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Washing soda (natron), $Na_2CO_3 \cdot 10H_2O$, revised: crystal structures at low and ambient temperatures

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Summary

Crystals of natron, $Na_2CO_3 \cdot 10H_2O$, were grown by slow evaporation of a saturated sodium carbonate solution at room temperature. A single-crystal fragment was measured on a CCD X-ray four-circle diffractometer at 110, 270 and 295 K. Whereas the crystal structure of natron at room temperature had first been published in 1969 with $R = 18\%$, in the present investigation the non-centrosymmetric structure was solved by direct methods and refined subsequently to $R1 = 1.9\%$ (110 K), 2.5% (270 K), and 3.5% (295 K). In contrast to the previous structure description, even the hydrogen atoms were located and refined with isotropic displacement parameters. Space group is *Cc*, lattice parameters are $a = 12.740(1)/12.763(1)/12.750(2)$ Å, $b = 8.816(1)/8.955(1)/9.001(2)$ Å, $c = 12.571(1)/12.593(1)/12.590(2)$ Å, $\beta = 115.97(1)/115.89(1)/115.83(1)^\circ$ at 110/270/295 K.

The structure is composed of pairs of edge-sharing $Na(H_2O)_6$ octahedra forming $Na_2(H_2O)_{10}$ units, and CO_3 molecules. These units are connected by hydrogen bonds ($d_{O\cdots O} > 2.73$ Å) in a NaCl-like arrangement. The structure is pseudo-centric, only the carbonate groups and four H atoms violating a centric symmetry.

The CO_3 molecules are perfectly ordered at 110 K and show almost isotropic ADPs of the carbonate O atoms. The CO_3 position is constrained by hydrogen bonds, involving at least three H bonds per acceptor oxygen atom. At 270/295 K the carbonate groups still hold the former low-temperature position to 60/46%, whereas 40/54% are disordered into at least two different positions with large and strongly smeared anisotropic displacement parameters of the carbonate O atoms. However, a centrosymmetric equivalent of the low-temperature CO_3 position is occupied to only $\sim 10\%$.

A definite phase transition from ordered to partially disordered CO_3 groups was neither observed in differential scanning calorimetry, nor in temperature-dependent birefringence, IR and Raman spectroscopic measurements, as the process takes place over a wide temperature interval and without any change of the space group symmetry *Cc*.

Introduction

The mineral natron, $Na_2CO_3 \cdot 10H_2O$, which is commonly known and used as ''washing soda'', occurs naturally in terrestrial evaporites, i.e. as an evaporation product of natron lakes at low temperatures (*Ramdohr* and *Strunz*, 1980). At moderate to high temperatures in arid climates, the mineral thermonatrite, $Na_2CO_3 \cdot H_2O$, is formed either as a primary evaporite or by dehydration of natron. In addition, three other hydrous sodium carbonate minerals are known in nature: trona, $Na_3(CO_3)(HCO_3) \cdot 2H_2O$, nahcolite, $Na(HCO_3)$, and wegscheiderite, $Na_5(CO_3)(HCO_3)_3$. Even the anhydrous sodium carbonate is known as the rare mineral natrite (*Mandarino*, 1999) that occurs together with some of the above mentioned minerals plus Na–Ca–carbonates in hyperagpaitic rocks of the Kola Peninsula (*Khomyakov*, 1995).

The structure of natron at room temperature has been solved in principle by *Taga* (1969), even though he obtained an *R* value as large as 18% and could not locate the hydrogen atom positions of the water molecules. Up to now, and to the best knowledge of the authors, *Taga's* (1969) paper has not been followed by any other refinement of natron at room temperature. This may be caused by the difficult handling of the material, as it dehydrates at room temperature and low humidity (*Zhang* et al., 1995), and melts in its own crystal water at only 305 K to $Na_2CO_3 \cdot 7H_2O$ + aqu. solution, and at 306 K to $Na_2CO_3 \cdot H_2O$ + aqu. solution (*Groenvold* and *Meisingset*, 1983). Nevertheless, a refinement of natron at 173 K has been published by *Mehta* and *Adam* (1998). In contrast to the room temperature structure description they observed an ordered arrangement of the anion groups. This was also confirmed in a preliminary investigation of natron at 110 K by *Libowitzky* and *Giester* (2000).

The structure of natron is composed of $Na(H_2O)_6$ octahedra, which are connected in pairs by a common edge to form $Na_2(H_2O)_{10}$ units, and by CO_3 molecules. The hydrated sodium units and the carbonate groups are interconnected by hydrogen bonds in a NaCl-like arrangement. *Taga* (1969) approximated the structure in the centrosymmetric space group $C2/c$ and refined the atom positions in space group Cc. He found that the carbonate ion occupies a center of symmetry in $C2/c$, and that it is disordered in space group Cc between two half-occupied positions ''rotated in its own plane''. A sketch of the structure, however, reveals that the latter statement by *Taga* (1969) is not true. (If ''rotated in its own plane'', the carbonate groups and consequently the whole structure would actually be centrosymmetric.) Thus, it is emphasized that the structure is pseudo-centric, but the disordered carbonate groups violate the centric symmetry.

The aim of the present study was to investigate the behavior of the carbonate groups at low temperatures and to provide accurate values of all atom positions (including the H atoms) in the structure of natron. The present investigation is part of a series of studies of minerals with disordered structural units at room temperature which become ordered at low temperatures, and which may be accompanied by phase transitions, e.g. H_2O and OH^- in lawsonite (*Libowitzky* and *Armbruster*, 1995), H_2O and OH^- in hemimorphite (*Libowitzky* and *Rossman*, 1997), $[SO_4]^{2-}$ in leonite (*Hertweck* et al., 2001).

Experimental

Crystals of natron were synthesized by slow evaporation of a saturated aqueous sodium carbonate solution at room temperature. One of the tabular crystals obtained with a size up to 1 cm was embedded in apiezone grease and cut into several pieces. A fragment with $\sim 0.35 \times 0.35 \times 0.40\,mm^3$ was selected and mounted with apiezone grease on a silica glass needle. The apiezone grease prevented dehydration of the natron crystal during preparation and all X-ray measurements, even at room temperature.

Single-crystal X-ray data were collected at 110, 270, and 295 K on a Nonius Kappa CCD diffractometer equipped with a 0.3 mm monocapillary optics collimator using monochromatized MoKα radiation. An Oxford Cryostream liquid nitrogen cooling device was used during the low-temperature experiments. A whole sphere of reflections was measured in reciprocal space ($N_{unique} > 4\sigma(F_o) =$ 3565/3084/2182 at 110/270/295 K), and lattice parameters (Table 1) were refined from all measured frames.

