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Structure and Electron Density of Pentasodium Trihydrogentetracarbonate

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Abstract

$Na_5H_3(CO_3)_4$, $M_r = 358·1$, triclinic, $P\bar{1}$, $a = 3·4762\ (1)$, $b = 10·0393\ (2)$, $c = 15·5969\ (3)$ Å, $\alpha = 107·770\ (2)$, $\beta = 95·589\ (2)$, $\gamma = 95·028\ (2)°$, $V = 511·90\ (2)$ Å^3, $Z = 2$, $D_x = 2·32$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·379$ mm^{-1}, $F(000) = 356$, $T = 298$ K, $R(F^2) = 0·0287$ for 8956 unique reflections. The carbonate groups are linked by hydrogen bonds to form two independent $[H_3(CO_3)_4]^{5-}$ fragments. There are four hydrogen bonds in the asymmetric unit, two of which are asymmetric with O···O distances of 2·572 (1) and 2·597 (1) Å. The other two are symmetric with O···O distances of 2·492 (1) and 2·507 (1) Å. Apparently, the H atoms in these symmetric hydrogen bonds are not located at inversion centres. Deformation densities in the covalent bonds of the carbonate groups are correlated with C—O bond order.

Introduction

The present study is part of a series of studies of short hydrogen bonds in hydrogen carbonates. Previous work has involved $KMgH(CO_3)_2.4H_2O$ and $KNiH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1988, 1990).

The salt $Na_2CO_3.3NaHCO_3$ is reported to occur as the mineral wegscheiderite (Fahey & Yorks, 1963), a name given in honour of Wegscheider who was the first to synthesize it. Cell dimensions for the mineral and the synthetic crystal have been determined by Appleman (1963); optical properties have been measured by Fahey & Yorks (1963). Phase-equilibrium studies of the system Na_2CO_3–$NaHCO_3$–H_2O have been performed by Hill & Bacon (1927) and by Waldeck, Lynn & Hill (1934). Differential thermal analysis (Barral & Rogers, 1966) shows that it is an intermediary product of the decomposition of $NaHCO_3$. From Raman and IR spectral studies of undeuterated and deuterated powder samples at 298 and 93 K, Bertoluzza, Monti, Morelli & Battaglia (1981) predicted the main structure of the anion as discrete $[H_3(CO_3)_4]^{5-}$ units.

Experimental

The phase diagram of the ternary system $NaHCO_3$–Na_2CO_3–H_2O has been studied at several temperatures, from 298 to 323 K by Hill & Bacon (1927) and from 373 to 473 K by Waldeck, Lynn & Hill (1934). On this basis a composition was chosen such that the two phases in equilibrium at 373 K would be a saturated solution and the solid $Na_5H_3(CO_3)_4$. At room temperature Na_2CO_3 was completely dissolved in water and then $NaHCO_3$ was added. The system was sealed and kept in an electric oven at 373 K. After two weeks the solid material consisted of fibrous and needle-like crystals as was reported for the natural compound (Fahey & Yorks, 1963). A crystal with well developed faces of size $0·10 \times 0·14 \times 0·29$ mm was selected and checked for twinning *etc.* by the Weissenberg technique. All subsequent X-ray measurements were performed on an automated Stoe–Philips four-circle diffractometer, graphite monochromator, λ(Mo $K\alpha$) = 0·71073 Å. Unit-cell parameters were determined from the refinement of 2θ angles of 104 reflections, $10 \le 2\theta \le 30°$; they agree qualitatively with the values reported for the mineral (Appleman, 1963). In this work the sequence of the unit-cell axes was chosen in agreement with the conventions for defining a reduced basis (*Inter-*

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national Tables for Crystallography, 1983). Data collection was performed in the ω–2θ scan mode, step width in ω equal to 0·010°, 96 steps at a rate from 1·0 to 3·0 s step^{-1}; $K\alpha$ splitting was considered, 15 242 reflections were measured, $-8 \le h \le 8$, $-23 \le k \le 23$, $-35 \le l \le 35$. The complete reciprocal-lattice sphere was investigated in the interval $0 < \sin\theta/\lambda \le 0{\cdot}9044$ Å^{-1}; in the interval $0{\cdot}9044 < \sin\theta/\lambda \le 1{\cdot}1237$ Å^{-1} a unique set was recorded for those reflections which had $I \ge 2\sigma(I)$ in the pre-scan measurements.

The data set was corrected for background effects (Lehmann & Larsen, 1974), and for Lorentz, polarization and absorption effects (transmission factors 0·944–0·965). The intensities of five standard reflections, measured at 6 h intervals, decreased linearly with time, $I_t = (0{\cdot}9778 - 0{\cdot}5823 \times 10^{-4}t)I_0$, where I_t is the intensity recorded at time t, in h, and I_0 is the estimated intensity at $t = 0$. The appropriate correction for this effect was applied to all measured reflections ($I \ge 0$) and resulted in an agreement factor $R_{\rm int} = 0{\cdot}0123$, compared with $R_{\rm int} = 0{\cdot}0275$ before this correction. A total of 8956 unique reflections were obtained. The variance V of an averaged reflection was taken as the larger of $V_1 = [\sum w_i(I_i - \langle I\rangle)^2]/\sum w_i$ or $V_2 = \sum\sigma_i^2/n$, where $w_i = 1/\sigma_i^2$ and σ_i^2 is the variance due to counting statistics and the above corrections; I_i is the measured (corrected) intensity; and $\langle I\rangle$ is the mean intensity. The inverse of V was used as weight in the least-squares refinements.

