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Thermal Changes in the Structure of Sodium Sesquicarbonate

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Accurate structure determinations of sodium sesquicarbonate in projection on (010) have been carried out at 18° C. and −170° C., using intensities measured with a Geiger counter. Hydrogen atoms have been located at both temperatures. Changes with temperature of all interatomic distances and the angles between them have been inferred from the two-dimensional results, and the justification for this process is discussed. Anisotropic thermal vibrations are found for Na and H_2O, and their variation with temperature is examined.

Results obtained for thermal expansion and electronic distribution in the three crystallographically distinct hydrogen bonds are compared with values for these quantities found in other structures.

1. Introduction

An approach to a better understanding of the nature of the hydrogen bond can be made by investigating its thermal properties, for these may give information about changes of energy with temperature. It is therefore of interest to study the effect of changing temperature on the relative positions of the atoms involved in such a bond, and to measure (for oxygen–oxygen bonds) both the O–O and O–H lengths at various temperatures.

Hitherto, with few exceptions, measurements have been concerned only with the overall thermal expansion of a structure. For simple, highly symmetrical structures, where all the bonds are equivalent and bond-angle changes are not permitted by the symmetry, the actual atomic movements can be deduced from these measurements. For complex structures, where bonds of different type contribute to the overall expansion, and dimensional changes may result from changes in bond angle, the interpretation of the results is more difficult. A correlation can be made, however, between the anisotropy of expansion of the crystal and changes in atomic position by assuming that an individual bond will behave very much as does a similar bond in a simple structure. Applying such an assumption to a structure containing hydrogen bonds, it is possible to estimate the expansions of the other bonds in the structure, and hence to find the expansions of the hydrogen bonds from the difference between the observed and estimated expansion coefficient in an appropriate direction. This method is usually simple to carry out experimentally, but conclusions based on it are not rigorously derived.

The deductions about the behaviour of the hydrogen bond drawn from results of thermal expansion measurements are contradictory. Robertson & Ubbelohde (1939) attributed the observed expansion of oxalic acid dihydrate in the (010) plane to a particularly large expansion of the short hydrogen bond, but the overall expansion in afwillite (Shaw, 1953) indicates no such effect for the short bonds. It is clearly preferable to measure changes in atomic positions directly, but it is in general a difficult experimental problem to obtain the necessary accuracy. The only determination so far made is that for potassium dihydrogen phosphate (Frazer & Pepinsky, 1953; Pease & Bacon, private communication).

Although there have been so few direct measurements of changes in bond lengths with temperature, many data now exist for O–O lengths at room temperature, and in some cases for O–H lengths. The accuracy of the results obtained varies widely, but at the best the presence of hydrogen in the bond can be directly demonstrated and the atomic position found (see, for example, Cochran, 1953; Bacon & Pease, 1953).

The work described in this paper was undertaken with the purpose of making direct measurements of changes with temperature in the position of the oxygen atoms, and, if possible, of the hydrogen atoms also. Complete structure determinations at two different temperatures were thus involved. The substance chosen for investigation was sodium sesquicarbonate (Brown, Peiser & Turner-Jones, 1949), and accurate determinations were made at 18° C. and at −170° C.

Sodium sesquicarbonate (Fig. 1) has a fairly simple and symmetrical structure with a very short repeat distance (3·49 Å) along y. The space group is $C2/c$. The cell contains four formula-units $Na_2CO_3 . NaHCO_3 . 2H_2O$; one sodium atom (denoted Na_1) and one hydrogen atom lie in special positions, the rest in general positions. There are three crystallographically distinct hydrogen bonds: two 'long' ones joining the oxygen of the water molecule to an oxygen of the carbonate group, and one 'short' one joining two carbonate

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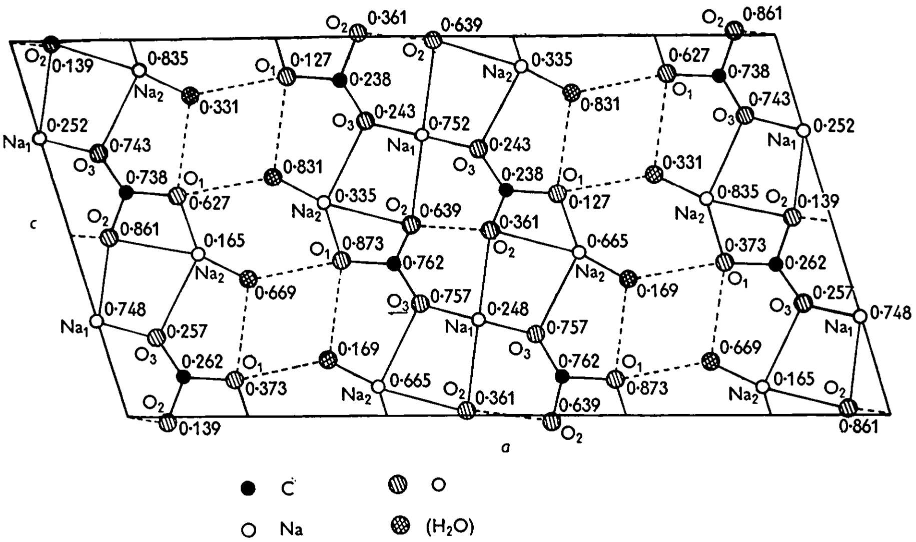

Fig. 1. Projection of unit cell of sodium sesquicarbonate on (010). Heights of atoms above this plane are given as fractions of *b*. Hydrogen bonds are denoted by dashed lines.

groups across a centre of symmetry. These bonds are all nearly parallel to the (010) plane.

The structure is thus a very suitable one for this investigation. The experimental work is simplified because the arrangement of the hydrogen bonds allows information about their behaviour to be deduced fairly reliably from two-dimensional data (although there is the corresponding disadvantage that it would be difficult to extend the work to three dimensions). A more important point is that sodium sesquicarbonate contains both long and short hydrogen bonds, whose differences can thus be compared under at least approximately similar conditions.

2. Thermal expansion and cell dimensions

The crystals used in this work were obtained by recrystallization from warm aqueous solution of material kindly supplied by Dr Brown.

The determination of the thermal expansion coefficients in the (010) plane was carried out in the same way as for afwillite (Shaw, 1953) except that Fe $K\alpha$ radiation was used, and the temperature range was from −170° C. to 18° C. The results obtained are given in Table 1.

Table 1. *Principal expansion coefficients: mean values for the range* −170° C. *to* 18° C.

