of Torino with the programs of the X-RAY system (Stewart, Kundell & Baldwin, 1970) and with a modified version of ORFLS (Busing, Martin & Levy, 1962).

Refinement

$P1$ model

A difference map following a structure factor calculation with the X-ray heavy-atom parameters (Dickens *et al.*, 1972) showed H(1) on the symmetry centre, H(2) in a general position and bonded to O(1), and H(3) statistically bonded to both O(6) and O(6'). However, the H(3) peak ($-51 \times 10^{-14} \text{ cm}^3 \text{ \AA}^{-3}$) was less than $\frac{1}{3}$ of those corresponding to H(1) and H(2) (-168 and $-183 \times 10^{-14} \text{ cm}^3 \text{ \AA}^{-3}$) respectively. The isotropic ($R = 0.090$) and anisotropic ($R = 0.046$) full-matrix least-squares refinements converged rapidly. A correction for secondary extinction by least-squares interpolation of the function $I_c/I_o = k(1 + gI_c)$ yielded $k = 0.900$ and $g = 32 \times 10^{20} \text{ cm}^{-2}$; the refinement converged then to $R = 0.0283$. Unit weights were used because of the satisfactory constant value of Δ^2 averaged over groups vs $|F_o|$ and $\sin \theta$. Very weak reflexions showed $|F_o| > |F_c|$ almost systematically, presumably because of the multiple scattering contribution to $|F_o|$; no correction was made for thermal diffuse scattering.

$P1$ models

The full-matrix least-squares refinements in $P1$ were performed by minimizing the quantity $\sum_i w_i |F_o - F_c|^2$ instead of $\sum_i w_i (|F_o| - |F_c|)^2$ (Rae, 1974). The high covariance between parameters in pseudo-symmetric structures, or even singularities when parameters are exactly symmetry-related, is avoided by this method.

A $P1$ model for CaHPO_4 can be obtained (Denne & Jones, 1971) by ordering H(3), so that the inversion centre must disappear; the whole H(3) atom was then attached to O(6), and a subsequent Fourier map showed H(1) very slightly closer to O(7'). The refinement converged ($R = 0.080$ and $R = 0.042$ for the isotropic and anisotropic cases respectively) with H(1) linked to O(7'); O(8) and O(8') were appreciably non-centrosymmetric, but the other atoms practically centrosymmetric; the position of P(1) was kept fixed in order to define the origin. At this stage the O atoms

related to H(3) and H(1) [*i.e.* O(6), O(6') and O(7), O(7')] were given shifts along their respective lines of maximum thermal motion, so as to lengthen the P—OH bond with respect to P—O; the refinement was continued without substantial improvement of *R* which, however, dropped to 0.0286 after a secondary extinction correction ($k = 0.933$, $g = 21 \times 10^{20} \text{ cm}^{-2}$).

Refinements were tried for two different models, and *R* did not change significantly: (i) H(1) and H(3) bonded to the same tetrahedron — appreciable shifts of the O atoms could not be observed; (ii) H(1) bonded to O(7') and H(3) disordered over O(6) and O(6') — refining the occupancy factors of H(3) and H(3') showed only a slight preference, about 4%, for the half-atom bonded to O(6).

The final fractional coordinates and the B_{ij} thermal coefficients of the expression

$$\exp\left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*\right)$$

are given in Table 1 for both the $P\bar{1}$ and the $P1$ refinements.† $P1$ parameters are reported only for the ordered case with H(1) and H(3) attached to different PO_4 tetrahedra, as it seems to be the simplest and extreme model.

† A list of $|F_o|$ and F_c (for $P\bar{1}$ only) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32206 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates ($\times 10^4$) and vibrational parameters ($\text{\AA}^2 \times 10^2$) for the $P\bar{1}$ (first line) and the $P1$ (second and third lines) models