The crystal structure was determined by direct methods using SHELXS-97 (*Sheldrick*, 1997a) and subsequent Fourier and difference Fourier syntheses. Final structure parameters were obtained by full-matrix least-squares techniques on F^2 using SHELXL-97 (*Sheldrick*, 1997b). Because of the good data quality and the

Table 1. *Parameters of the X-ray single-crystal refinements of natron at 110, 270, and 295 K*

	110 K	270 K	295 K
Space group	*Cc*	*Cc*	*Cc*
a (Å)	12.740(1)	12.763(1)	12.750(2)
b (Å)	8.816(1)	8.955(1)	9.001(2)
c (Å)	12.571(1)	12.593(1)	12.590(2)
β (°)	115.97(1)	115.89(1)	115.83(1)
V (Å^3)	1269.4(2)	1294.8(2)	1300.5(4)
Z	4	4	4
μ [MoKα] (mm^{-1})	0.21	0.21	0.21
$2\theta_{max}$(°)	61	61	56.5
R_{int}	0.014	0.014	0.019
N_{unique}	3717	3767	3107
N [with $F_o > 4\sigma(F_o)$]	3565	3084	2182
$N_{parameters}$	226	297	297
$N_{restraints}$	2	22	22
$R1$ [for $F_o > 4\sigma(F_o)$]	0.019	0.025	0.035
$R1$ [for all F_o]	0.021	0.038	0.067
$wR2$ [for $F_o > 4\sigma(F_o)$]	0.047	0.049	0.055
$wR2$ [for all F_o]	0.047	0.054	0.063
GooF	1.060	0.960	1.022
$\rho_{min/max}$ (eÅ^{-3})	−0.15/0.13	−0.13/0.09	−0.14/0.13

$R1 = \Sigma\|\|F_o| - |F_c\|| / \Sigma|F_o|$
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.2P]$
$P = (F_o^2 + 2F_c^2)/3$

generally low scattering cross section of the participating light elements (Na, C, O), it was possible to refine atomic positions and even isotropic displacement parameters (U_{iso}) of the 20 hydrogen atom sites. All other atoms were refined with anisotropic displacement parameters (ADPs, U_{ij}). Because of the disordered structures at 270 and 295 K, certain restraints in hydrogen bond lengths (O–H = 0.80(5) Å) and constraints on a common site occupancy of the three oxygen atoms of the carbonate group were applied and facilitated a stable refinement. The refinements converged to $R1 = 1.9/2.5/3.5\%$ at 110/270/295 K. Details of measurements and refinement procedures are listed in Table 1.

Results and discussion

Atomic fractional coordinates and isotropic displacement parameters for natron at 110/270/295 K are presented in Table 2. A list of ADPs for all atoms except hydrogen is summarized in Table 3 (deposited) and can be obtained from the authors upon request. The ADPs of the atoms of the (disordered) carbonate groups, however, are given in Table 4. Interatomic distances and angles are summarized in Table 5 (around Na and C) and Table 6 (hydrogen bond system).

Table 2. *Atomic coordinates and displacement parameters U_{eq}/U_{iso} with e.s.d.'s in parentheses and site occupation factors (s.o.f.'s) of natron at 110/270/295 K (in consecutive rows)*

Atom	x	y	z	U_{eq}/U_{iso}	s.o.f.
Na1	0.13371(3)	− 0.03546(4)	0.12779(3)	0.01322(8)	1.0
	0.13386(4)	− 0.02541(9)	0.12738(5)	0.03635(16)	1.0
	0.13393(10)	− 0.0219(2)	0.12711(11)	0.0442(4)	1.0
Na2	− 0.13346(3)	0.03418(4)	− 0.12709(3)	0.01354(8)	1.0
	− 0.13561(5)	0.02545(9)	− 0.13032(5)	0.03727(17)	1.0
	− 0.13637(11)	0.0227(2)	− 0.13155(11)	0.0449(4)	1.0
C	− 0.00839(9)	0.50611(12)	− 0.01460(8)	0.01146(15)	1.0
	− 0.00535(18)	0.5025(3)	− 0.00727(18)	0.02735(18)	1.0
	− 0.0049(4)	0.5003(7)	− 0.0059(5)	0.0330(4)	1.0
O1	− 0.19218(7)	0.13536(9)	− 0.32302(6)	0.01519(14)	1.0
	− 0.19546(13)	0.1271(2)	− 0.32652(13)	0.0406(3)	1.0
	− 0.1962(3)	0.1242(4)	− 0.3272(3)	0.0497(9)	1.0
O2	0.18774(6)	− 0.14186(9)	0.31986(6)	0.01503(14)	1.0
	0.19050(12)	− 0.13147(18)	0.32001(12)	0.0397(3)	1.0
	0.1918(2)	− 0.1286(4)	0.3200(2)	0.0471(8)	1.0
O3	− 0.06433(6)	− 0.12442(9)	0.04647(6)	0.01540(14)	1.0
	− 0.06143(12)	− 0.12262(17)	0.04777(12)	0.0407(4)	1.0
	− 0.0608(2)	− 0.1222(4)	0.0492(3)	0.0502(9)	1.0
O4	0.06179(6)	0.12966(8)	− 0.04666(6)	0.01580(14)	1.0
	0.05814(11)	0.12547(18)	− 0.05265(12)	0.0419(4)	1.0
	0.0568(2)	0.1230(4)	− 0.0535(2)	0.0487(9)	1.0