α_{11}	$(13{\cdot}7 \pm 1{\cdot}2) \times 10^{-6}$	$(°\text{C.})^{-1}$
α_{33}	$(18{\cdot}6 \pm 1{\cdot}5) \times 10^{-6}$	$(°\text{C.})^{-1}$
ψ	$-4 \pm 5°$	

ψ is the angle between α_{33} and z; it is positive if it lies in the obtuse angle β.

A Geiger-counter diffractometer (Cochran, 1950) was used to determine the cell constants a, c and β at 18° C. and at −170° C. These constants were found from the angular settings of the crystal for which reflexion took place on either side of the incident beam from planes of the type (h00) and (00l). The values are given in Table 2.

Table 2. *Cell dimensions*

	18° C.	−170° C. (from thermal expansion)	−170° C. (independent determination)
a	20·346±0·015 Å	20·298 Å	20·335±0·015 Å
c	10·296±0·008	10·265	10·270±0·008
β	106° 26′±1·5′	106° 33′	106° 34′±1·5′

The cell dimensions at −170° C. were also calculated from the 18° C. values, using the measured values of the expansion coefficient in the appropriate directions. These values did not differ significantly from those determined directly (see Table 2). Since the differences in cell dimensions at the two temperatures are known more accurately than their absolute values, and since the interest of this work lies in the study of differences rather than absolute values of individual bond lengths, these calculated values of the cell dimensions at −170° C. have been used in what follows.

3. Structure determinations: experimental procedure

A good crystal (of linear dimensions 0·6 × 0·2 × 0·2 mm., with the direction of elongation along the y axis) was selected from the recrystallized material, and used for structure determinations at 18° C. and −170° C.

Preliminary photographic measurements showed that visual estimation of intensities was not sufficiently accurate; a Geiger counter was therefore used. The construction of the apparatus was such that

75 hOl reflexions with $\theta < 55°$ for Cu $K\alpha$ radiation could be measured.

One structure determination was made just above the temperature of boiling oxygen, and the other at room temperature, safely below the point at which dehydration started.

In the low-temperature determination, the crystal was cooled by a stream of cold oxygen from a Dewar vessel supported over the crystal. The apparatus was an adaptation of the thermostat described by Ubbelohde & Woodward (1946). A steady temperature of $-170 \pm 2°$ C. was maintained. Precautions were taken to prevent the formation of ice in the paths of the incident or reflected X-ray beams.

For the room-temperature observations, frequent measurements of the ambient temperature showed that it did not vary from 18° C. by more than 2° C.

Lorentz and polarization corrections were applied separately to the two groups of measured intensities. Corrections for absorption of the X-ray beam were found by Albrecht's method (1939) and were the same for both sets of intensities.

The intensities were obtained on an absolute scale by the comparison of F_o with F_c, starting from the F_c values given by Brown *et al.* The scaling factor thus obtained was constant for all sin θ. Both the very large and the very small intensities were omitted from the comparison: the large because they might be affected by extinction, and the small because the percentage error in their measurement was greater. The discrepancy between F_o and F_c for the six strongest reflexions was so much greater than the estimated experimental error that the low values of F_o were ascribed to extinction, and F_o was replaced by F_c for these terms in all computations of electron density (Cochran, 1948). The F_o's were rescaled after each stage of the refinement. Full details of the procedure are available elsewhere (Shaw, 1955).

4. Refinement of the structure

The refinement of the structure was accomplished by using a series of (F_o-F_c) syntheses. Though slow, this method had the advantage that the detailed effects of changes in the parameters of the structure could be seen. A full description of the course of the refinement is available elsewhere (Shaw, 1955) and will not be repeated here. An outline of the operations is given in Table 3, and the methods of dealing with certain important points are considered below.

(i) *Choice of atomic scattering factors*

Hartree atomic scattering factors, multiplied by a temperature factor, were used in the first place for all atoms at both temperatures. The curve for neutral oxygen appeared to be quite satisfactory, but although the curve for Na$^+$ was better than that for Na, neither fitted the experimental data very well, and on the $(\varrho_o-\varrho_c)$ map there seemed always to be rings round the sodium positions that no adjustment of the temperature factor could remove. At the very end of the refinement, therefore, empirical scattering-factor curves for sodium were deduced independently for the two temperatures. These curves were used in deriving the final sets of F_c and the final $(\varrho_o-\varrho_c)$ maps (§ 4(iv)).

Table 3. *Refinement of* (010) *projection*

Data	Operations	R	$\sigma(F)$
125 hOl terms estimated photographically at 18° C.	Scaled by comparison with F_c obtained by Brown *et al.*	0·196	7·9
	Two (F_o-F_c) syntheses	0·152	5·3
75 hOl terms measured with Geiger counter at 18° C.	F_c unchanged from above	0·125	5·2
	Twelve (F_o-F_c) syntheses	0·045	1·89
75 hOl terms measured with Geiger counter at −170° C.	Eight (F_o-F_c) syntheses	0·048	1·90

(ii) *Hydrogen atoms*

The peaks corresponding to the hydrogens of the water molecule could easily be seen on the first

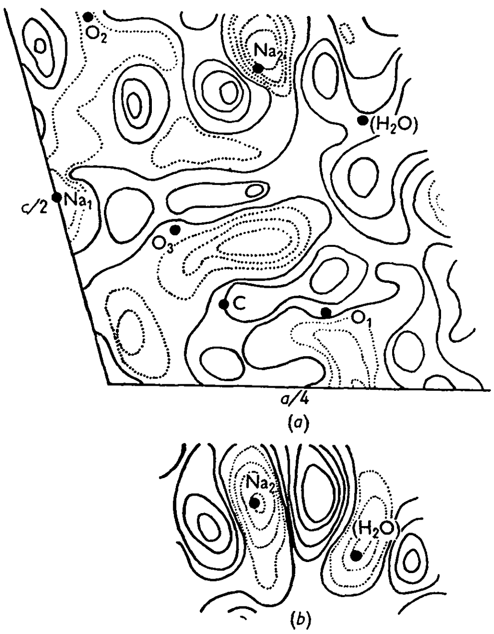

Fig. 2. (*a*) The first difference map at 18° C. computed with accurate values of F_o. Two positive regions corresponding to hydrogen atoms near (H_2O) may be identified by comparison with later figures; there is no definite peak at $(0, \frac{1}{2})$, the expected position of the third hydrogen. Contours at intervals of 0·2 e.Å^{-2}.

(*b*) Part of difference map, at an intermediate stage of refinement, showing anisotropic electron distribution round Na_2 and (H_2O) at 18° C. Contours at intervals of 0·1 e.Å^{-2}.

$(\varrho_o-\varrho_c)$ map computed with accurate F_o's (Fig. 2(*a*)), but the third hydrogen, which is associated with the centre of symmetry at the origin, did not show up so convincingly at any stage of the refinement.