The e.s.d.'s ($P1$ in parentheses) are as follows for positional and thermal parameters, in the order: 0.0001 (0.0002), 0.02 (0.04) for Ca, P and O; 0 (0.0004), 0.08 (0.08) for H(1); 0.0002 (0.0004), 0.05 (0.08) for H(2); 0.0008 (0.0008), 0.22 (0.20) for H(3).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P(1)	2077	3790	7207	43	47	52	1	16	4
	2077	3790	7207	40	44	47	-1	15	-1
	-2077	-3791	-7200	39	40	51	2	16	9
P(2)	2962	9436	2082	75	76	62	18	17	2
	2955	9425	2089	79	69	61	19	19	-4
	-2971	-9452	-2076	71	75	57	18	14	5
Ca(1)	2947	4353	2719	62	120	95	3	25	-26
	2925	4369	2719	60	113	88	5	20	-23
	-2968	-4337	-2717	55	112	95	3	23	-30
Ca(2)	1754	8373	6664	114	56	91	-4	3	17
	1762	8370	6662	103	52	90	-5	0	11
	-1745	-8375	-6657	110	53	87	-2	2	19
O(1)	3234	3322	9373	100	119	55	19	19	22
	3228	3335	9385	98	108	53	22	20	22
	-3239	-3309	-9358	97	118	53	18	15	17
O(2)	3514	4919	6324	65	90	82	-14	28	24
	3503	4915	6328	64	86	83	-11	31	28
	-3523	-4925	-6321	61	86	80	-16	29	19
O(3)	1390	1806	5964	94	56	97	-8	12	-14
	1377	1793	6006	93	50	91	-10	16	-11
	-1403	-1820	-5919	91	55	91	-5	11	-14
O(4)	394	5228	7459	58	76	131	16	32	2
	388	5224	7491	57	71	126	16	30	3
	-402	-5234	-7428	50	71	124	17	29	2
O(5)	3329	8363	168	95	179	75	35	14	-37
	3348	8406	164	92	158	71	29	20	-35
	-3307	-8315	-174	86	167	73	32	14	-36
O(6)	4592	1042	3007	90	134	176	-35	13	-52
	4589	1018	3069	85	135	167	-38	16	-55
	-4598	-1067	-2946	85	125	161	-32	6	-40
O(7)	994	673	1637	83	136	79	48	16	3
	987	628	1666	82	124	74	52	18	6
	-1001	-721	-1608	77	124	78	47	15	4
O(8)	2880	7917	3537	230	125	159	74	113	85
	2779	7863	3475	191	115	123	53	79	61
	-2977	-7972	-3598	186	111	127	55	78	75
H(1)	0	0	0	189	261	337	70	115	67
	-34	16	-76	182	251	305	73	113	73
	4605	2588	9506	233	236	144	3	42	16
H(2)	4615	2580	9537	238	229	142	6	51	18
	5406	7407	522	224	241	143	6	41	53
	5293	1160	4683	515	653	467	320	328	274
H(3)	5278	1164	4677	489	644	461	292	319	238

Comparison between the refinements

In view of the reasonable equal R values for both refinements, and taking into account that the number of variables is nearly doubled in changing from $P\bar{1}$ (133) to $P1$ (262), the centrosymmetric model seems to be supported by the diffraction experiment; we can, however, emphasize and discuss some further features. (i) The lower R for $P1$ before the secondary extinction correction, compared to the equal final values for $P1$ and $P\bar{1}$, can be interpreted by assuming that such a correction is taken into account, in part, by extra degrees of freedom in $P1$. (ii) The $P1$ refinement should be favoured by the better F_o/F_c agreement for weak reflexions (Rae, 1975), but this effect may also be due to the higher number of variables. (iii) Thermal factors of the atoms are not very different in the two models, except for O(8), which also shows the greatest positional shift; however, higher anisotropy of thermal motion in the coordination tetrahedron of P(2), which is common to both $P\bar{1}$ and $P1$ models, would support a disordered model since only the atoms close to H(3) are involved. (iv) Although average positions of pseudo-centrosymmetric pairs of atoms in $P1$ and corresponding atomic positions in $P\bar{1}$ are not significantly different, single coordinates differ by several e.s.d.'s from the average value. Important differences in bond distances and angles may therefore arise, whose crystal-chemical meaning should be crucial in choosing the model.