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	U_{eq}/U_{iso}	s.o.f.
O5	− 0.33836(6)	− 0.04574(8)	− 0.19489(6)	0.01514(14)	1.0
	− 0.33757(12)	− 0.05796(18)	− 0.18797(14)	0.0421(3)	1.0
	− 0.3372(2)	− 0.0625(4)	− 0.1862(3)	0.0514(8)	1.0
O6	0.33045(6)	0.05279(8)	0.17553(7)	0.01559(14)	1.0
	0.33212(11)	0.06248(17)	0.17770(13)	0.0401(3)	1.0
	0.3327(2)	0.0652(4)	0.1780(3)	0.0465(7)	1.0
O7	0.08137(6)	0.18169(9)	0.20779(6)	0.01647(14)	1.0
	0.08233(13)	0.1905(2)	0.20716(13)	0.0442(3)	1.0
	0.0830(3)	0.1943(5)	0.2073(3)	0.0534(8)	1.0
O8	− 0.08963(7)	− 0.18571(8)	− 0.21313(7)	0.01708(14)	1.0
	− 0.09159(14)	− 0.1951(2)	− 0.21520(14)	0.0442(3)	1.0
	− 0.0916(3)	− 0.1970(4)	− 0.2152(3)	0.0510(8)	1.0
O9	− 0.21528(7)	0.26685(9)	− 0.08754(7)	0.01925(15)	1.0
	− 0.21227(14)	0.2590(2)	− 0.08929(14)	0.0498(4)	1.0
	− 0.2114(3)	0.2555(5)	− 0.0890(3)	0.0584(9)	1.0
O10	0.20505(7)	− 0.26755(10)	0.08047(7)	0.02046(16)	1.0
	0.20235(14)	− 0.2547(2)	0.07712(15)	0.0523(4)	1.0
	0.2021(3)	− 0.2514(5)	0.0775(3)	0.0615(9)	1.0
O11	− 0.10167(5)	0.54697(7)	− 0.00619(5)	0.01487(12)	1.0
	− 0.1003(4)	0.5420(6)	− 0.0035(4)	0.0409(8)	0.60(1)
	− 0.1001(11)	0.5461(13)	− 0.0009(11)	0.055(3)	0.46(2)
O12	0.00493(6)	0.54031(7)	− 0.10682(6)	0.01938(14)	1.0
	0.0079(2)	0.5420(6)	− 0.0990(2)	0.0514(12)	0.60(1)
	0.0093(7)	0.5461(16)	− 0.0971(7)	0.060(3)	0.46(2)
O13	0.07225(6)	0.43262(8)	0.07036(6)	0.02036(14)	1.0
	0.0784(4)	0.4569(8)	0.0854(4)	0.0562(13)	0.60(1)
	0.0784(8)	0.4704(16)	0.0902(8)	0.051(3)	0.46(2)
Q1	–	–	–	–	0.0
	0.0042(17)	0.578(3)	0.0824(14)	0.050(8)	0.08(1)
	0.002(3)	0.586(4)	0.080(2)	0.066(12)	0.12(1)
Q2	–	–	–	–	0.0
	0.0889(5)	0.4453(10)	− 0.0092(6)	0.045(3)	0.19(1)
	0.0878(9)	0.4430(18)	− 0.0044(14)	0.066(8)	0.26(1)
Q3	–	–	–	–	0.0
	− 0.0158(10)	0.459(2)	0.0896(9)	0.045(6)	0.12(1)
	− 0.0164(19)	0.463(3)	0.0893(13)	0.052(10)	0.15(1)
Q4	–	–	–	–	0.0
	− 0.0839(7)	0.5469(15)	− 0.0951(10)	0.071(5)	0.23(1)
	− 0.0839(13)	0.543(3)	− 0.0968(19)	0.081(9)	0.27(2)
Q5	–	–	–	–	0.0
	− 0.0073(7)	0.4375(18)	− 0.0971(6)	0.060(4)	0.25(1)
	− 0.0071(9)	0.440(3)	− 0.0945(9)	0.075(7)	0.34(2)
Q6	–	–	–	–	0.0
	− 0.0858(15)	0.589(2)	− 0.013(2)	0.094(7)	0.25(1)
	− 0.083(2)	0.583(3)	− 0.016(3)	0.129(11)	0.34(3)

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	U_{eq}/U_{iso}	s.o.f.
Q7	–	–	–	–	0.0
	0.0630(10)	0.4057(10)	0.0591(13)	0.041(2)	0.22(1)
	0.0688(16)	0.407(2)	0.065(2)	0.052(5)	0.26(2)
H1	− 0.1879(15)	0.227(2)	− 0.3233(15)	0.031(4)	1.0
	− 0.193(2)	0.212(2)	− 0.325(2)	0.044(6)	1.0
	− 0.195(3)	0.208(3)	− 0.327(3)	0.034(8)	1.0
H2	− 0.2623(14)	0.1194(17)	− 0.3621(12)	0.020(3)	1.0
	− 0.2567(17)	0.108(2)	− 0.3642(17)	0.032(5)	1.0
	− 0.257(2)	0.111(4)	− 0.366(3)	0.034(10)	1.0
H3	0.2635(17)	− 0.119(2)	0.3766(17)	0.049(5)	1.0
	0.258(2)	− 0.118(4)	0.367(3)	0.083(10)	1.0
	0.262(3)	− 0.102(7)	0.365(4)	0.11(2)	1.0
H4	0.1842(14)	− 0.232(2)	0.3108(14)	0.033(4)	1.0
	0.184(3)	− 0.228(3)	0.313(3)	0.083(10)	1.0
	0.183(6)	− 0.219(4)	0.306(5)	0.16(3)	1.0
H5	− 0.0764(16)	− 0.211(2)	0.0253(14)	0.031(4)	1.0
	− 0.055(3)	− 0.212(3)	0.047(3)	0.100(12)	1.0
	− 0.063(8)	− 0.199(7)	0.015(7)	0.27(4)	1.0
H6	− 0.0933(11)	− 0.1175(16)	0.0901(12)	0.017(3)	1.0
	− 0.0925(18)	− 0.114(2)	0.0859(19)	0.042(6)	1.0
	− 0.088(5)	− 0.111(7)	0.095(4)	0.12(2)	1.0
H7	0.1004(17)	0.132(2)	− 0.0923(18)	0.054(6)	1.0
	0.093(2)	0.115(4)	− 0.097(3)	0.080(10)	1.0
	0.094(3)	0.113(4)	− 0.090(3)	0.036(9)	1.0
H8	0.0627(14)	0.2248(19)	− 0.0281(14)	0.028(4)	1.0
	0.066(2)	0.214(2)	− 0.032(2)	0.056(6)	1.0
	0.0579(17)	0.213(3)	− 0.0440(18)	0.025(5)	1.0
H9	− 0.3812(15)	− 0.0191(18)	− 0.1585(15)	0.033(4)	1.0
	− 0.376(3)	− 0.042(4)	− 0.148(3)	0.104(11)	1.0
	− 0.380(5)	− 0.048(7)	− 0.149(5)	0.16(3)	1.0
H10	− 0.3722(16)	− 0.0136(19)	− 0.2555(17)	0.036(4)	1.0
	− 0.3756(17)	− 0.033(2)	− 0.2485(17)	0.034(5)	1.0
	− 0.377(2)	− 0.047(3)	− 0.248(2)	0.025(8)	1.0
H11	0.3586(14)	0.0416(16)	0.1282(14)	0.027(4)	1.0
	0.361(2)	0.046(2)	0.1406(18)	0.038(5)	1.0
	0.362(2)	0.055(3)	0.139(2)	0.031(7)	1.0
H12	0.3815(16)	0.027(2)	0.2409(17)	0.040(5)	1.0
	0.383(3)	0.042(3)	0.244(2)	0.087(9)	1.0
	0.374(4)	0.032(6)	0.242(4)	0.11(2)	1.0
H13	0.0643(13)	0.2587(19)	0.1642(14)	0.028(4)	1.0
	0.069(2)	0.266(3)	0.167(2)	0.048(7)	1.0
	0.070(3)	0.260(4)	0.167(3)	0.047(13)	1.0