Contributions from the hydrogen atoms were omitted from the first few sets of F_c. When the hydrogen peaks on the difference maps became comparable in value with the peaks due to other causes, contributions from the hydrogen atoms were included in the F_c's.

(iii) *Choice of temperature factors*

It became obvious early in the refinement that the temperature factor was not the same for all the atoms, either at 18° C. or at −170° C. At −170° C. all atoms had an electron distribution which was (within experimental error) isotropic, but at 18° C. Na_2 and probably (H_2O) were appreciably anisotropic (Fig. 2(*b*)).

The isotropic temperature factors were chosen independently for the separate atoms so that the ripples round the atomic positions were reduced. The anisotropic temperature-factor parameters for Na_2 and (H_2O) were found by a least-squares method, after the manner described by Cochran (1951).

(iv) *Determination of an empirical scattering factor curve for sodium*

At a late stage in the refinement it was assumed for purposes of calculation that all differences between F_o and F_c were due to inaccuracies in the scattering-factor curves for sodium, and that the anisotropy of Na_2 at 18° C. was correctly represented by the selected values of β and ψ. If the two sodium atoms have coordinates $(0, \frac{1}{4})$ and (x, z) and isotropic temperature factors α and $\alpha+\Delta\alpha$ respectively, and if the contribution of all the other atoms in the unit cell to F_c is denoted by F_c', then

$$\begin{aligned}F_o-F_c' = {} & 8f_{\mathrm{Na}}\exp\left[-\alpha s^2\right]\{\tfrac{1}{2}\cos 2\pi l/4 \\ & +\cos 2\pi(hx+lz)\exp\left[-\Delta\alpha s^2\right] \\ & \times\exp\left[-\beta\sin^2(\varphi-\psi)s^2\right]\}\,,\end{aligned}$$

where β, φ, ψ, are defined as in Cochran's paper (1951), and $2s$ is the radius of a reciprocal space specified by $d^* = \lambda/d$. An estimate of $\Delta\alpha$ can be obtained from the difference in the most satisfactory isotropic temperature factors for the two atoms when the Hartree curves are used and all the other quantities in the bracket are known, so that the product $f_{\mathrm{Na}}\exp\left[-\alpha s^2\right]$ can be determined at a number of s-values.

All reflexions, except those for which the total sodium contribution was small, were grouped according to their values of s, and the mean value of $f_{\mathrm{Na}}\exp\left[-\alpha s^2\right]$ was found at $s = 0{\cdot}2, 0{\cdot}3, \ldots, 0{\cdot}7$. A smooth curve was drawn through the resulting points. Though this curve did not differ much from the Hartree curve, the standard deviation of the experimental value of f for a given reflexion was 0·15 for the former and 0·30 for the latter.

The factors f_{Na} and $\exp\left[-\alpha s^2\right]$ cannot be determined separately, but the difference $\delta\alpha$ in α at 18° C. and −170° C. can be derived at a series of values of s from the ratios of $f_{\mathrm{Na}}\exp\left[-\alpha s^2\right]$ at the two temperatures. It is recorded in Table 4. Reasonably constant values of $\delta\alpha$ are obtained, variations being less than experimental error. This is of interest, as it suggests that an empirical f-curve independent of temperature can be combined with a conventional Gaussian temperature factor. Such a curve can be constructed from the experimental f-curve at each temperature by assuming the same value of α as gave the best fit with the Hartree f-curve. The Hartree f-curve, and the empirical zero-temperature f-curves determined independently from the two available empirical curves, are listed as functions of $\sin\theta/\lambda$ in Table 4.

5. Results

The final values of the atomic parameters x and z are given in Table 5, and the temperature factors in Table 6. Lists of observed and calculated F's are given in Table 7. The $(\varrho_o-\varrho_c)$ maps obtained using these values are shown in Fig. 3. The corresponding $(\varrho_o-\varrho_c)$ maps in which contributions to F_c from the hydrogen atoms are omitted are shown in Fig. 4.

The projected lengths on (010) are given in Table 8 together with bond lengths in three dimensions calculated as described below. Bond angles are given in Table 9. The derivation of these values needs explanation as neither b nor any of the y coordinates was measured in the present investigation. The small value of b, 3·49 Å, which makes the determination

Table 4. *Comparison of Hartree and empirical f-curves for* Na^+

$\sin\theta/\lambda$	0	0·1	0·2	0·3	0·4	0·5
$\delta\alpha$ from empirical curves	—	—	0·20	0·19	0·21	0·25
Hartree f-curve (uncorrected for thermal motion)	10·0	9·5	8·2	6·7	5·25	4·05
Zero-temperature empirical curves						
(i) from 18° C. curve	—	9·72*	7·96	6·58	5·31	4·05
(ii) from −170° C. curve	—	9·54*	7·88	6·50	5·28	4·07
(iii) mean f-curve	—	9·63*	7·92	6·54	5·30	4·06

* These values are unreliable as only a few observed $h0l$ terms have values of $\sin\theta/\lambda$ in the range 0–0·15.

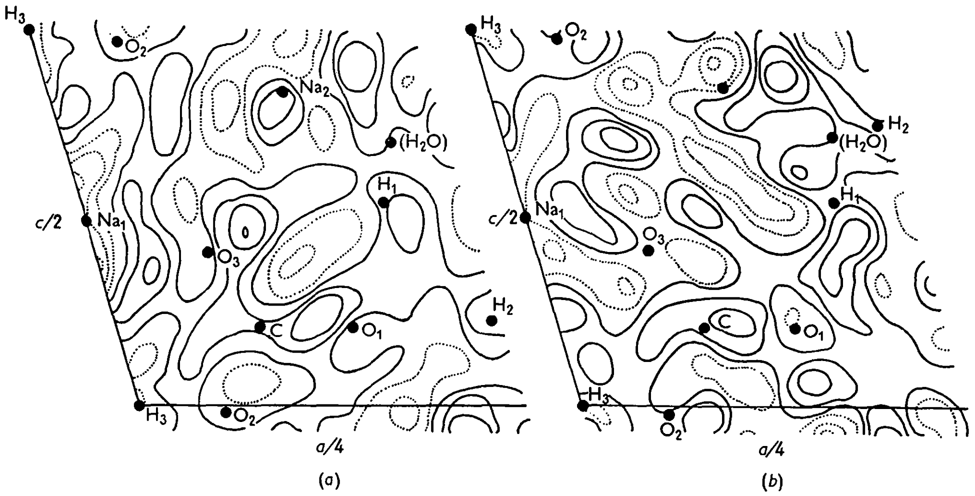

Fig. 3. (a) Final $\varrho_o - \varrho_c$ map at 18° C. Contours at intervals of 0·1 e.Å^{-2}. (Note.—The position marked H_2 is not that of the atom whose coordinates are given in Table 5, which lies just outside the portion of the cell illustrated. It is related to it by the diad axis through ($\frac{1}{4}$, $\frac{1}{4}$).)