Conventional refinements

The structure was solved by direct methods using the program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Neutral-atom scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Full-matrix least-squares refinement was performed using the scale factor and positional and anisotropic thermal parameters for non-H atoms; the function minimized was $\sum w(F_o^2 - kF_c^2)^2$. The H atoms were located from difference Fourier syntheses and their thermal parameters refined isotropically. Extinction corrections could be neglected. The programs used in the computations have been described by Lundgren (1982). Stereoscopic illustrations were drawn using *ORTEP*II (Johnson, 1969).

The data set included 322 reflections with negative intensities. These reflections could have been included in the refinement as it was performed in F^2. However, their true intensities must be non-negative. Therefore, the data set was processed by a Bayesian method (French & Wilson, 1978) in order to bring all intensities to non-negative values (*cf.* Schwarzenbach *et al.*, 1989). The FORTRAN routine used to calculate the (*a posteriori*) expected value and variance of the intensity of a reflection is one of those written by French & Wilson (deposited as SUP 33352). The reliability indices for a refinement according to this procedure are shown in Table 1 (refinement *A*).

Table 1. *Details of the refinements*

A, free-atom model refinement. *B*, deformation refinement, 128 deformation coefficients. $\Delta = |F_o|^2 - |F_c|^2$, $\sigma = \sigma(F_o^2)$, $w = 1/\sigma^2$, $(\sin\theta/\lambda)_{\rm max} = 1{\cdot}1218$ Å^{-1}, n (number of observations) = 8956.

	A	*B*
k (scale factor × F_o)	3·0151 (17)	3·0023 (43)
p (number of refined parameters)	200	318
$R = \sum\lvert\Delta\rvert/\sum F_o^2$	0·0438	0·0287
$wR = (\sum w\Delta^2/\sum wF_o^4)^{1/2}$	0·0595	0·0347
$S = [\sum w\Delta^2/(n-p)]^{1/2}$	1·933	1·136
Number of reflections with $\lvert\Delta\rvert > 4{\cdot}0\sigma$	285	28
Ratio of maximum least-squares shift to e.s.d. in final refinement cycle	$1{\cdot}2 \times 10^{-3}$	$< 0{\cdot}5 \times 10^{-3}$
Minimum and maximum heights in difference maps (e Å^{-3})	−0·50, 0·63	−0·25, 0·29

The two hydrogen bonds across the centres of symmetry are relatively long, O6···O6 [2·494 (1) Å], O12···O12 [2·507 (1) Å]. Therefore the H atoms might vibrate in a double potential well rather than in a single one. Furthermore, their thermal parameters were larger than others (*cf.* Table 2). A refinement with H2 and H4 as half atoms in general positions was therefore performed. The value of wR showed a significant improvement at the 0·001 significance level (Hamilton, 1965). A further refinement was made of a model which also included two sites for H1 and H3 in the asymmetric O···O bonds [2·572 (1) and 2·597 (1) Å], but the occupancies of alternative minority sites were judged to be non-significant.

Deformation refinements

The scattering model of all atoms was improved by adding to the spherical scattering factors a set of functions, according to the Hirshfeld (1971, 1977) formalism. In this model the atomic multipole functions are of the type

$$\rho_n(r_a,\theta_k) = N_n r_a^n \exp(-\alpha_a r_a)\cos^n\theta_k$$

where a indicates an atomic centre, $0 \le n \le 4$, r_a is the distance of a point r from the nucleus a, α_a is the shape parameter, θ_k is the angle between the vector r_a and specified polar axis k, and N is a normalizing constant.

Functions for $n \le 2$ were used for the H atoms in the symmetric hydrogen bonds; $n \le 3$ for H1 and H3; $n \le 4$ for all C, O and Na atoms. The site symmetry assigned to each atom was: 'spherical' for all Na; 'axial' for all H atoms along the O—H bonds; $mm2$ for C1, C3, O1, O2, O5, O7, O8 and O11; m for C2, C4, O3, O4, O6, O9, O10 and O12. All Na atoms shared the same deformation functions, and a chemical equivalence between the two $H_3(CO_3)_4$ fragments was assumed. Therefore the number of deformation atom types was nine.

Since the thermal parameters of H atoms derived from X-ray data are in general biased, Hirshfeld (1976) suggests that they should be estimated from other observations of internal and external vibrations. However, reliable thermal parameters for the H atoms are not available and therefore the thermal parameters of the H atoms were arbitrarily fixed at $B = 3{\cdot}50$ Å^2.

A series of refinements with different models for the distribution of the H atoms in the hydrogen bond were carried out. The number of deformation coefficients refined in any model was 128.

The reliability indices and deformation maps from these different refinements were literally equal and therefore the deformation maps and data reported in the tables correspond to the refinement in which the H atoms in the symmetric hydrogen bonds were fixed at the centre of symmetry. Further relaxation of symmetry and chemical constraints did not improve the reliability indices.