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	U_{eq}/U_{iso}	s.o.f.
H14	0.0269(12)	0.1720(14)	0.2296(12)	0.024(3)	1.0
	0.0318(15)	0.1802(18)	0.2284(15)	0.052(5)	1.0
	0.034(2)	0.181(3)	0.230(2)	0.068(9)	1.0
H15	− 0.0658(14)	− 0.2746(19)	− 0.1787(14)	0.031(4)	1.0
	− 0.073(3)	− 0.271(3)	− 0.180(3)	0.082(11)	1.0
	− 0.076(4)	− 0.281(4)	− 0.179(4)	0.084(17)	1.0
H16	− 0.1491(14)	− 0.2036(16)	− 0.2693(14)	0.029(4)	1.0
	− 0.1515(15)	− 0.2138(17)	− 0.2735(15)	0.047(4)	1.0
	− 0.152(2)	− 0.219(2)	− 0.275(2)	0.048(7)	1.0
H17	− 0.1813(16)	0.360(2)	− 0.0658(16)	0.045(5)	1.0
	− 0.169(3)	0.327(4)	− 0.074(3)	0.133(16)	1.0
	− 0.165(3)	0.310(5)	− 0.088(4)	0.114(17)	1.0
H18	− 0.2773(15)	0.2831(16)	− 0.1491(14)	0.031(4)	1.0
	− 0.2701(17)	0.272(2)	− 0.1475(16)	0.057(5)	1.0
	− 0.269(2)	0.270(3)	− 0.146(2)	0.069(9)	1.0
H19	0.1683(16)	− 0.338(2)	0.0613(16)	0.046(5)	1.0
	0.173(2)	− 0.332(3)	0.058(2)	0.071(8)	1.0
	0.174(3)	− 0.328(4)	0.053(3)	0.093(13)	1.0
H20	0.2279(15)	− 0.2577(19)	0.0321(15)	0.036(4)	1.0
	0.225(2)	− 0.240(3)	0.0299(19)	0.077(7)	1.0
	0.222(2)	− 0.244(3)	0.028(2)	0.063(9)	1.0

Approximately centrosymmetric atom pairs are (hypothetical center of symmetry at the origin): Na1–Na2, O1–O2, O3–O4, O5–O6, O7–O8, O9–O10, O11–Q2*, O12–Q3*, O13–Q4*, H1–H4, H2–H3, H5–H8, H6–H7, H9–H11, H10–H12, H13–H15, H17–H19. *Only with low site occupation factor at 270 and 295 K

The ordered crystal structure of natron at 110 K

An important result of the structure refinement of the 110 K X-ray data set is that the crystal structure of natron is completely ordered, which is quite different from previous findings at room temperature (*Taga*, 1969), but in agreement with the findings of *Mehta* and *Adams* (1998) at 173 K. (However, the latter gave no atom coordinates in their published abstract contribution.) The ordered low-temperature structure is confirmed also by the small values and the almost isotropic behavior of the ADPs (Tables 3 and 4), by the low residual electron density in a difference Fourier map (without any remaining significant density maxima) after complete refinement, and finally by the obtained low agreement (R) values.

The crystal structure of natron at 110 K is displayed in Fig. 1. This view parallel to a^*, projected onto the (100) plane, makes evident that one bond of the carbonate group (i.e. C–O12) points uniformly along the [− 1 0 0] axis direction without exception, and thus determines the non-centrosymmetric space group symmetry, even if the rest of the structure is almost centrosymmetric. Table 2, which lists the (approximately) centrosymmetric pairs of atoms in the structure, also shows that

Table 3. *Anisotropic displacement parameters U_{ij} with e.s.d.'s in parentheses for natron at 110/270/295 K (in consecutive rows)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	0.01234(17)	0.01369(17)	0.01358(17)	0.00008(13)	0.00564(14)	0.00043(14)
	0.0294(3)	0.0425(4)	0.0369(3)	−0.0001(3)	0.0143(3)	0.0001(3)
	0.0354(7)	0.0525(11)	0.0444(8)	0.0000(8)	0.0171(6)	−0.0008(8)
Na2	0.01276(17)	0.01396(18)	0.01374(17)	−0.00024(13)	0.00564(14)	−0.00031(14)
	0.0309(3)	0.0418(4)	0.0390(3)	0.0020(3)	0.0150(3)	−0.0001(3)
	0.0393(7)	0.0491(10)	0.0472(8)	0.0022(8)	0.0196(6)	−0.0001(8)
C	0.0110(3)	0.0093(3)	0.0133(4)	−0.0032(3)	0.0046(3)	−0.0022(3)
	0.0257(4)	0.0259(4)	0.0298(4)	−0.0038(3)	0.0114(3)	−0.0035(3)
	0.0315(9)	0.0320(8)	0.0359(9)	−0.0056(7)	0.0150(8)	−0.0052(7)
O1	0.0141(3)	0.0144(4)	0.0181(3)	0.0012(2)	0.0080(3)	−0.0006(3)
	0.0363(8)	0.0421(10)	0.0448(8)	0.0013(6)	0.0189(7)	−0.0007(7)
	0.046(2)	0.048(2)	0.055(2)	0.0020(16)	0.0226(18)	−0.0010(16)
O2	0.0155(3)	0.0134(3)	0.0159(3)	−0.0001(2)	0.0067(3)	0.0002(3)
	0.0365(8)	0.0416(9)	0.0422(7)	−0.0002(6)	0.0183(7)	0.0013(6)
	0.0422(18)	0.054(2)	0.0483(18)	−0.0022(15)	0.0229(16)	−0.0001(14)
O3	0.0166(3)	0.0154(3)	0.0164(3)	−0.0010(3)	0.0091(3)	−0.0016(3)
	0.0369(8)	0.0456(10)	0.0451(8)	0.0031(6)	0.0230(7)	−0.0003(6)
	0.047(2)	0.059(2)	0.0509(19)	0.0072(15)	0.0274(16)	0.0015(15)
O4	0.0163(3)	0.0164(3)	0.0170(3)	−0.0008(3)	0.0094(3)	−0.0018(3)
	0.0388(8)	0.0475(10)	0.0453(9)	−0.0002(6)	0.0238(7)	−0.0043(6)
	0.045(2)	0.054(2)	0.057(2)	−0.0028(15)	0.0308(16)	−0.0057(15)
O5	0.0148(3)	0.0159(3)	0.0162(3)	0.0012(3)	0.0082(3)	0.0023(3)
	0.0369(7)	0.0470(9)	0.0455(8)	0.0004(7)	0.0208(7)	0.0018(6)
	0.0440(18)	0.060(2)	0.0499(19)	−0.0001(18)	0.0201(16)	0.0001(16)
O6	0.0146(3)	0.0176(3)	0.0156(3)	0.0004(3)	0.0077(3)	0.0000(3)
	0.0339(7)	0.0477(9)	0.0414(7)	−0.0031(7)	0.0190(6)	0.0002(6)
	0.0410(17)	0.054(2)	0.0490(17)	−0.0012(16)	0.0240(15)	0.0011(14)
O7	0.0178(3)	0.0159(3)	0.0179(3)	0.0008(3)	0.0098(3)	0.0029(3)
	0.0427(8)	0.0461(10)	0.0488(8)	0.0022(7)	0.0246(7)	0.0070(7)
	0.0540(18)	0.056(3)	0.056(2)	0.0023(17)	0.0296(16)	0.0052(16)
O8	0.0179(4)	0.0154(3)	0.0183(3)	−0.0001(3)	0.0082(3)	0.0009(3)
	0.0409(8)	0.0457(10)	0.0458(8)	−0.0002(7)	0.0188(7)	0.0008(7)
	0.0456(16)	0.053(2)	0.0546(19)	0.0013(16)	0.0218(15)	0.0012(15)
O9	0.0173(3)	0.0175(4)	0.0194(4)	−0.0041(3)	0.0047(3)	0.0000(3)
	0.0392(7)	0.0475(9)	0.0542(9)	−0.0084(7)	0.0125(7)	−0.0044(7)
	0.0472(15)	0.058(2)	0.065(2)	−0.0071(16)	0.0197(15)	−0.0048(16)
O10	0.0182(4)	0.0184(4)	0.0265(4)	−0.0084(3)	0.0114(3)	−0.0063(3)
	0.0445(7)	0.0493(9)	0.0641(10)	−0.0175(8)	0.0248(7)	−0.0131(7)
	0.0520(16)	0.062(2)	0.072(2)	−0.0207(18)	0.0284(15)	−0.0149(17)
O11	0.0132(3)	0.0172(3)	0.0155(3)	−0.0003(2)	0.0074(2)	0.0021(2)
	0.0327(11)	0.0560(19)	0.0366(14)	0.0008(14)	0.0177(10)	0.0083(12)
	0.042(4)	0.085(5)	0.045(5)	0.009(4)	0.026(3)	0.012(3)