(b) Final $\varrho_o - \varrho_c$ map at −170° C. Contours at intervals of 0·1 e.Å^{-2}. (Note.—At this temperature the atom H_2 whose coordinates are given in Table 5 comes within the portion of the cell illustrated.)

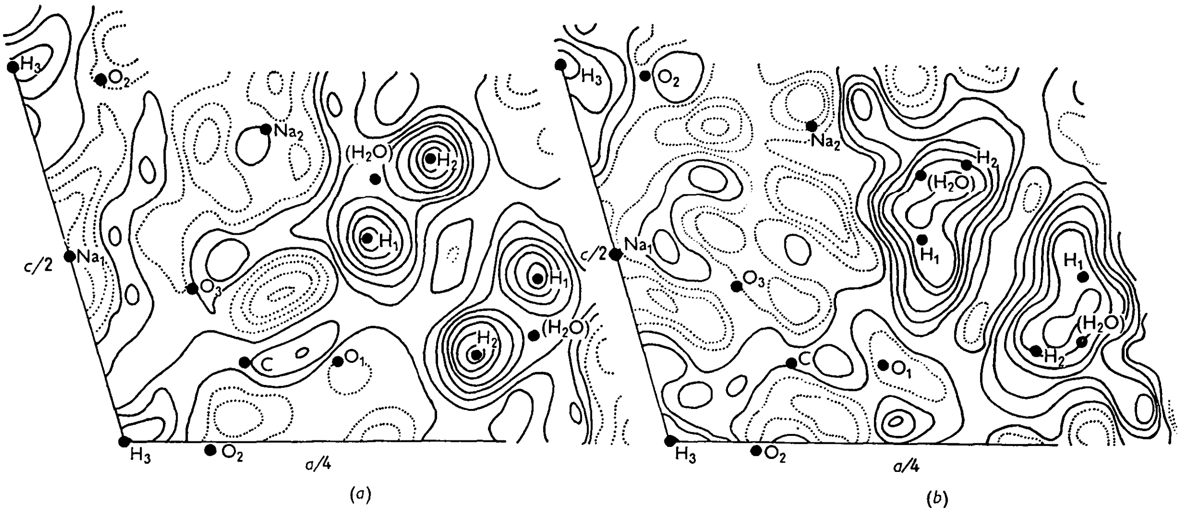

Fig. 4. Hydrogen peaks (a) at 18° C., (b) at −170° C. Contours at intervals of 0·1 e.Å^{-2}.

Table 5. *Atomic parameters*

(The y parameters at 18° C. are taken from Brown *et al*, 1949.)

	18° C.			−170 C.	
Atom	x	y	z	x	z
Na_1	0	0·748	0·2500	0	0·2500
Na_2	0·1509	0·165	0·4260	0·1507	0·4268
O_1	0·1514	0·373	0·1018	0·1517	0·1016
O_2	0·0547	0·139	0·9892	0·0540	0·9879
O_3	0·0720	0·257	0·2070	0·0732	0·2065
(H_2O)	0·2120	0·669	0·3542	0·2127	0·3550
H_1	0·196	—	0·272	0·203	0·270
H_2	0·257	—	0·385	0·243	0·375
H_3	0	—	0	0	0
C	0·0932	0·262	0·1040	0·0932	0·1035

Table 6. *Temperature factors*

	18° C.			−170° C.	
	α	β	ψ	α	β
Na_1	0·68	0	—	0·42	0
Na_2	0·75	0·40	90°	0·51	0
(H_2O)	0·59	0·40	−48°	0·51	0
All other atoms	0·51	0	—	0·51	0

The values of α quoted for Na_1 and Na_2 are those which gave the most satisfactory agreement of F_o and F_c when Hartree f-curves for Na^+ were used to calculate F_c.

ψ is the angle between the direction of maximum vibration and the z axis, and is positive if it lies within the obtuse angle β.

Table 7. *Comparison of F_o and F_c*

	18° C.		−170° C.	
hkl	F_o	F_c	F_o	F_c
002	24·3	24·1	24·3	22·8
004	18·3	−16·6	18·4	−16·8
006	54·0	−52·3	55·4	−55·4
008	19·5	17·5	19·1	17·2
$20\bar{8}$	12·3	−12·5	11·9	−13·2
$20\bar{6}$	24·1	−21·0	23·6	−23·7
$20\bar{4}$	67·1	67·1	68·5	65·0
$20\bar{2}$	5·7	− 6·9	0·0	− 3·3
200	28·5	28·6	28·0	30·7
202	36·6	−35·5	37·0	−35·6
*204	125·0	149·2	136·3	156·2
206	17·2	15·8	14·7	15·7
208	53·0	53·4	58·5	55·1
$4,0,\overline{10}$	45·4	−46·1	54·6	−52·6
$40\bar{8}$	17·7	19·5	20·7	24·3
$40\bar{6}$	67·7	66·4	62·3	64·5
$40\bar{4}$	33·2	32·8	32·7	29·7
$40\bar{2}$	16·0	13·8	15·4	14·6
400	52·3	−53·0	47·2	−50·1
*402	121·5	−144·0	127·4	−145·1
404	82·9	83·5	80·6	81·5
406	34·1	33·4	34·8	33·4
408	49·4	48·4	58·1	57·0
$6,0,\overline{10}$	48·2	−47·4	52·9	−54·9
$60\bar{8}$	35·0	−33·4	37·4	−34·4
$60\bar{6}$	38·7	−39·4	42·0	−41·5
$60\bar{4}$	9·8	− 5·8	3·2	5·1
$60\bar{2}$	25·6	−25·3	26·2	−25·0
600	26·6	29·2	30·4	27·8
602	53·2	52·0	61·5	56·7
604	22·1	−24·2	23·5	−23·9
*606	84·4	−92·6	87·5	−103·4
608	15·8	16·2	16·9	17·0
$8,0,\overline{10}$	7·8	− 8·3	6·3	− 6·3
$80\bar{8}$	35·5	30·6	36·7	32·8
*$80\bar{6}$	108·0	−116·4	116·8	−125·4
$80\bar{4}$	65·6	−66·5	66·4	−65·9
$80\bar{2}$	22·4	−24·2	22·4	−22·7
800	31·9	−29·9	31·9	−27·3
802	10·4	−11·4	9·0	− 8·9
804	20·9	22·2	26·7	26·8
806	11·1	−10·2	9·5	− 7·4
$10,0,\bar{8}$	46·6	44·8	51·3	50·1
$10,0,\bar{6}$	11·3	12·7	14·3	15·6
$10,0,\bar{4}$	41·1	37·1	41·6	41·2
*$10,0,\bar{2}$	116·8	−141·5	114·2	−154·0
10,0,0	52·2	−52·4	51·2	−54·3
10,0,2	43·6	−42·3	46·8	−45·1
10,0,4	20·9	−22·9	21·0	−21·0
10,0,6	9·1	9·5	11·1	11·4
$12,0,\bar{8}$	6·0	7·2	6·1	5·3
$12,0,\bar{6}$	61·6	−62·0	63·9	−63·7
$12,0,\bar{4}$	56·7	59·8	60·3	63·3
$12,0,\bar{2}$	13·6	−14·5	7·3	− 9·2
12,0,0	36·7	39·0	39·6	41·4
12,0,2	41·4	−40·2	47·0	−47·6
12,0,4	26·8	−25·6	30·0	−28·1
12,0,6	43·1	−43·2	47·0	−51·7
$14,0,\bar{8}$	0·0	− 2·4	0·0	− 2·5
$14,0,\bar{6}$	49·5	−49·1	50·8	−51·2
$14,0,\bar{4}$	9·9	− 6·8	11·1	−12·5
$14,0,\bar{2}$	0·0	− 2·9	4·8	− 5·4
*14,0,0	91·4	109·1	92·5	106·0
14,0,2	33·3	−33·8	31·7	−32·7
14,0,4	2·8	− 2·1	0·0	2·9
$16,0,\bar{8}$	8·1	5·1	9·9	10·8
$16,0,\bar{6}$	42·6	43·4	44·3	43·8
$16,0,\bar{4}$	57·0	62·2	61·0	63·0
$16,0,\bar{2}$	34·9	−34·5	37·8	−39·5
16,0,0	26·5	−24·8	30·4	−33·6
16,0,2	19·9	−23·3	26·0	−26·9
$18,0,\bar{6}$	42·4	42·6	39·8	43·8
$18,0,\bar{4}$	19·6	18·7	22·7	25·5
$18,0,\bar{2}$	13·9	13·4	17·8	18·1
18,0,0	12·6	16·0	14·7	15·9