From Table 1 it can be seen that a model which takes into account the non-spherical distribution of the valence electrons nicely fits the experimental data. The positional and equivalent isotropic displacement parameters are shown in Table 2.*

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^2) *from the deformation refinement*

For non-H atoms, $\langle u^2\rangle = (1/6\pi^2)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$\langle u^2\rangle$
Na1	0·78632 (5)	0·67317 (2)	0·04873 (1)	1·898 (5)
Na2	0·81130 (5)	0·18185 (2)	0·09932 (1)	2·000 (6)
Na3	0·18047 (4)	0·71800 (2)	0·27916 (1)	1·813 (5)
Na4	0·42761 (4)	0·21298 (2)	0·30787 (1)	1·853 (5)
Na5	0·77185 (5)	0·74803 (2)	0·47762 (1)	1·780 (5)
O1	0·28749 (9)	0·55431 (4)	0·09748 (3)	2·201 (10)
O2	0·37640 (8)	0·34347 (5)	0·10976 (2)	1·874 (9)
O3	0·62239 (16)	0·54136 (7)	0·22131 (5)	1·733 (11)
O4	0·94197 (15)	0·38381 (7)	0·30290 (5)	1·703 (11)
O5	0·18035 (8)	0·60058 (5)	0·39492 (2)	1·565 (8)
O6	0·30491 (16)	0·40970 (8)	0·43290 (5)	1·691 (11)
O7	0·30385 (9)	0·85333 (4)	0·05650 (3)	1·947 (9)
O8	0·30195 (8)	0·06961 (5)	0·15427 (2)	1·728 (8)
O9	0·07345 (13)	0·87712 (7)	0·18646 (6)	1·772 (11)
O10	0·88991 (12)	0·06120 (7)	0·32907 (5)	1·803 (11)
O11	0·73764 (7)	0·86380 (5)	0·36291 (2)	1·512 (8)
O12	0·64812 (13)	0·07382 (7)	0·45689 (5)	1·705 (11)
C1	0·41972 (12)	0·47544 (4)	0·13898 (4)	1·291 (9)
C2	0·13807 (12)	0·46837 (5)	0·37668 (4)	1·216 (9)
C3	0·23680 (11)	0·93709 (4)	0·12978 (3)	1·322 (9)
C4	0·75976 (10)	0·99593 (5)	0·38122 (4)	1·149 (9)
H1*	0·715	0·469	0·248	4·4
H1†	0·708 (3)	0·474 (1)	0·246 (1)	3·3 (4)
H2*	0·500	0·500	0·500	4·4
H2†				6·2 (7)
H3*	0·009	0·955	0·239	4·4
H3†	0·018 (3)	0·945 (1)	0·232 (1)	1·6 (3)
H4*	0·500	0·000	0·500	4·4
H4†				6·6 (8)

* Distances O3—H1 and O9—H3 extended and fixed to 1·0 Å (*cf.* Olovsson & Jönsson, 1976). Hydrogen thermal parameters not refined, see text.

† Refined hydrogen parameters derived from the free-atom model.

Discussion

The structure of NaHCO$_3$ contains infinite chains of HCO$_3^-$ (Sharma, 1965), whereas the structure reported here contains two independent [H$_3$(CO$_3$)$_4$]$^{5-}$ fragments in which the carbonate groups are linked *via* hydrogen bonds. A stereoscopic view of the unit-cell contents is shown in Fig. 1, a list of interatomic distances and angles is given in Table 3. The oxygen arrangement around the Na atoms is shown in Fig. 2; the Na—O distances range from 2·29 to 2·66 Å. The coordination number of the Na atoms is not equal: considering the Na—O contacts less than 2·7 Å, Na1 has a coordination number equal to seven, Na2 equal to five and finally Na3–Na5 equal to six (Na2 has a sixth neighbour, O4, which completes the octahedron but it is 3·17 Å apart). The survey by Brown (1988) shows that the coordination number of Na varies between four and eight. On the other hand, it is noticeable that all 12 O atoms have the same coordination, four neighbours.

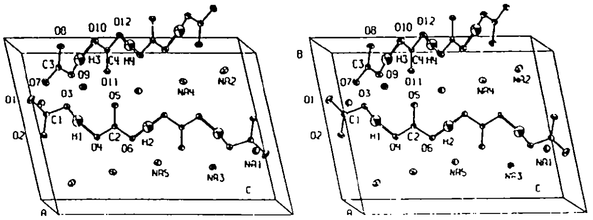

Fig. 1. The unit-cell contents of Na$_5$H$_3$(CO$_3$)$_4$. In this and the following figures the thermal vibration ellipsoids are drawn to include 50% probability (results from the deformation refinement).

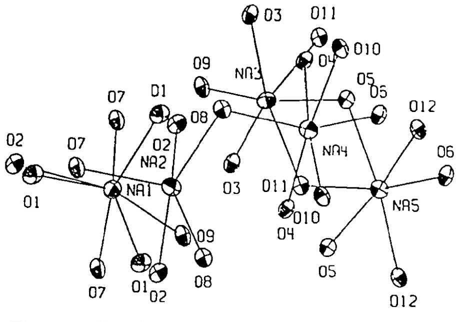

Fig. 2. The coordination around the Na ions in Na$_5$H$_3$(CO$_3$)$_4$.

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* Lists of structure factors, deformation coefficients and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52743 (80 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *from the deformation refinement*

C1—O1	1·255 (1)	O9—H3	1·000
C1—O2	1·252 (1)	O10···H3	1·604 (1)
C1—O3	1·344 (1)	O12···H4	1·253 (1)
C2—O4	1·288 (1)	O12···O12	2·507 (1)
C2—O5	1·261 (1)		
C2—O6	1·315 (1)	O1—C1—O2	125·32 (5)
C3—O7	1·252 (1)	O1—C1—O3	115·67 (5)
C3—O8	1·260 (1)	O2—C1—O3	119·01 (5)
C3—O9	1·352 (1)	O4—C2—O5	123·17 (5)
C4—O10	1·281 (1)	O4—C2—O6	116·40 (6)
C4—O11	1·262 (1)	O5—C2—O6	120·41 (5)
C4—O12	1·317 (1)	O7—C3—O8	126·32 (4)
O3···O4	2·572 (1)	O7—C3—O9	115·63 (5)
O3—H1	1·000	O8—C3—O9	118·04 (5)
O4···H1	1·590 (1)	O10—C4—O11	122·99 (5)
O6···H2	1·246 (1)	O10—C4—O12	116·65 (6)
O6···O6	2·492 (1)	O11—C4—O12	120·37 (5)
O9···O10	2·597 (1)	O3—H1···O4	165·97 (4)
		O9—H3···O10	171·19 (5)