(*continued*)

Table 3 (*continued*)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O12	0.0187(3)	0.0242(3)	0.0194(3)	0.0068(2)	0.0122(3)	0.0053(2)
	0.0497(15)	0.065(3)	0.0502(13)	0.0153(14)	0.0316(11)	0.0141(14)
	0.056(5)	0.073(7)	0.063(4)	0.023(4)	0.038(3)	0.013(4)
O13	0.0160(3)	0.0285(3)	0.0147(3)	0.0055(3)	0.0050(2)	0.0088(3)
	0.0356(16)	0.086(3)	0.041(2)	0.021(2)	0.0115(14)	0.012(2)
	0.037(4)	0.067(6)	0.038(4)	0.008(4)	0.007(3)	0.017(4)
Q1	–	–	–	–	–	–
	0.057(11)	0.068(17)	0.020(8)	−0.026(8)	0.012(7)	0.018(9)
	0.10(2)	0.048(18)	0.030(13)	−0.028(10)	0.010(11)	0.013(12)
Q2	–	–	–	–	–	–
	0.024(4)	0.073(6)	0.038(4)	−0.004(4)	0.013(3)	0.018(3)
	0.023(6)	0.111(13)	0.055(11)	−0.012(9)	0.007(6)	0.024(6)
Q3	–	–	–	–	–	–
	0.043(7)	0.078(14)	0.027(5)	0.034(6)	0.028(5)	0.045(7)
	0.067(16)	0.08(2)	0.020(8)	0.014(9)	0.025(8)	0.045(12)
Q4	–	–	–	–	–	–
	0.043(4)	0.111(9)	0.061(6)	0.040(6)	0.023(3)	0.039(5)
	0.054(9)	0.123(17)	0.069(13)	0.034(12)	0.029(7)	0.043(9)
Q5	–	–	–	–	–	–
	0.050(4)	0.094(10)	0.033(3)	−0.010(3)	0.013(2)	0.014(4)
	0.060(6)	0.120(18)	0.047(6)	−0.013(6)	0.026(4)	0.015(7)
Q6	–	–	–	–	–	–
	0.071(8)	0.089(11)	0.096(12)	−0.032(8)	0.011(6)	0.033(7)
	0.089(12)	0.170(19)	0.096(19)	−0.064(14)	0.010(9)	0.070(11)
Q7	–	–	–	–	–	–
	0.037(4)	0.031(4)	0.047(5)	0.007(3)	0.011(4)	0.009(3)
	0.073(8)	0.041(9)	0.059(10)	0.029(7)	0.046(8)	0.037(6)

only the CO_3 group plus four H atom sites (H14, H16, H18, H20) contradict a centrosymmetric arrangement.

Investigation of the two NaO_6 octahedra shows quite similar Na–O distances between 2.39 and 2.45 Å (Na1) or 2.47 Å (Na2) and thus might suggest almost centrosymmetric behavior. However, a closer look at single Na–O bonds reveals the deviation towards a non-centrosymmetric geometry. For example, even if the pairs Na1/Na2 and O3/O4 have almost centrosymmetric fractional coordinates (a hypothetical center of symmetry is assumed at the origin), the Na2–O3 distance of 2.41 Å is among the three shortest bonds of the Na2 polyhedron, whereas Na1–O4 with a distance of 2.45 Å is the longest bond in the Na1 octahedron. In general, the Na–O distances are well within the range of Na–O bonds in other sodium carbonate (hydrate) minerals. Whereas the bond lengths of 2.39–2.47 Å in natron (this paper) are equal in nahcolite (*Sharma*, 1965) and almost equal (2.36–2.45 Å) in trona (*Choi* and *Mighell*, 1982; *Pertlik*, 1986), they show wider scattering in thermonatrite with 2.30–2.57 Å (*Wu* and *Brown*, 1975), in wegscheiderite with

Table 4. *Anisotropic displacement parameters U_{ij} with e.s.d.'s in parentheses of the atoms of the (disordered) carbonate groups in natron at 110/270/295 K (in consecutive rows)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C	0.0110(3)	0.0093(3)	0.0133(4)	−0.0032(3)	0.0046(3)	−0.0022(3)
	0.0257(4)	0.0259(4)	0.0298(4)	−0.0038(3)	0.0114(3)	−0.0035(3)
	0.0315(9)	0.0320(8)	0.0359(9)	−0.0056(7)	0.0150(8)	−0.0052(7)
O11	0.0132(3)	0.0172(3)	0.0155(3)	−0.0003(2)	0.0074(2)	0.0021(2)
	0.0327(11)	0.0560(19)	0.0366(14)	0.0008(14)	0.0177(10)	0.0083(12)
	0.042(4)	0.085(5)	0.045(5)	0.009(4)	0.026(3)	0.012(3)
O12	0.0187(3)	0.0242(3)	0.0194(3)	0.0068(2)	0.0122(3)	0.0053(2)
	0.0497(15)	0.065(3)	0.0502(13)	0.0153(14)	0.0316(11)	0.0141(14)
	0.056(5)	0.073(7)	0.063(4)	0.023(4)	0.038(3)	0.013(4)
O13	0.0160(3)	0.0285(3)	0.0147(3)	0.0055(3)	0.0050(2)	0.0088(3)
	0.0356(16)	0.086(3)	0.041(2)	0.021(2)	0.0115(14)	0.012(2)
	0.037(4)	0.067(6)	0.038(4)	0.008(4)	0.007(3)	0.017(4)
Q1	–	–	–	–	–	–
	0.057(11)	0.068(17)	0.020(8)	−0.026(8)	0.012(7)	0.018(9)
	0.10(2)	0.048(18)	0.030(13)	−0.028(10)	0.010(11)	0.013(12)
Q2	–	–	–	–	–	–
	0.024(4)	0.073(6)	0.038(4)	−0.004(4)	0.013(3)	0.018(3)
	0.023(6)	0.111(13)	0.055(11)	−0.012(9)	0.007(6)	0.024(6)
Q3	–	–	–	–	–	–
	0.043(7)	0.078(14)	0.027(5)	0.034(6)	0.028(5)	0.045(7)
	0.067(16)	0.08(2)	0.020(8)	0.014(9)	0.025(8)	0.045(12)
Q4	–	–	–	–	–	–
	0.043(4)	0.111(9)	0.061(6)	0.040(6)	0.023(3)	0.039(5)
	0.054(9)	0.123(17)	0.069(13)	0.034(12)	0.029(7)	0.043(9)
Q5	–	–	–	–	–	–
	0.050(4)	0.094(10)	0.033(3)	−0.010(3)	0.013(2)	0.014(4)
	0.060(6)	0.120(18)	0.047(6)	−0.013(6)	0.026(4)	0.015(7)
Q6	–	–	–	–	–	–
	0.071(8)	0.089(11)	0.096(12)	−0.032(8)	0.011(6)	0.033(7)
	0.089(12)	0.170(19)	0.096(19)	−0.064(14)	0.010(9)	0.070(11)
Q7	–	–	–	–	–	–
	0.037(4)	0.031(4)	0.047(5)	0.007(3)	0.011(4)	0.009(3)
	0.073(8)	0.041(9)	0.059(10)	0.029(7)	0.046(8)	0.037(6)