* These large reflexions probably show considerable extinction.

of x and z coordinates easy, makes the accurate determination of the y coordinates difficult. On the other hand, the lengths of bonds lying nearly parallel to (010) will not be greatly affected by small changes in y parameters. The following procedure was adopted in order to obtain three-dimensional values.

For the 18° C. structure the values of b and the y coordinates obtained by Brown *et al.* were used. For the −170° C. structure, it was assumed that a reasonable estimate of b would be obtained by taking the thermal expansion coefficient α_{22} as equal to the mean coefficient in the (010) plane (16×10^{-6} (°C.)$^{-1}$ for this temperature range). It was further assumed that none of the y coordinates changed with temperature. It is obvious that there is no strict justification for this assumption, but reasons for accepting it as a legitimate approximation will be given in § 6(ii), where the errors in bond lengths will be discussed in detail.

6. Errors

(i) *In projected values*

The standard deviations in projected electron density, $\sigma(\varrho)$, and in atomic position, $\sigma(x_r)$, were found from the formulae quoted by Cochran (1951), assuming a Gaussian electron-density distribution near the centre of the atom, given by $\varrho_r = \varrho \exp[-pr^2]$. The value of $\sigma(\varrho)$ is 0·11 e.Å^{-2}. The values of $\sigma(x_r)$ are:

Na, 0·0038 Å; O, 0·0056 Å; C, 0·024 Å; H, 0·123 Å.

These represent means of values calculated by Cochran's two methods for each of the two temperatures independently, the separate values being in satisfactory agreement; the 18° C. value of p was used throughout, as likely to give an upper estimate of the error, except for hydrogen, where some of the atoms were less well resolved at −170° C. In this case, the mean value of p for H_1 and H_2 at −170° C. and 18° C. was used. The standard deviation in the projected bond lengths other than O–H is given in Table 8; for O–H, it is 0·125 Å.

(ii) *In three-dimensional values*

In order to estimate the error in the 18° C. bond lengths, it is necessary to know the error in y as

Table 8. *Changes in bond lengths with temperature*

(All lengths are in Å)

Bond	Projected length 18° C.	Projected length −170° C.	Contraction on cooling	Standard deviation in projected length	Angle with (010) (°)	Actual bond length 18° C.	Actual bond length −170° C.	Contraction on cooling	Error in actual length at 18° C.
$\mathrm{C-O_1}$	1·191	1·193	−0·002	0·025	18	1·253	1·254	−0·001	0·027
$\mathrm{C-O_2}$	1·220	1·226	−0·006	0·025	19	1·293	1·298	−0·005	0·027
$\mathrm{C-O_3}$	1·253	1·240	0·013	0·025	1	1·254	1·241	0·013	0·027
$\mathrm{Na_1-O_2}$	2·400	2·374	0·026	0·006	9	2·432	2·406	0·026	0·010
$\mathrm{Na_1-O_3}$	1·646	1·669	−0·023	0·006	47	2·422	2·434	−0·012	0·040
$\mathrm{Na_1-O_3}$	1·646	1·669	−0·023	0·006	46	2·376	2·388	−0·012	0·040
$\mathrm{Na_2-O_1}$	1·808	1·788	0·020	0·006	46	2·607	2·589	0·018	0·040
$\mathrm{Na_2-O_1}$	1·808	1·788	0·020	0·006	42	2·422	2·404	0·018	0·034
$\mathrm{Na_2-O_2}$	2·231	2·225	0·006	0·006	25	2·470	2·463	0·007	0·021
$\mathrm{Na_2-O_3}$	2·370	2·357	0·013	0·006	8	2·392	2·379	0·013	0·008
$\mathrm{Na_2-(H_2O)}$	1·616	1·630	−0·014	0·006	47	2·389	2·394	−0·005	0·040
$\mathrm{Na_2-(H_2O)}$	1·616	1·630	−0·014	0·006	47	2·368	2·374	−0·006	0·040
$\mathrm{O_1 \cdots H_1 \cdots (H_2O)}$	2·543	2·541	0·002	0·007	22	2·745	2·742	0·003	0·019
$\mathrm{O_1 \cdots H_2 \cdots (H_2O)}$	2·687	2·660	0·027	0·007	15	2·780	2·753	0·027	0·013
$\mathrm{O_2 \cdots H_3 \cdots O_2}$	2·300	2·275	0·025	0·009	23	2·495	2·472	0·023	0·020
$\mathrm{H_1-(H_2O)}$	0·82	0·83	−0·01	0·12	*	0·88	0·90	−0·02	*
$\mathrm{H_2-(H_2O)}$	0·88	0·58	0·30	0·12	*	0·91	0·60	0·30	*
$\mathrm{H_3-O_2}$	1·15	1·14	0·01	0·12	*	1·25	1·24	0·01	*
$\mathrm{O_1-O_2}$	1·979	1·992	−0·013	0·007	22	2·140	2·153	−0·013	0·019
$\mathrm{O_2-O_3}$	2·168	2·158	0·010	0·007	10	2·207	2·197	0·010	0·010
$\mathrm{O_3-O_1}$	2·186	2·194	−0·008	0·007	10	2·223	2·231	−0·008	0·010

The smaller expansions of certain bonds in three dimensions in comparison with those in projection are explained by the large components of these bonds parallel to y and the overall contraction of the structure.