Discussion*Crystal-chemical considerations*

The disordered $P\bar{1}$ model must represent an average image, such as is revealed by diffraction effects, over two structural configurations that are distinct in neighbouring cells or small groups of cells. The disorder is assumed to be static, because $H(3) \cdots H(3') = 1.7 \text{ \AA}$ seems to be too long for dynamic effects. The two configurations should respectively show H(3) bonded to O(6) only and to O(6') only; other atomic shifts would adjust distances and angles according to the position of H(3): in particular, in each configuration the two tetrahedra of P(2) and P(2') are chemically inequivalent, so that H(1) links to one of them preferentially and the symmetric hydrogen bond disappears (Catti & Ferraris, 1976). In this context $O(6)-H(3) = 1.153 \text{ \AA}$, which is remarkably long for a hydrogen bridge $O \cdots O$ of $2.658(1) \text{ \AA}$, can be understood.

The crystal-chemical consistency of the ordered $P1$ model with H(3) linked to O(6) can be tested by comparing pseudocentrosymmetric bond lengths directly involved with H(1) and H(3) (Tables 2, 3, 4). The two bonds $P(2)-O(6)^{iv}$ and $P(2')-O(6')^{vi}$, approximately equal, are the weak point of this model; the former would have been expected to be longer than the latter. By contrast, a satisfactory behaviour is shown by other pairs of pseudosymmetric bonds, where significant differences of length can be observed; besides, $O(6)-$

Table 2. *Interatomic distances and O-P-O angles for the P tetrahedra*

Under $P1$ the two columns refer to the polyhedron reported for $P\bar{1}$ and to its pseudo-centrosymmetric polyhedron. The e.s.d.'s are 0.001 \AA (0.002 \AA) and 0.1° for distances ($P1$ in parentheses) and angles respectively.

	$P\bar{1}$		$P1$			
P(1)-O(1)	1.595 Å		1.599 Å		1.591 Å	
P(1)-O(2)	1.538		1.530		1.546	
P(1)-O(3)	1.516		1.514		1.520	
P(1)-O(4)	1.513		1.520		1.506	
Average	1.541		1.541		1.541	
O(1)-O(2)	2.533 Å	107.9°	2.533 Å	108.1°	2.534 Å	107.8°
O(1)-O(3)	2.534	109.0	2.524	108.4	2.543	109.7
O(1)-O(4)	2.493	106.6	2.482	105.4	2.504	107.9
O(2)-O(3)	2.522	111.3	2.532	112.6	2.512	110.1
O(2)-O(4)	2.465	107.8	2.472	108.4	2.456	107.2
O(3)-O(4)	2.538	113.9	2.539	113.7	2.538	114.0
Average	2.514	109.4	2.514	109.4	2.515	109.4
P(2)-O(5)	1.519 Å		1.520 Å		1.519 Å	
P(2)-O(6) ^{iv}	1.546		1.549		1.545	
P(2)-O(7) ^{iv}	1.552		1.539		1.567	
P(2)-O(8)	1.521		1.522		1.523	
Average	1.535		1.533		1.539	
O(5)-O(6) ^{iv}	2.519 Å	110.6°	2.519 Å	110.3°	2.524 Å	111.0°
O(5)-O(7) ^{iv}	2.511	109.7	2.505	110.0	2.520	109.5
O(5)-O(8)	2.500	110.7	2.507	111.0	2.496	110.3
O(6) ^{iv} -O(7) ^{iv}	2.451	104.6	2.458	105.5	2.446	103.6
O(6) ^{iv} -O(8)	2.520	110.5	2.544	111.9	2.501	109.3
O(7) ^{iv} -O(8)	2.525	110.5	2.475	108.0	2.575	112.9
Average	2.504	109.4	2.501	109.4	2.510	109.4

H(3), 1.107(5) Å, seems to fit the corresponding O...O contact of 2.563(2) Å better than in the $P\bar{1}$ model. With respect to the Ca—O bonds (Table 3), only Ca(1)—O(7) and Ca(1')—O(7') do not conform clearly to the requirement for O bonded to H atoms.

Choice of the model

In order to interpret the results of diffraction experiments, a few other chemical-physical properties of monetite should be taken into account.