2.29–2.56 Å (*Fernandes* et al., 1990), and in natrite with 2.31–2.67 Å (*van Aalst* et al., 1976).

A closer investigation of the carbonate group reveals regular distances (1.279–1.290 Å) and angles (119.8–120.1°) at 110 K. The aplanarity of the CO_3 group, i.e. the distance d of the central carbon atom from the plane defined by the three O atoms, amounts to only 0.006(1) Å and is therefore within the range of usual carbonates ($d \leq 0.03$ Å, *Zemann*, 1981). The very low d value, compared to

Table 5. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses for natron at 110/270/295 K (in consecutive rows)*

Na1–O7	2.3892(8)	Na2–O4	2.3907(8)	C–O12	1.2790(11)
	2.3997(17)		2.4004(16)		1.288(4)
	2.408(4)		2.396(3)		1.305(9)
Na1–O2	2.3933(8)	Na2–O8	2.4018(8)	C–O13	1.2865(12)
	2.4037(16)		2.4252(17)		1.258(5)
	2.409(3)		2.424(4)		1.243(10)
Na1–O3	2.4015(8)	Na2–O3	2.4099(8)	C–O11	1.2897(12)
	2.4069(16)		2.4145(16)		1.283(5)
	2.413(3)		2.429(3)		1.308(13)
Na1–O10	2.4166(9)	Na2–O1	2.4100(8)	O12–C–O13	119.77(9)
	2.422(2)		2.4225(17)		122.0(3)
	2.425(4)		2.418(4)		122.5(7)
Na1–O6	2.4353(8)	Na2–O9	2.4485(9)	O12–C–O11	120.08(9)
	2.4543(15)		2.458(2)		117.0(3)
	2.457(3)		2.457(4)		115.5(8)
Na1–O4	2.4511(8)	Na2–O5	2.4676(8)	O13–C–O11	120.14(8)
	2.4466(15)		2.4688(16)		119.3(3)
	2.427(3)		2.466(3)		116.0(9)

Table 6. *The hydrogen bond system in natron at 110/270/295 K (in consecutive rows). Distances in (Å), angles in (°), D = donor, A = acceptor, H–D–H = angle of the H_2O molecule, e.s.d.'s in parentheses*

D–H···A	D–H	H···A	D–A	D–H–A	H–D–H
O1–H1···O6	0.813(17)	1.953(17)	2.7652(11)	176.9(17)	103.1(16)
	0.76(2)	2.04(2)	2.799(2)	174(2)	106(3)
	0.76(3)	2.07(3)	2.817(5)	172(3)	101(4)
O1–H2···O13	0.822(16)	1.951(16)	2.7640(11)	170.2(13)	
	0.735(19)	2.002(19)	2.707(5)	161(2)	
	0.72(3)	2.06(3)	2.732(11)	155(4)	
O2–H3···O11	0.937(19)	1.818(19)	2.7462(11)	170.0(18)	107.4(18)
	0.82(3)	1.95(3)	2.744(5)	163(3)	104(3)
	0.86(4)	1.90(4)	2.732(13)	163(5)	114(6)
O2–H4···O5	0.800(17)	1.979(18)	2.7706(11)	170.6(16)	
	0.87(3)	1.94(3)	2.800(2)	173(3)	
	0.83(4)	1.99(4)	2.801(5)	165(5)	
O3–H5···O11	0.803(18)	2.166(18)	2.9634(10)	172.0(16)	103.0(15)
	0.81(3)	2.29(3)	3.067(5)	160(3)	101(3)
	0.81(4)	2.34(6)	3.047(12)	148(9)	125(7)
O3–H6···O1	0.787(14)	2.002(14)	2.7739(10)	167.0(14)	
	0.75(2)	2.05(2)	2.793(2)	169(2)	
	0.79(4)	2.02(4)	2.782(4)	161(6)	

(*continued*)

Table 6 (*continued*)