* Unknown.

Table 9. *Bond angles*

(Subscripts U and L are used to distinguish atoms lying respectively above and below the atom at which the angle is subtended.)

Atoms concerned	Bond angle 18° C,	Bond angle −170° C:	Estimated error at 18° C.
$\mathrm{O_1-C-O_2}$	116° 38′	116° 44′	46′
$\mathrm{O_1-C-O_3}$	123 2	122 30	44
$\mathrm{O_2-C-O_3}$	120 19	120 43	44
$\mathrm{O_3-Na_1-O_3}$	86 40	*	51
$\mathrm{O_3-Na_1-O_3}$	93 20	*	51
$\mathrm{O_2-Na_1-O_{3\mathit{U}}}$	86 31	86 37	51
$\mathrm{O_2-Na_1-O_{3\mathit{L}}}$	100 9	100 16	51
$\mathrm{O_2-Na_1-O_{3\mathit{U}}}$	79 48	79 41	51
$\mathrm{O_2-Na_1-O_{3\mathit{L}}}$	93 19	93 12	51
$\mathrm{O_2-Na_2-O_{1\mathit{L}}}$	49 57	50 23	15
$\mathrm{O_2-Na_2-O_{1\mathit{U}}}$	85 48	86 17	32
$\mathrm{O_1-Na_2-O_1}$	87 51	*	51
$\mathrm{O_{1\mathit{L}}-Na_2-(H_2O)_\mathit{L}}$	77 52	77 44	8
$\mathrm{O_{1\mathit{U}}-Na_2-(H_2O)_\mathit{U}}$	81 14	81 5	8
$\mathrm{(H_2O)-Na_2-(H_2O)}$	94 22	*	51
$\mathrm{(H_2O)_\mathit{U}-Na_2-O_3}$	83 1	82 40	19
$\mathrm{(H_2O)_\mathit{L}-Na_2-O_3}$	94 19	93 58	19
$\mathrm{O_2-Na_2-O_3}$	86 18	86 34	16
$\mathrm{(H_2O)_\mathit{U}-O_1-(H_2O)_\mathit{L}}$	77 22	77 29	13
$\mathrm{(H_2O)_\mathit{L}-O_1-Na_{2\mathit{L}}}$	74 48	74 44	32
$\mathrm{(H_2O)_\mathit{L}-O_1-Na_{2\mathit{U}}}$	94 47	94 55	32
$\mathrm{(H_2O)_\mathit{U}-O_1-Na_{2\mathit{U}}}$	111 20	111 21	32

Table 9 (*cont.*)

Atoms concerned	Bond angle 18° C.	Bond angle −170° C.	Estimated error at 18° C.
$\mathrm{Na_2-O_1-Na_2}$	87 51	*	51
$\mathrm{Na_{2\mathit{U}}-O_1-C}$	112 39	112 48	40
$\mathrm{Na_{2\mathit{L}}-O_1-C}$	87 7	87 13	40
$\mathrm{C-O_1-(H_2O)_\mathit{U}}$	107 43	107 31	32
$\mathrm{C-O_1-(H_2O)_\mathit{L}}$	146 48	146 42	32
$\mathrm{O_2-O_2-C}$	111 52	111 35	32
$\mathrm{C-O_2-Na_2}$	93 27	92 50	32
$\mathrm{Na_1-O_2-Na_2}$	88 25	88 41	14
$\mathrm{Na_1-O_2-O_2}$	89 24	90 16	14
$\mathrm{Na_1-O_2-C}$	149 5	148 52	32
$\mathrm{O_2-O_2-Na_2}$	130 29	130 44	32
$\mathrm{Na_1-O_3-Na_1}$	93 20	*	51
$\mathrm{Na_{1\mathit{U}}-O_3-Na_2}$	101 53	101 21	32
$\mathrm{Na_{1\mathit{L}}-O_3-Na_2}$	90 29	90 4	32
$\mathrm{Na_2-O_3-C}$	120 1	121 40	40
$\mathrm{Na_{1\mathit{U}}-O_3-C}$	121 41	121 13	40
$\mathrm{Na_{1\mathit{L}}-O_3-C}$	123 0	122 33	40
$\mathrm{Na_2-(H_2O)-Na_2}$	94 22	*	51
$\mathrm{Na_{2\mathit{U}}-(H_2O)-O_{1\mathit{U}}}$	110 33	110 45	32
$\mathrm{Na_{2\mathit{L}}-(H_2O)-O_{1\mathit{U}}}$	136 14	136 29	32
$\mathrm{O_{1\mathit{U}}-(H_2O)-O_{1\mathit{L}}}$	114 18	114 11	13
$\mathrm{O_{1\mathit{L}}-(H_2O)-Na_{2\mathit{L}}}$	83 15	83 2	32
$\mathrm{O_{1\mathit{L}}-(H_2O)-Na_{2\mathit{U}}}$	115 51	115 37	32

* Changes in these angles will depend very much on the y coordinates; hence they have been left out of consideration.

determined by Brown *et al.*, which was not explicitly stated by these authors. A reasonable estimate is 0·05 Å, and this has been used in constructing the final column of Table 8.

It is also necessary to obtain some idea of the errors introduced into the bond lengths at −170° C. as a result of the assumptions specified in § 5. Since none of the bonds is inclined at more than 50° to (010), and most of them very much less, it seems reasonable to assume that the observed changes in projection give a reliable picture, statistically speaking, of what happens in three dimensions. Several of the Na–O bonds occur in pairs linking the same oxygen atom to two Na's which are related by the translation repeat b. Here a change of y coordinate would lengthen one bond and shorten the other. Since there is no physical reason for expecting this, it is assumed that any differences thus introduced are of the same order of magnitude as the differences actually observed in the projected lengths. Table 8 shows that these range from a contraction (on cooling) of 0·026 Å to an expansion of 0·023 Å. It may also be noted that the changes in O–O distances of the CO_3 group are not significantly greater than the standard deviation.