Table 4. *Mean-square vibration amplitudes* ($Å^2 \times 10^4$) *of covalently bonded non-*H *atoms A and B in the direction of bond A—B for rigid-bond tests of vibration parameters*

	Free-atom model refinement			Deformation refinement		
A *B*	z_A^2	z_B^2	$\lvert z_A^2 - z_B^2 \rvert$	z_A^2	z_B^2	$\lvert z_A^2 - z_B^2 \rvert$
C1—O1	144 (3)	120 (4)	24 (5)	125 (2)	120 (2)	5 (3)
C1—O2	137 (2)	115 (2)	22 (2)	120 (1)	117 (1)	3 (2)
C1—O3	146 (2)	128 (2)	18 (2)	142 (1)	132 (1)	10 (2)
C2—O4	135 (2)	122 (1)	13 (2)	123 (1)	120 (1)	3 (2)
C2—O5	117 (2)	104 (2)	14 (3)	104 (1)	103 (1)	2 (2)
C2—O6	125 (3)	116 (3)	9 (4)	116 (2)	113 (2)	3 (3)
C3—O7	151 (2)	131 (2)	20 (3)	131 (1)	130 (1)	2 (2)
C3—O8	137 (2)	120 (2)	17 (2)	122 (2)	120 (1)	2 (2)
C3—O9	126 (3)	114 (3)	12 (4)	123 (2)	119 (2)	4 (3)
C4—O10	124 (3)	111 (3)	13 (4)	113 (2)	110 (3)	3 (3)
C4—O11	115 (2)	98 (2)	17 (3)	101 (1)	10 (1)	1 (2)
C4—O12	122 (2)	113 (2)	9 (3)	110 (2)	109 (2)	1 (2)

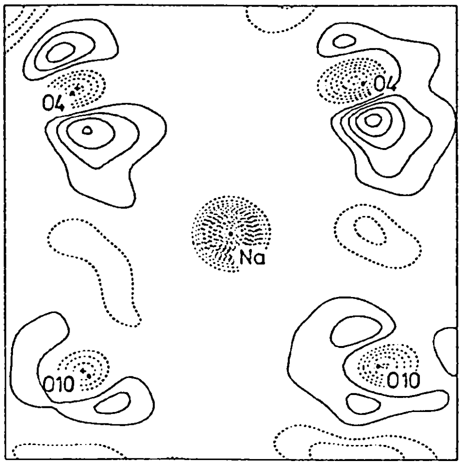
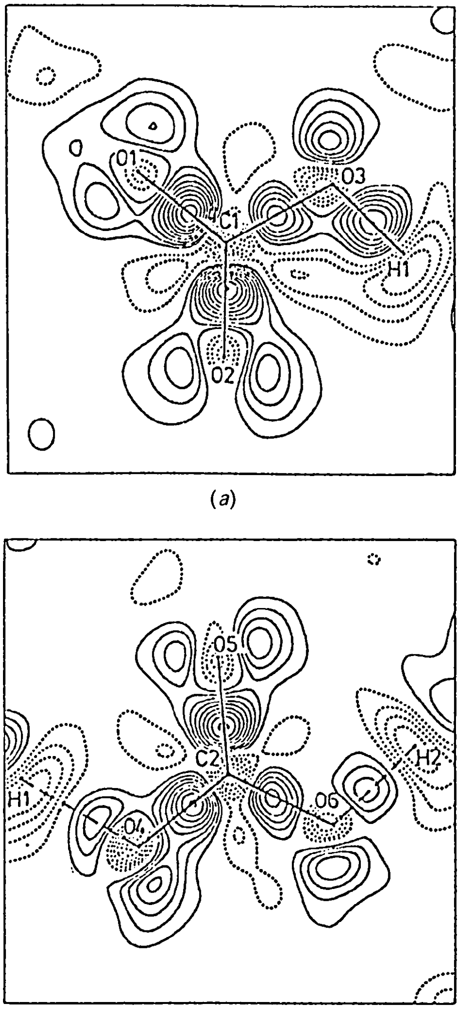


Fig. 3. Dynamic deformation density in a plane defined by Na4, O4 and O10. Another O4 and O10 lie 0·10–0·15 Å above the plane; they are indicated by +. Contours here and in the following figures are at intervals of 0·05 e Å^{-3}. Solid and dashed lines denote positive and negative contours, respectively; the zero level has been omitted.

There are four hydrogen bonds, out of which O3—H1···O4, 2·572 (1) and O9—H3···O10, 2·597 (1) Å are asymmetric. The two symmetric hydrogen bonds are shorter, O6···H2···O6, 2·491 (1) and O12···H4···O12, 2·507 (1) Å. All carbonate groups are planar, the maximum deviation from a least-squares plane through the atoms occurs in the C2—O4—O5—O6 plane, 0·007 (1) Å. However, the entire $H_3(CO_3)_4$ fragment is not at all planar. For example, the angle between the C1—O1—O2—O3 and C2—O4—O5—O6 planes is 4·0°, and the angle between the C3—O7—O8—O9 and C4—O10—O11—O12 planes is 7·9°. The C—O distances are of the same magnitude as in other hydrogencarbonate systems, for example $KHCO_3$ (Thomas, Tellgren & Olovsson, 1974), $KMgH(CO_3)_2.4H_2O$ (Fernandes,



(*a*)

(*b*)

Fig. 4. Dynamic deformation densities in the least-squares planes of two of the carbonate groups (*a*) C1, O1, O2, O3; (*b*) C2, O4, O5, O6. Contours as in Fig. 3.