A study of the heat capacity vs temperature curve (Egan & Wakefield, 1964) showed that it had a jump between a maximum at 273 K and a minimum at 287 K; shifts of a few degrees for these values were observed in different samples. Such an anomaly could approximate a discontinuous change of heat capacity involving a second-order phase transition; e.g. an order/disorder transformation where only H positions would be significantly affected, since no variations of the X-ray powder spectrum were detected. The phase

transition seems to be supported by approximate measurements of the dielectric constant in the range 300 to 220 K: indeed, after a rapid decrease between 300 and 270 K, it becomes stable at lower temperatures.

Besides the already mentioned piezoelectricity tests (Denne & Jones, 1971), new measurements, based on the second optical harmonic generation by non-centrosymmetric crystals, were performed by a Nd laser with $\lambda = 1.06 \mu\text{m}$ at the Centro di Studio per la Cristallografia Strutturale del CNR (Pavia); a very small signal, yet significantly above the noise, was detected.

The following explanation could account for all the experimental results: monetite shows a low-temperature ordered phase and a high-temperature disordered phase, which correspond substantially to the $P\bar{1}$ and $P1$ structural models discussed above. The diffraction data were collected at room temperature, just at the upper end of the phase transition, when some fractions of the crystals were still in the ordered arrangement. In this light, most features of the problem are interpretable: (i) the successful $P\bar{1}$ refinement; (ii) some crystal-chemical inconsistencies of the ordered $P1$ refinement; (iii) feeble physical effects characteristic of non-centrosymmetry. Structurally, then, the presence of a small quantity of $P1$ phase seems to be detected better by the displacement of H(1) off the centre than by the ordering of H(3).

It should be added that in both $P\bar{1}$ and $P1$ final difference maps the two largest negative peaks (-14 and $-8 \times 10^{-14} \text{ cm } \text{\AA}^{-3}$) appeared in a cavity delimited by O(6), O(8), O(6') and O(8'); they lay in the centre of the cavity, at 1.59 and 2.05 Å from O(6) and O(8), and on the line O(6)...O(8') at 1.01 Å from O(8'). These peaks could account for 10% of a proton approximately, and their positions might be involved in the disorder of H(3), in view of the reduced height of the corresponding peak observed on Fourier maps.

KKM effect and thermal motion

From the heavy-atom parameters and the observed structure factors published in the X-ray work (Dickens

Table 3. *Interatomic distances in the Ca coordination polyhedra*

For explanation and e.s.d.'s see Table 2.

	$P\bar{1}$	$P1$	
Ca(1)—O(1) ⁱ	2.419 Å	2.415 Å	2.424 Å
Ca(1)—O(2)	2.447	2.448	2.447
Ca(1)—O(6)	2.448	2.481	2.417
Ca(1)—O(7)	2.764	2.794	2.731
Ca(1)—O(8)	2.370	2.321	2.420
Ca(1)—O(2') ⁱⁱ	2.425	2.430	2.421
Ca(1)—O(4') ⁱⁱⁱ	2.293	2.286	2.301
Average	2.452	2.454	2.452
Ca(2)—O(2)	2.575	2.569	2.579
Ca(2)—O(3) ^v	2.374	2.359	2.389
Ca(2)—O(4)	2.482	2.496	2.467
Ca(2)—O(5) ^v	2.435	2.432	2.445
Ca(2)—O(8)	2.478	2.482	2.472
Ca(2)—O(3') ⁱⁱⁱ	2.485	2.478	2.488
Ca(2)—O(6') ⁱⁱ	2.518	2.499	2.536
Ca(2)—O(7') ⁱⁱⁱ	2.503	2.521	2.489
Average	2.481	2.480	2.483

Table 4. *Interatomic distances (Å) and angles (°) in the hydrogen bonds*

For each set of bonds the first line refers to the $P\bar{1}$ model, the second and third lines refer to the corresponding and to the pseudo-centrosymmetric bond in the $P1$ model respectively