With the above assumptions, it may be shown that the standard deviation of the length of the two long hydrogen bonds is 0·008 Å, not very different from the error involving x and z coordinates only. Since the two bonds join symmetry-related atoms, it is necessary to enquire whether there may be any systematic effect on the difference of their lengths; it can be shown, however, that any such effect is very small and may be neglected.

For the short hydrogen bond, the estimate is less accurate. This bond joins two atoms of type O_2 related by a symmetry centre, whose y coordinate is fairly sensitive to small amounts of tilt of the CO_3 group. The standard deviation is 0·019 Å.

7. Comparison of the structure at the two temperatures

(i) *Changes in geometry*

(*a*) *The hydrogen bonds.*—The short hydrogen bond $O_2 \cdots H_3 \cdots O_2$ undergoes a contraction of 0·023 Å on cooling, and the long hydrogen bond $O_1 \cdots H_2 \cdots (H_2O)$ one of 0·027 Å. Both changes correspond to an expansion coefficient of about 50×10^{-6} (°C.)$^{-1}$ for this temperature range but only the latter is probably significant. The other long bond $O_1 \cdots H_1 \cdots (H_2O)$ undergoes no significant change with changing temperature.

The angle at (H_2O) between the two hydrogen bonds at −170° C. is somewhat greater than the tetrahedral angle; it increases slightly with rising temperature (see Table 9), though this change is not significantly outside the experimental error. The same is true of the angle at O_2 between the covalent bond to C and the short hydrogen bond.

(*b*) *The* CO_3 *group.*—The changes observed in the carbonate group at the two temperatures are not significant since the carbon atom has not been located as accurately as the heavier atoms. The coordination of the carbon is not regular at either temperature, for there is no doubt that the differences between the interbond angles are real. The apparent difference in bond length between C–O_2 and the other two bonds is not significant at either temperature considered by itself, but since there are two independent determinations, the difference becomes possibly significant. The atom O_2 is that involved in the short hydrogen bond and may well undergo some electronic rearrangement which weakens the bond to C. The CO_3 group is planar within experimental error: the calculated distance of C from the plane containing O_1, O_2 and O_3 is 0·009 Å.

(*c*) *The environment of* Na.—From the changes which are observed in the (010) plane, it looks as though the arrangement of oxygens round the sodium atoms tends to become more regular with decreasing temperature. Changes in Na–O bond lengths range from a contraction on cooling of 0·026 Å (corresponding to a mean thermal expansion coefficient of 51×10^{-6} (°C.)$^{-1}$) to an expansion of 0·012 Å (see Table 8). Expansions are observed only in Na–O bonds that are shorter than the average for this structure. There must be some doubt about the actual values for the expansions, as these bonds are all rather steeply inclined to (010), and their lengths are sensitive to small errors in the y coordinates of the atoms involved. Nevertheless, it seems likely that the order of magnitude is correct, and that Na_1–O_3 and Na_2–(H_2O) bonds do not in any case undergo any appreciable contraction on cooling. For Na_2–O bonds, the extreme range in value is 0·239 Å at 18° C. and 0·215 Å at −170° C. There are also slight changes in bond angle which result in a more evenly spaced distribution of oxygens round Na_2 at the lower temperature.

It also appears that the mean lengths of bonds from Na_1 and Na_2 become more nearly equal as the temperature decreases. At 18° C. the mean length of those from Na_1 is 2·410 Å and of those from Na_2 2·441 Å. (It is perhaps worth noticing that the larger value is associated with the atom with the larger temperature factor and the larger thermal anisotropy (see Table 6).) At −170° C. the corresponding values are 2·409 Å and 2·434 Å respectively.

These conclusions are only tentative, because of possible errors in the y coordinates, but the results do seem to indicate a tendency towards a more regular arrangement with decreasing temperature.

(ii) *Changes in the electronic distribution*

(*a*) *The hydrogen atoms.*—At 18° C., the hydrogen atoms of the water molecule are well-resolved, with circular symmetry in projection, but at −170° C. the atoms appear to overlap, and it is not possible to pick out round hydrogen peaks.

The electron cloud of H_3 has the same distribution, within experimental error, at both temperatures. There is a maximum of electron density at the centre of the bond, with some slight extension along the bond. Differences in electron density at a given radial distance from the origin are not, however, outside the experimental error in the determination of ϱ.

The peak heights and numbers of electrons associated with each hydrogen atom are given in Table 10.

Table 10. *Electron counts for hydrogen*

	No. of electrons		Peak height (e.Å^{-2})	
Atom	18° C.	−170° C.	18° C.	−170° C.
H_1	0·68	—	0·64	0·60*
H_2	0·71	—	0·72	0·62*
H_1+H_2	1·39	1·44	—	—
H_3	0·28	0·34	0·30	0·33

Uncertainty in number of electrons associated with a given area on map is 0·13 e.Å^{-2}.

Uncertainty in peak height is 0·11 e.Å^{-2}.

H_1 and H_2 are not resolved in projection at −170° C., and the values marked with an asterisk are not as reliable as the others.

The atoms H_1 and H_2 are closely similar, but H_3 has values which are much lower. There are no appreciable changes with temperature.

(*b*) *The heavier atoms.*—Two atoms, Na_2 and (H_2O) show markedly anisotropic vibration at 18° C., but not at −170° C. (see Table 6). The direction of maximum vibration for Na_2 is that in which there are no bonds to neighbouring atoms. For the water molecule, the direction is approximately parallel to the line bisecting the obtuse angle between the hydrogen bonds (and presumably also between the two Na_2–(H_2O) bonds, though this cannot be proved from two-dimensional data). The other cation, Na_1, has an isotropic thermal vibration, the amplitude of which increases with rising temperature. None of the atoms belonging to the carbonate group shows a change with temperature; hence there can be no appreciable thermal movement of the group as a whole, nor of the oxygens relative to the carbon, in the plane of the group, but movements perpendicular to this plane remain as possibilities.

8. Discussion

(i) *Thermal expansion of the hydrogen bonds*

It is rather surprising that two long hydrogen bonds, of very similar length, should behave so differently with changing temperature. This difference is probably a consequence of the different environments of the two types of bond.