Tellgren & Olovsson, 1988) and $KNiH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1990).

Experimental deformation densities

The distance between positions obtained in the spherical-atom and deformation refinements, the asphericity shift, has a maximum value of 0·003 (1) Å for O2.

According to the rigid-bond postulate (Hirshfeld, 1976), the difference $|z_A^2 - z_B^2|$ shall vanish for a pair of covalently bonded atoms A and B, where z_A^2 and z_B^2 are the mean-square amplitudes of vibration of the atoms A and B along the A—B bond. In Table 4 these quantities are listed and for comparison the results obtained in the spherical-atom refinement are also given. It is notable that z_C^2 is consistently larger than z_O^2 which could be an indication that the neutral-atom model assumed is not absolutely true. It appears that the rigid-bond postulate is verified after the deformation refinement, since $|z_A^2 - z_B^2|$ is not significantly different from zero for most pairs of atoms. This means that the deformation refinement has succeeded in distinguishing between non-spherical valence-electron distributions and effects of thermal smearing. However, in this data set some systematic errors have not been minimized, for example *TDS* effects (Willis & Pryor, 1975).

Deformation density maps are shown in Figs. 3–9. In these maps the estimated error calculated from the variance–covariance matrix (Rees, 1977) is 0·05 e Å^{-3} outside a radius of 0·20 Å around each nucleus (except H). In regions inside this radius the errors are larger than the contours. For the H atoms this radius is 0·15 Å. In Fig. 3 a section passing through Na4 is shown. A circular depletion around

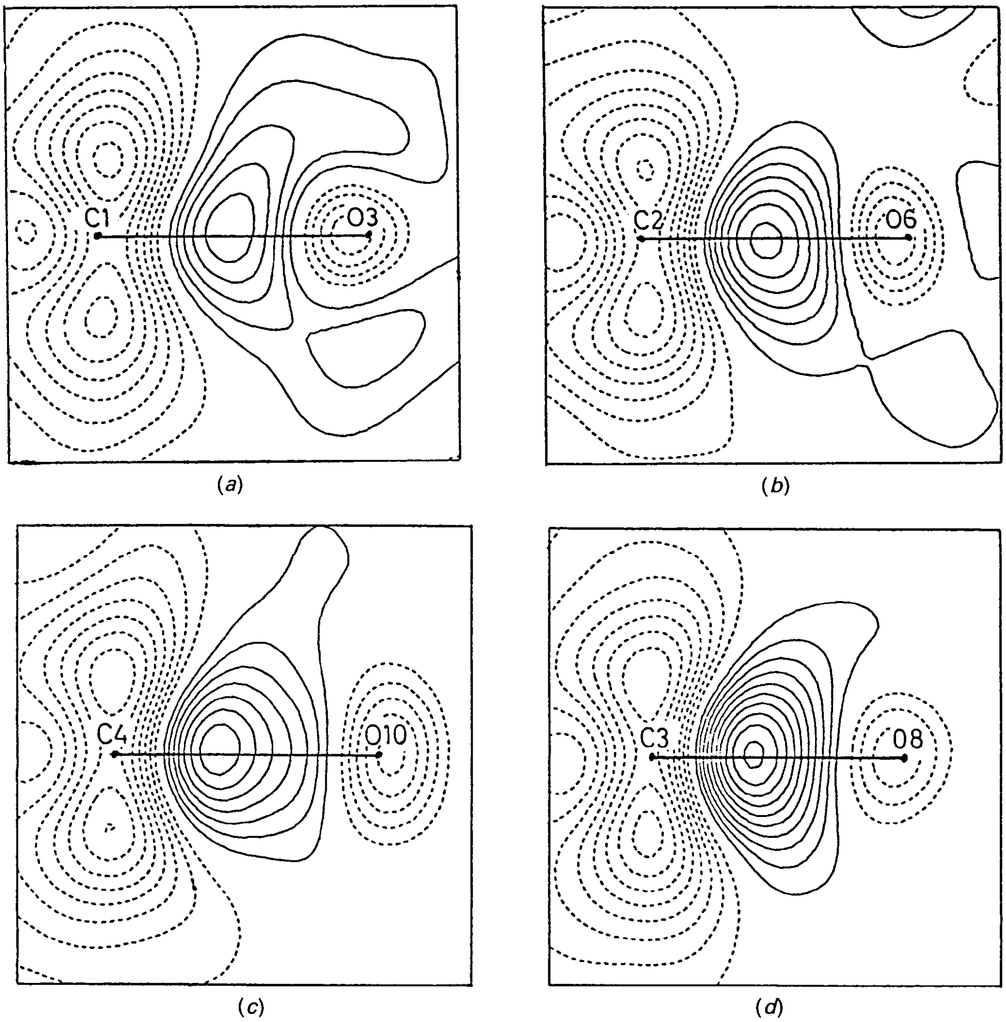


Fig. 5. (*a*)–(*d*) Dynamic deformation density in sections through the C—O bonds, perpendicular to the least-squares plane of the respective carbonate group. Contours as in Fig. 3.

Na is observed. This feature may be interpreted as a consequence of the spherical scattering factor used, that is, the number of electrons around Na is less than the number of electrons in a neutral Na atom.