A	B	C	D	BC	CD	BD	∠ABC	∠BCD
P(1)—O(1)—H(2)...O(5') ⁱⁱ				1.042 (2)	1.521 (2)	2.560 (1)	117.0 (1)	175.6 (1)
				1.057 (3)	1.515 (3)	2.568 (2)	117.3 (2)	174.8 (3)
				1.027 (3)	1.529 (3)	2.553 (2)	116.9 (2)	175.3 (2)
P(2) ^{vi} —O(6)—H(3)...O(8') ⁱⁱ				1.153 (6)	1.627 (6)	2.658 (1)	119.3 (3)	145.5 (5)
				1.107 (5)	1.560 (5)	2.563 (2)	122.1 (3)	147.4 (4)
				—	—	2.753 (2)	—	—
P(2) ^{vi} —O(7)—H(1)—O(7')				1.230 (1)	1.230 (1)	2.459 (1)	108.1 (1)	180
				1.283 (3)	1.182 (3)	2.461 (2)	—	173.5 (3)
				1.182 (3)	1.283 (3)	2.461 (2)	106.7 (2)	173.5 (3)

et al., 1972), a calculation of F_c gave $R = 0.037$; the scale factor obtained was 1.024, and secondary extinction and anomalous scattering were not taken into account. The syntheses ΔF_X , ΔF_N and $F_X - F_N$ were then calculated in space group $P\bar{1}$, omitting the contribution of all H atoms for ΔF_X and of H(1) only for ΔF_N ; the corresponding maps about the origin are shown in Fig. 2(a), (b) and (c). According to Dickens *et al.* (1972), H(1) was located as a single peak at the origin $0.77 \text{ e } \text{\AA}^{-3}$ high; the different height in our ΔF_X calculation can be explained by a change of scale factor; the multiple peaks may have been missed by the above authors through use of a coarse grid.

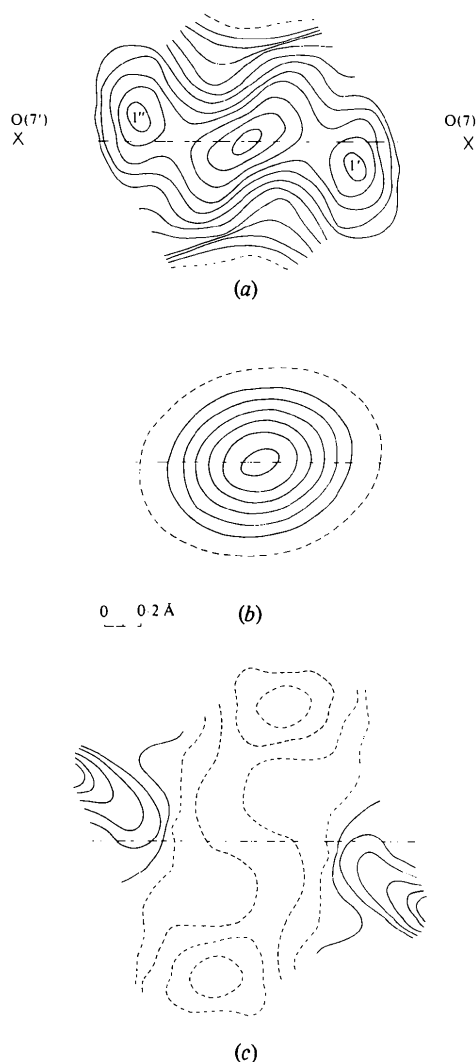


Fig. 2. Difference synthesis maps in the plane determined by the c axis and the $\text{O}(7) \cdots \text{O}(7')$ direction (dashed line). Contours are drawn at intervals of $0.05 \text{ e } \text{\AA}^{-3}$, $30 \times 10^{-14} \text{ cm } \text{\AA}^{-3}$, and $0.10 \text{ e } \text{\AA}^{-3}$ for (a) ΔF_X , (b) ΔF_N and (c) $F_X - F_N$ respectively; zero and negative lines are broken. Distances and angles relevant to the maxima $1'$ and $1''$ in (a) are: $\text{O}(7) \cdots (1') = 0.68$, $(1') \cdots \text{O}(7') = 1.81$, $(1') \cdots (1'') = 1.19 \text{ \AA}$, $\angle \text{O}(7)-(1') \cdots \text{O}(7') = 161^\circ$.