The bond $(H_2O)\cdots H_1\cdots O_1$ is effectively jammed by interactions of the oxygen atoms with Na_2. If, with rising temperature, it expanded by more than the average expansion of the cell as a whole, it would force a contraction of the Na_2–(H_2O) bonds. These bonds are already shorter than the average Na–O bond (not longer, as the fact that (H_2O) is involved in hydrogen bonds might have led one to expect) and it seems likely that the structure could not tolerate any further contraction here. Hence an expansion in the hydrogen bond cannot take place. Evidently, therefore, energy changes with bond length may be less in a hydrogen bond than in a neighbouring electrostatic bond, and in such a case the hydrogen bond will not exhibit its characteristic thermal properties.

The environment of $(H_2O)\cdots H_2\cdots O_1$ is quite different. Bonds of this type join one slab of electrostatically-bonded atoms to the next, across the cleavage plane, and it would be expected that interactions between such units of structure would impose no severe limitations on the length of the bond, since they would be of the nature of long-range electrostatic or van der Waals forces varying rather slowly with distance. It may therefore be assumed that the behaviour of $(H_2O)\cdots H_2\cdots O_1$ approximates to that of an isolated bond, i.e. a bond unconstrained by anything other than those homopolar or ionic forces which directly affect its polarization and which are allowed for in specifying its nature and identity as a structure-building unit. The observed changes in $(H_2O)\cdots H_2\cdots O_1$ are thus attributable to the nature of the bond itself.

It also appears, from a detailed examination of the Na_1–O and Na_2–O bond lengths, that the short hydrogen bond $O_2\cdots H_3\cdots O_2$ is unlikely to be constrained by interactions between O_2 and other atoms, and that its expansion is determined principally by the nature of the bond.

It therefore seems safe to conclude that an expansion coefficient of approximately 50×10^{-6} (°C.)$^{-1}$ is characteristic of long hydrogen bonds for this temperature range, but that this may be suppressed where the atoms concerned are clamped by stronger cation–anion forces. There is no evidence for a different coefficient for the short bond in this structure, and in particular there is no evidence for any abnormally great expansion.

(ii) *Thermal expansion of the crystal as a whole*

The anisotropy of thermal expansion is not very great for sodium sesquicarbonate (see Table 1), and there is no obvious correlation between the direction of maximum vibration for the crystal as a whole and the directions of any particular bonds in the structure. The bond Na_1–O_2, which undergoes a big change with temperature, does indeed lie somewhere near the direction of maximum expansion, but the other bonds which show comparable changes, namely $(H_2O)\cdots H_2\cdots O_1$ and $O_2\cdots H_3\cdots O_2$, lie approximately at 90° to it. It can be seen from Fig. 1 that there are four bonds of the type Na_1–O_2 lying within the repeat distance *c*, and two each of $(H_2O)\cdots H_2\cdots O_1$ and $O_3\cdots H_2\cdots O_2$ lying within the repeat distance *a*. Since *a* is twice as long as *c*, the proportion of bonds lying near the direction of *a* and having large expansions is half as great as that of comparable bonds lying nearly parallel to *c*. The somewhat larger thermal expansion coefficient parallel to *z* can thus be explained in a qualitative way. There is, however, no particular correlation with the hydrogen bonds considered by themselves.

There are two atoms Na_2 and (H_2O) which show marked anisotropy of thermal vibration. Again there is no obvious relation between the directions of maximum vibration and of maximum thermal expansion. Since, however, the directions of maximum vibration are those in which the atoms make no bonds, it is quite reasonable that such anisotropic vibrations should have no direct influence on the anisotropy of thermal expansion.

(iii) *Electronic distribution in the hydrogen bonds*

At 18° C. the electronic distribution in the long bonds approximates to that in an isolated hydrogen atom, although the peak heights and number of electrons associated with both H_1 and H_2 are somewhat lower than the calculated values. The O–H distances of 0·88 and 0·91 Å are in good agreement with the value of 0·91 Å obtained for one of the O–H bonds in salicylic acid (Cochran, 1953). They are, however, rather shorter than the values obtained in preliminary neutron experiments on sodium sesquicarbonate (Bacon, private communication) which indicate O–H distances of approximately the value calculated for a free O–H bond. Although this difference is not significantly outside the experimental error of the X-ray determination, it should be pointed out that neutron diffraction experiments give proton positions, which do not necessarily coincide with the maxima of electron density located by X-ray methods. There is also a possible source of error in the assumption of a spherical electron distribution at absolute zero for the oxygen atom; actual departures from this may be sufficiently large to affect the apparent position of the hydrogen atom.

When the temperature is lowered to −170° C., H_2 appears to undergo a movement towards the nearer oxygen. The *y* coordinate of H_2 has not been determined, and the shortening of the projected distance might, therefore, represent an angular displacement rather than a shortening of the true distance. In any case, however, the shift is only possibly significant compared with the standard deviation in O–H bond length. The atom H_1 retains its original position with respect to the nearer oxygen. Peak heights and electron counts (which are difficult to estimate because of the overlapping of H_1 and H_2) are again rather low, and do not differ significantly from their 18° C. values (Table 10).

The results show an interesting difference between the hydrogens in the long bonds on the one hand and that in the short bond on the other. At both temperatures, H_3 has peak heights and associated number of electrons that are only half as great as the values for H_1 and H_2. The hydrogen in the short bond must therefore be appreciably ionized. The question of a double equilibrium position for H_3 cannot be answered from these results, for any departures from spherical symmetry about the origin are not significantly outside the experimental error. The maximum of electron density is at the origin at both temperatures, but the peak value is so low compared with $\sigma(\varrho)$ that this hydrogen cannot be located very precisely.

The results for sodium sesquicarbonate indicate, therefore, that there is an inherent difference between the electronic distribution in a long bond and that in a short one, but that nevertheless, under favourable conditions, both types of hydrogen bonds have similar values of the thermal expansion coefficient.

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References

Albrecht, G. (1939). *Rev. Sci. Instrum.* **10**, 221.
Bacon, G. E. & Pease, R. S. (1953). *Proc. Roy. Soc.* A, **220**, 397.
Brown, C. J., Peiser, H. S. & Turner-Jones, A. (1949). *Acta Cryst.* **2**, 167.
Cochran, W. (1948). *Nature, Lond.* **161**, 765.
Cochran, W. (1950). *Acta Cryst.* **3**, 268.
Cochran, W. (1951). *Acta Cryst.* **4**, 81.
Cochran, W. (1953). *Acta Cryst.* **6**, 260.
Frazer, B. C. & Pepinsky, R. (1953). *Acta Cryst.* **6**, 273.
Robertson, J. M. & Ubbelohde, A. R. (1939). *Proc. Roy. Soc.* A, **170**, 241.
Shaw, R. (1953). *Acta Cryst.* **6**, 428.
Shaw, R. (1955). Thesis, Cambridge University.
Ubbelohde, A. R. & Woodward, I. (1946). *Proc. Roy. Soc.* A, **185**, 448.