Owing to the uncertainty in the position and thermal parameters of the H atoms, the dynamic deformation density is reported in this work, although the rigid-bond test (Table 4) would allow a static deformation density calculation. Since symmetry and chemical constraints were imposed, only a set of independent sections is shown. Fig. 4 presents the experimental dynamic deformation density in the mean molecular planes of two carbonate groups; the C2—O4—O5—O6 group is linked to another *via* a symmetric hydrogen bond and to C1—O1—O2—O3 *via* a symmetric hydrogen bond and to C1—O1—O2—O3 *via* an asymmetric hydrogen bond. It is observed that in the C1—O1, C1—O2, C2—O4 and C2—O5 bonds the peaks are higher than the peaks in C1—O3 and C2—O6, which we interprete as a consequence of the larger π character present in the former bonds. In addition to the bond peaks, there are two maxima outside each O atom, O1, O2 and O5, and a single peak outside O3, O4 and O6. These peaks may be assigned as oxygen non-bonding electrons. Fig. 5 shows deformation densities in sections through selected C—O bonds perpendicular to the carbonate group planes, where it can be seen that the peak height diminishes as the C—O bond length increases. Double maxima associated with non-bonding electrons perpendicular to the C2—O5 bond and 0·1 Å behind the O atom can be seen in Fig. 6. Similar maps (not shown) have been obtained for O1, O2, O7, O8 and O11. The non-bonding density peaks near O4, O6 and O9 are shown in Fig. 7 in sections perpendicular to the corresponding

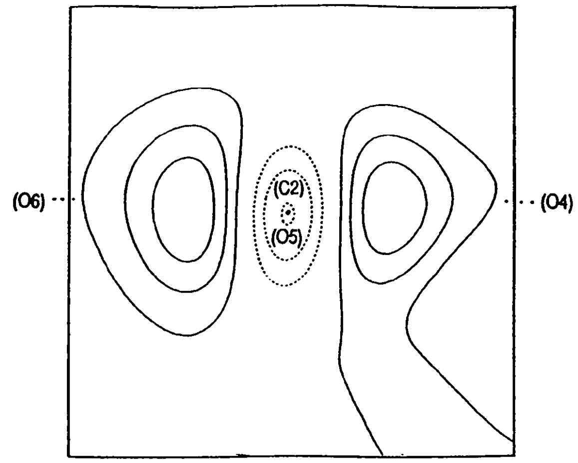


Fig. 6. Dynamic deformation density in a section perpendicular to the C2—O5 bond, 0·1 Å behind the O atom. Contours as in Fig. 3.

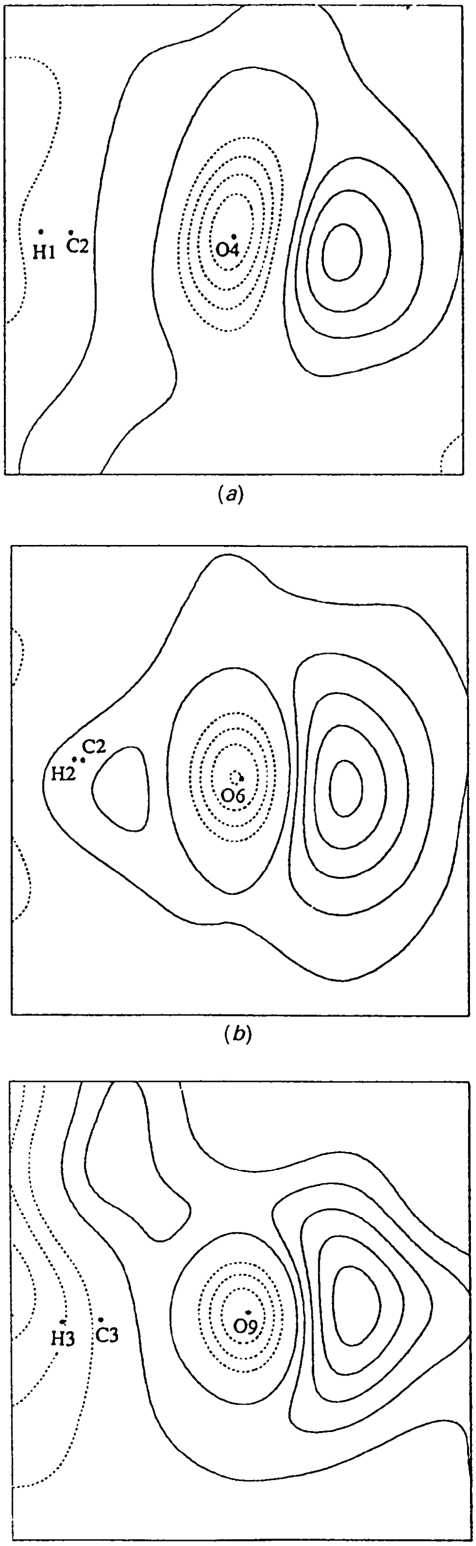


Fig. 7. Dynamic deformation density in a section perpendicular to selected C—O—H or C—O···H planes and bisecting these angles: (*a*) C2—O4···H1; (*b*) C2—O6···H2; (*c*) C3—O9—H3. Contours as in Fig. 3.

C—O—H or C—O···H planes and bisecting those angles (these O atoms are also engaged in hydrogen bonds, in contrast to O5 *etc*.). These peaks are considerably higher than the double maxima peaks found in O5 (Fig. 6). A comparison of the density distribution around O4 and O5 gives clear evidence that O4 could be interpreted as being sp^3 and O5 as sp^2 hybridized. The overall features in the carbonate groups resemble those found in $KNiH(CO_3)_2.4H_2O$ (Fernandes, Tellgren & Olovsson, 1990).