D–H···A	D–H	H···A	D–A	D–H–A	H–D–H
O4–H7···O2	0.90(2)	1.88(2)	2.7857(10)	176.7(18)	101.7(16)
	0.86(3)	1.95(3)	2.792(2)	168(3)	107(3)
	0.80(3)	2.02(3)	2.808(4)	170(3)	103(3)
O4–H8···O13	0.870(16)	2.184(17)	3.0239(11)	162.2(14)	
	0.83(2)	2.59(2)	3.392(7)	163(2)	
	0.82(2)	2.81(3)	3.563(15)	153.5(19)	
O5–H9···O12	0.884(17)	1.905(17)	2.7791(10)	170.1(16)	102.5(16)
	0.85(3)	1.99(3)	2.806(3)	160(3)	106(3)
	0.87(4)	1.98(4)	2.821(9)	161(6)	103(5)
O5–H10···O13	0.748(19)	2.108(19)	2.8384(10)	165.5(18)	
	0.738(19)	2.026(19)	2.728(6)	159(2)	
	0.73(2)	1.99(3)	2.671(11)	155(3)	
O6–H11···O11	0.824(17)	1.965(17)	2.7746(10)	167.2(15)	106.4(16)
	0.730(19)	2.08(2)	2.776(5)	161(2)	102(3)
	0.75(3)	2.01(3)	2.741(12)	164(3)	109(4)
O6–H12···O12	0.827(19)	1.962(19)	2.7883(11)	177.9(17)	
	0.82(3)	2.07(3)	2.882(4)	171(3)	
	0.80(4)	2.13(4)	2.921(11)	169(5)	
O7–H13···O13	0.839(17)	1.964(17)	2.7777(10)	163.1(15)	106.0(13)
	0.81(2)	2.03(2)	2.824(6)	166(2)	109(2)
	0.74(3)	2.16(3)	2.877(14)	164(4)	113(4)
O7–H14···O8	0.855(14)	1.916(14)	2.7628(8)	170.2(12)	
	0.804(16)	1.995(17)	2.7893(11)	169.5(16)	
	0.80(2)	2.01(2)	2.7924(19)	167(2)	
O8–H15···O12	0.883(17)	1.891(17)	2.7679(10)	171.9(15)	104.4(14)
	0.79(3)	2.00(3)	2.770(5)	166(3)	105(3)
	0.86(3)	1.92(4)	2.746(12)	160(5)	100(4)
O8–H16···O10	0.793(16)	2.003(16)	2.7929(12)	174.2(15)	
	0.814(17)	2.008(17)	2.820(3)	175.6(16)	
	0.83(2)	1.99(2)	2.822(5)	174(2)	
O9–H17···O11	0.91(2)	1.91(2)	2.8182(11)	174.8(17)	104.8(15)
	0.79(3)	2.14(4)	2.877(5)	156(4)	113(3)
	0.77(4)	2.37(4)	2.952(13)	133(4)	109(4)
O9–H18···O7	0.841(16)	1.934(17)	2.7748(12)	179.0(16)	
	0.789(19)	2.001(19)	2.789(2)	178.2(19)	
	0.78(3)	2.01(3)	2.792(6)	179(3)	
O10–H19···O13	0.75(2)	2.39(2)	3.1109(12)	160.6(18)	103.5(18)
	0.77(3)	2.35(3)	3.054(7)	153(2)	102(3)
	0.78(3)	2.34(4)	3.001(13)	144(4)	92(3)
O10–H19···O12	-”-	2.47(2)	3.1074(11)	143.9(17)	
	-”-	2.45(3)	3.096(5)	142(3)	
	-”-	2.41(4)	3.081(13)	145(4)	
O10–H20···O9	0.785(17)	1.946(18)	2.7314(9)	180(2)	
	0.78(2)	1.99(2)	2.7548(14)	170(2)	
	0.77(2)	2.00(2)	2.763(2)	173(3)	

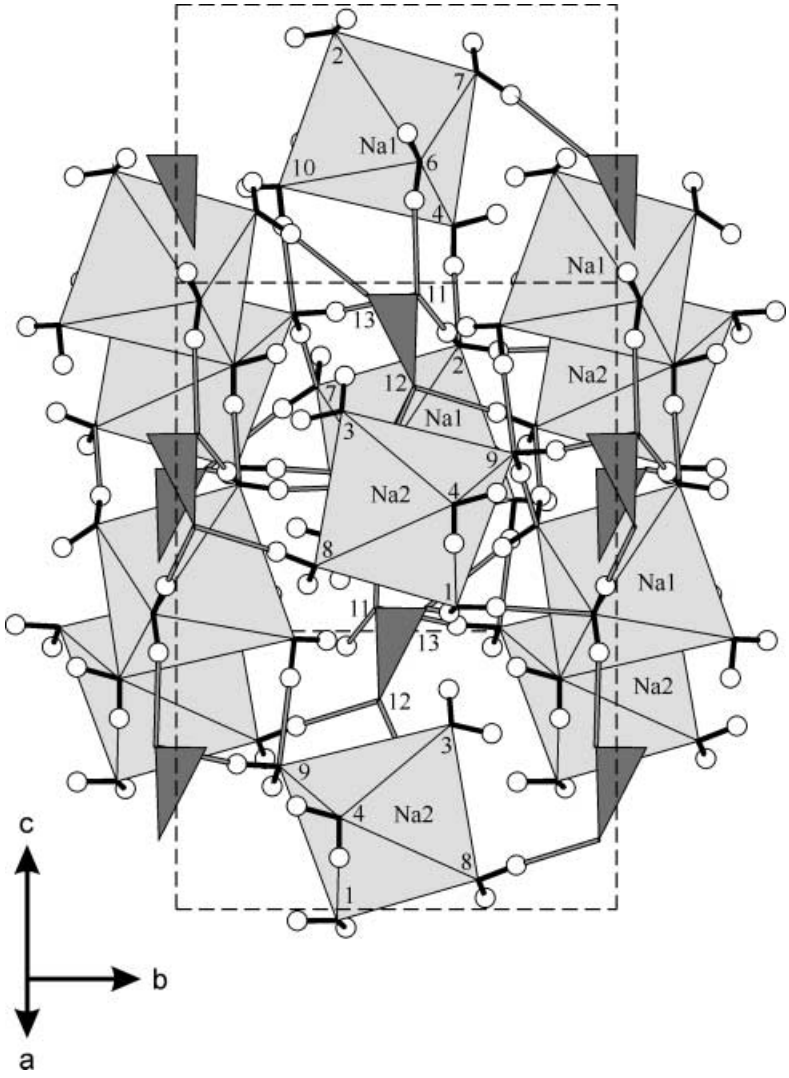

Fig. 1. The crystal structure of natron at 110 K in a projection parallel to a^* onto the (100) plane. Small spheres represent hydrogen atoms, hydrated Na octahedra and CO_3 groups are plotted as polyhedra. Bold lines are O–H bonds, whereas grey lines indicate H · · · O bonds. Numbers denote the different oxygen atom sites

aplanarities of up to 0.06 Å in some particular carbonate minerals (*Winkler* et al., 2000), is in agreement with the rather regular environment around the CO_3 group in natron.

The hydrogen bond system in the ordered low-temperature structure of natron is characterized by shortest donor–acceptor distances between 2.73 and 3.11 Å (Table 6). The H bonds connect mutually between O atoms of two sodium octahedra, and between Na polyhedra and carbonate groups. It is interesting to note that the H bonds are divided into a group with rather short distances of 2.73–2.84 Å (17 strong H bonds) and one with long distances of 2.96–3.11 Å (4 weak H bonds). Moreover, every O atom of the carbonate group (O11, O12,

O13) is acceptor for at least three short H bonds and a long one. By this multiple network of H bonds the structural building blocks, i.e. NaO_6 octahedra and carbonate groups, are held together. The hydrogen bond angles (D–H–A) are generally straight (160–180°), except for the second (long) bond of the H19 atom (O10–H19 $\cdots$ O12) where it amounts to only 144°. The O–H bond lengths (unconstrained during the low-temperature refinements) appear shorter (0.75–0.91 Å) than the true bond lengths (around 0.98 Å) in water molecules (*Franks*, 1973), but due to the fact that X-rays locate the shifted electron pairs rather than nuclei of H atoms, they show the usual values expected from X-ray refinements (*Lager* et al., 1987). For the same reason, an average value of 0.80(5) Å was assumed as an O–H distance restraint during the 270 and 295 K refinements of the disordered structures.