The peculiar aspects of Fig. 2 seem to be interpretable as a particular version of the KKM effect (MacDonald, Speakman & Hadži, 1972), differing both from the ordinary twin-peaks case in ΔF_X (Currie, Speakman, Kanters & Kroon, 1975; Ferraris & Franchini-Angela, 1973) and from the case found by MacDonald *et al.* (1972), with normal ΔF_X and $F_X - F_N$ showing multiple peaks. The unusual presence of three peaks in the ΔF_X map could be accounted for by the mixing of ordered and disordered phases discussed above. Probably, separate peaks can be detected in electronic but not in nuclear density maps because of electron polarizability effects (Catti & Ferraris, 1976).

The two ellipsoids representing the total motion and the difference motion [with respect to $\text{O}(7)$] of H(1) were compared; both show their directions of maximum displacement within about 10° of the $\text{O}(7) \cdots \text{O}(7')$ line. Such an effect probably should be related to the structural disorder, in this case, rather than to the shape of the potential well as in very short hydrogen bonds not suspected of disorder (Speakman, 1975). The root-mean-square displacements along principal directions of thermal vibration for all atoms (Table 5) are slightly smaller in the $P\bar{1}$ refinement, on average, than in $P1$, particularly for atoms which are involved directly in the order/disorder process.

Comparison of the X-ray and neutron parameters

Heavy-atom parameters from the $P\bar{1}$ neutron refinement and from the X-ray refinement (Dickens *et al.*, 1972) were compared statistically (Abrahams, 1974) through χ^2 tests (Table 6) and half- or full-normal

Table 5. Root-mean-square displacements ($\text{\AA} \times 10^3$) along the principal directions of vibration

	$P\bar{1}$	$P1$		$P\bar{1}$	$P1$
P(1)	77	72	O(5)	104	105
	83	82		169	158
	70	67		83	76
P(2)	90	93	O(6)	126	123
	111	111		173	172
	82	75		88	84
Ca(1)	97	95	O(7)	100	97
	139	134		148	145
	83	83		83	76
Ca(2)	103	99	O(8)	118	114
	130	127		194	171
	82	80		88	91
O(1)	106	102	H(1)	181	171
	129	126		215	210
	80	78		130	125
O(2)	102	101	H(2)	171	169
	114	114		175	175
	74	69		135	133
O(3)	109	109	H(3)	197	207
	121	114		353	343
	77	74		161	159
O(4)	104	102			
	130	127			
	75	73			

Table 6. χ^2 analysis for sets of structural parameters with ν degrees of freedom; δp_{\max} is the maximum value of the weighted $p_X - p_N$ difference for the set

	ν	δp_{\max}	χ^2	$\chi^2_{0.05}$
x	12	5.7	98.7	21
y	12	14.7	830.1	
z	12	16.3	680.2	
B_{11}	12	6.5	184.8	
B_{22}	12	6.7	63.6	
B_{33}	12	5.7	166.0	
B_{12}	12	4.2	44.3	
B_{13}	12	7.8	108.8	
B_{23}	12	2.1	11.9	
B_{ij}	36	6.7	414.4	
B_{ij}	36	7.8	265.0	
All coordinates	36	16.3	1609	
All B_{ij}	72	7.8	679.4	92
All parameters	108	16.3	2288	133
P(1)—O	4	1.8	7.5	9.5
P(2)—O	4	6.0	57.9	
Ca(1)···O	7	4.9	45.1	14.4
Ca(2)···O	8	4.8	79.2	15.5

probability plots (not reported); the second kind of plot was used to analyse B_{11} , B_{22} and B_{33} , since in this case the sign of the difference is relevant. The results of the two experiments appear to differ significantly, and this should not be due to a low reliability of the e.s.d.'s only, even if they are probably underestimated, since all the experimental values lie above the ideal straight line. In particular, the plot fails to be linear for positional parameters, and it fails to intersect the origin for diagonal thermal parameters. The latter effect is caused by B_{ii} values being larger for X-ray data (27 out of 36), and has been related (Hamilton, 1969) to the inadequacy of the spherical approximation for X-ray scattering factors. The significant difference between positional parameters from the two experiments (confirmed by comparing the P—O and Ca—O distances) could be accounted for by assuming that the measurements were performed on two samples with different amounts of order/disorder. Actually, the largest differences are shown by O(6), O(7) and O(8), which are involved in the disorder of the H atoms, while the atoms of the P(1) tetrahedron behave more regularly.

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