The hydrogen bonds

Deformation densities in sections passing through the asymmetric hydrogen bond O9—H3···O10 of 2·597 (1) Å, and the symmetric hydrogen bond O12···H4···O12 of 2·507 (1) Å, are shown in Fig. 8. An excess of charge density is found in the O9—H3 bond as well as near O10. Between H3 and O10 a depletion is observed. These features are typical for hydrogen bonds of moderate strength [see, for example, Delaplane, Tellgren & Olovsson (1990)]. The symmetric hydrogen bond (Fig. 8*b*) is different in the sense that it is ~0·10 Å shorter, the peak height between O12 and H4 is lower and the depletion is shifted to the midpoint of the hydrogen bond, which can be a result of the symmetry. However, these features are not a consequence of symmetry alone; as Hermansson (1987) has pointed out, the trough in an O···O bond approaches the centre as the O···O distance decreases.

The symmetric hydrogen bonds

A refinement with the H2 and H4 atoms located at the inversion centre gave the same reliability index as a refinement with two half atoms on each side of the inversion centres. Furthermore, the derived deformation maps were almost identical. However, in an attempt to get some more information on the nature of the symmetric hydrogen bonds, difference Fourier maps were calculated in which H2 and H4 had been omitted after the spherical-atom model refinement (Figs. 9*a* and 9*b*). Double maxima were observed in both cases. Although these maps resemble that reported in the study of $KMgH(CO_3)_2$ at room temperature (Fernandes, Tellgren & Olovsson, 1988) there are, at least, two differences: firstly, the maxima in Figs. 9(*a*) and 9(*b*) lie closer to the O···O line; secondly, the distance between the two maxima is ~0·50 Å, as compared with ~0·70 Å in $KMgH(CO_3)_2.4H_2O$. Looking at the C—O bond distances: C1—O3, 1·344 (1), C3—O9, 1·352 (1), C2—O6, 1·315 (1) and C4—O12, 1·317 (1) Å, it can be noticed that the C—OH distances in the symmetric hydrogen bond are significantly shorter than those in the asymmetric ones, but much longer than a C···O bond. This can be interpreted as an intermediate between a C—OH and a C···O bond, and a support for the off-centre model shown in Figs. 9(*a*) and 9(*b*). Similar difference Fourier maps were calculated after the deformation refinement and they are shown in Figs. 9(*c*) and 9(*d*) for H2 and H4, respectively. Although the electron distribution is now more concentrated around the inversion centre, the main features are the same and it seems probable that the equilibrium positions for H2 and H4 are indeed off the inversion centres.

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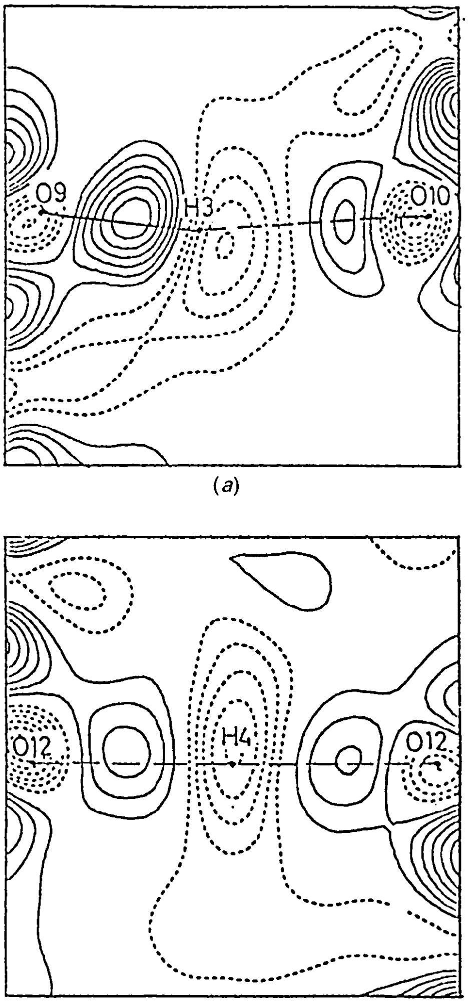

(*a*)

(*b*)

Fig. 8. (*a*), (*b*) Dynamic deformation density in a plane defined by atoms in selected hydrogen bonds. Contours as in Fig. 3.

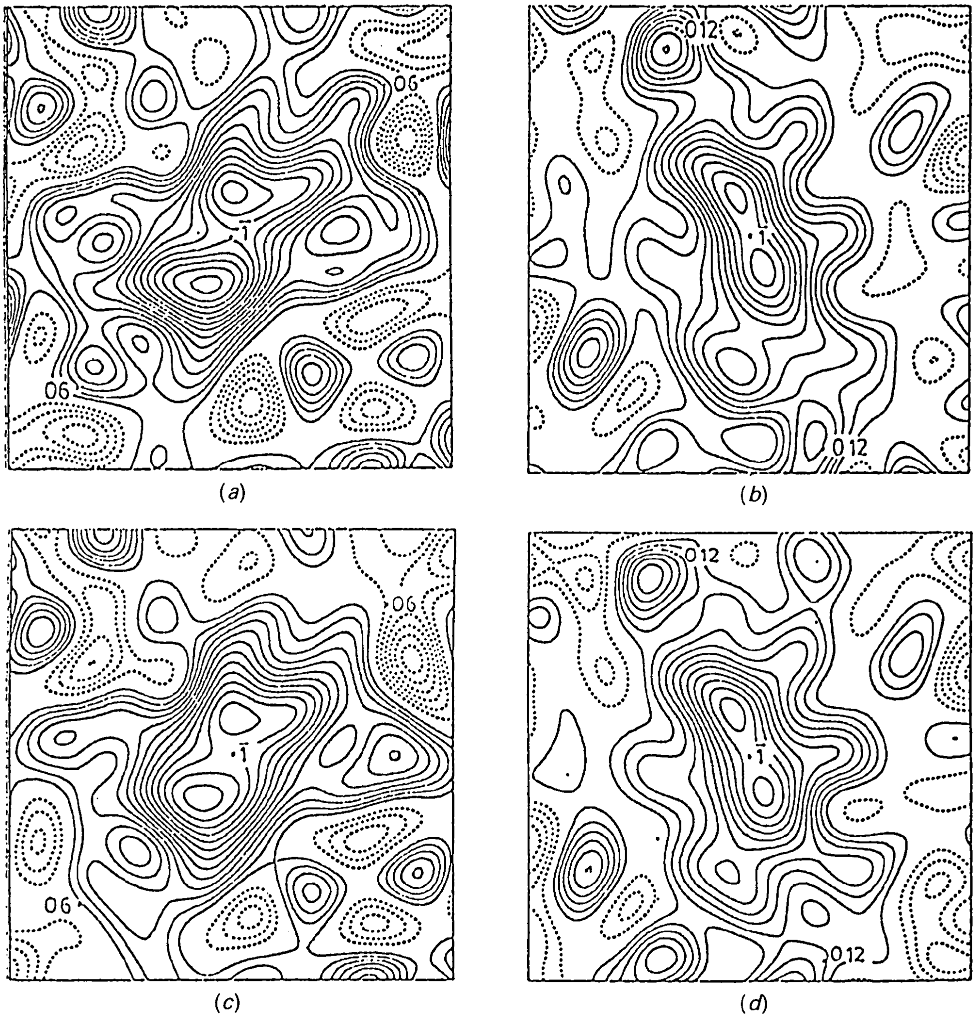

Fig. 9. Difference Fourier maps through the symmetric hydrogen bond in which the H atom has been omitted from F_c. (*a*) O6···O6, spherical-atom model; (*b*) O12···O12, spherical-atom model; (*c*) O6···O6, deformation refinement; (*d*) O12···O12, deformation refinement. Contours as in Fig. 3.

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Structure Refinement of Commensurately Modulated Bismuth Titanate, $Bi_4Ti_3O_{12}$

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Abstract

The displacive ferroelectric $Bi_4Ti_3O_{12}$ [$M_r = 1171{\cdot}6$, $a = 5{\cdot}450\,(1)$, $b = 5{\cdot}4059\,(6)$, $c = 32{\cdot}832\,(3)$ Å, $\beta = 90{\cdot}00°$, $Z = 4$, $D_x = 8{\cdot}045$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 747{\cdot}3$ cm^{-1}, $F(000) = 1976$] is described at room temperature as a commensurate modulation of an *Fmmm* parent structure derived from an idealized *I*4/*mmm* structure. Displacive modes of inherent *F*2*mm*, *Bmab* and *Bbab* symmetry are all substantial and reduce the space-group symmetry to *B*2*ab*. A further substantial displacive mode of *Bbam* symmetry reduces the space-group symmetry to *B*1*a*1 and induces minor displacive modes of *Fmm*2, *F*12/*m*1 and *Bmam* symmetry. A group-theoretical analysis of the problem details how the X-ray data can be classified so as to monitor the refinement. To a first-order approximation, the *F*2*mm* and *Bbab* symmetry components of atom displacements contribute only to the imaginary part of the structure factors. Because the structure factors have a predominant real component, it is easy to get the *F*2*mm* and *Bbab* displacive components of the O atoms wrong. False minima occur at values of 0·027 for $R_1 = \sum_{\mathbf{h}}||F_{\rm obs}(\mathbf{h})| - |F_{\rm calc}(\mathbf{h})||/\sum_{\mathbf{h}}|F_{\rm obs}(\mathbf{h})|$ but a corrrect solution was obtained with $R_1 = 0{\cdot}0177$ for 2839 unmerged data with $I(\mathbf{h}) > 2\sigma[I(\mathbf{h})]$. Criteria for a correct solution are evaluated and subsequently met. The final refinement used a 0·63:0·37 twin model.

Introduction

Within the family of so called Aurivillius phases (Aurivillius, 1949, 1950), there exists a large number of displacive ferroelectrics (Subbarao, 1973; Singh, Bopardikar & Atkare, 1988). These displacive ferroelectrics have room-temperature structures which can be described in terms of small displacive perturbations away from an *I*4/*mmm*, $a' = b' = 3{\cdot}85$ Å, prototype parent structure that consists of perovskite-like $A_{n-1}B_nO_{3n+1}$ slabs regularly interleaved with Bi_2O_2 layers (see Fig. 1 for $n = 3$). The parent structure is presumed to correspond to the crystal structure above the high-temperature phase transition which occurs at the so called Curie temperature. However, in several instances additional phase transitions are known to occur at different temperatures (Subbarao, 1973; Newnham, Wolfe & Dorrian, 1971). This poses questions as to the nature of these changes.

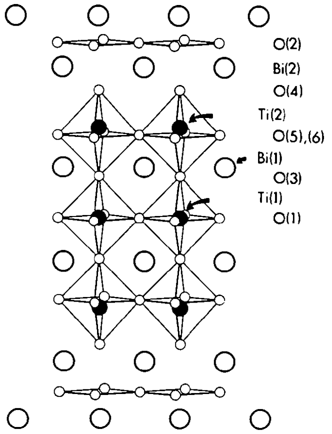

Fig. 1. A perspective drawing, approximately down ⟨110⟩, of the undistorted *Fmmm* parent structure of $Bi_4Ti_3O_{12}$. Only atoms between $\frac{1}{4}$**c** and $\frac{3}{4}$**c** are shown.