The disordered crystal structure of natron at 270 and 295 K

Refinements of the 270/295 K X-ray data sets using the 110 K atom positions as starting values lead to unsatisfactory agreement (R) values. Moreover, difference Fourier maps showed additional remaining density maxima in the vicinity of the C atoms. In addition, the sites of the carbonate O atoms (O11, O12, O13) were obviously not fully occupied. The distances between the remaining density maxima and the carbon atom were between 1.19 and 1.35 Å, thus suggesting additional oxygen positions of a disordered carbonate group. Therefore, seven density maxima, labeled Q1 to Q7, were included in the final refinement with unconstrained s.o.f.'s for Q1 to Q7 and restrained s.o.f.'s for O11, O12, O13 (for details see ''Experimental''). By this method, R values of 2.5 and 3.5% at 270/295 K were obtained.

The final results show that the conventional (low-temperature) oxygen positions O11, O12, O13 of the CO_3 group are occupied to only 60% (at 270 K) and 46% (at 295 K). The additional oxygen atom positions Q1 to Q7 are occupied between 8% (Q1 at 270 K) and 34% (Q5, Q6 at 295 K). Analysis of the positions and Q–C–Q angles of the Q sites provides strong evidence for at least two additional, dynamic positions of the CO_3 molecule. Approximately centrosymmetric positions to O11, O12, O13 are observed in Q2, Q3, Q4. However, as indicated by Q3, this position is occupied to only 12/15% at 270/295 K. The low site occupancy is in disagreement with the higher s.o.f.'s of Q2 and Q4 (average 21% at 270 K and 27% at 295 K). Inspection of Fig. 2 shows that Q2 and Q4 may be completed to a triangular molecule also by Q1 (in addition to Q3) which also shows a very low s.o.f., i.e. 8/12% at 270/295 K. Thus, Q1 and Q3 complete the Q2 and Q4 positions to two slightly different CO_3^{2-} positions. This model is confirmed (within e.s.d.'s) by the fact that the s.o.f. sum of Q1 + Q3 equals the average s.o.f. of Q2 and Q4, i.e. (Q2 + Q4)/2 (see also Table 2). Another CO_3^{2-} orientation is observed in the density maxima Q5, Q6, Q7 which are occupied to an average of 24/31% at 270/295 K.

However, as the large anisotropic displacement parameters (Table 4) show, there is considerable dynamic/positional disorder at ambient temperatures. The smeared probability ellipsoids of O11 to O13 and Q1 to Q7 in Fig. 2 suggest a dynamic motion or a positional disorder of the carbonate ion about its center of

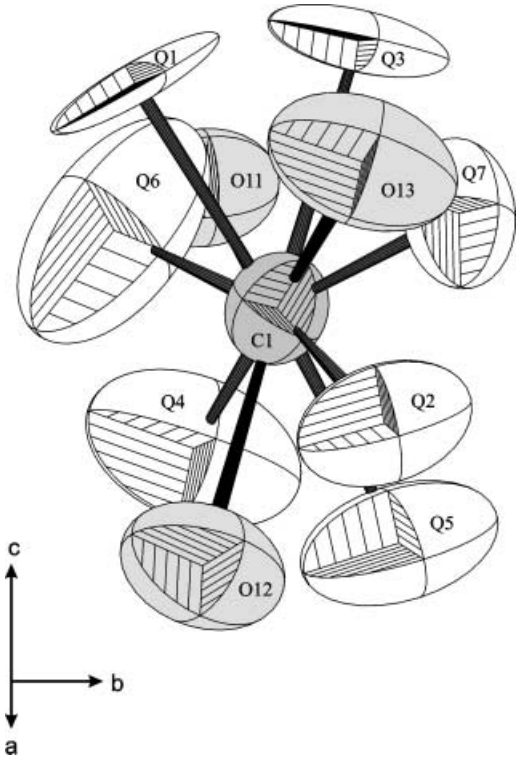

Fig. 2. The disordered CO_3 group at 270 K in the structure of natron. Shaded ellipsoids represent the position of the ordered CO_3 molecule (O11/O12/O13) in the low-temperature structure. Additional CO_3 orientations are Q2/Q3/Q4, Q2/Q1/Q4, and Q5/Q6/Q7

gravity, i.e. about the C atom, which shows a rather isotropic appearance even at 295 K (though increasing in ADPs). Even if disordered and only partially occupied, the distances of the oxygen atoms of the carbonate groups to the surrounding oxygen atoms of the hydrated Na octahedra are larger than 2.67(1) Å, except for Q7–O7 which amounts to 2.62(1) Å (270 K) and 2.57(1) Å (295 K). These distances are well within the range of usual strong hydrogen bonds.

The transition from the ordered to the disordered structure

The X-ray refinements at 110/270/295 K indicate that the carbonate molecules in the structure of natron change from an ordered static position at low temperatures to a partially dynamic/disordered behavior at ambient conditions. These changes do not result in a change of space group symmetry. In order to further investigate this peculiar behavior, the optical retardation (as a function of birefringence) of polished single-crystal plates of natron was pursued between 80 K and dehydration in the cooling stage at around 280 K. The applied technique is very sensitive to phase transitions and is described in detail by *Libowitzky* and *Armbruster* (1995). Because of decomposition of the plates under ambient conditions neither the exact thickness nor the orientation of the slabs could be determined. Nevertheless, it should be emphasized that the relative changes in retardation are sufficient to characterize the transition behavior.

Instead of a discontinuity or a break at a certain temperature (indicative for a phase transition), a peculiar, continuously changing slope and curvature of the retardation curves are obtained (Fig. 3). The retardation (equivalent to

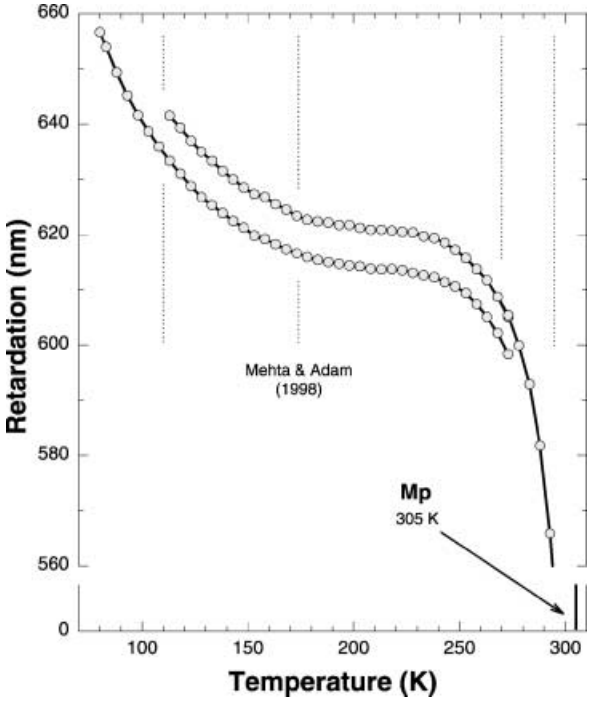

Fig. 3. Optical retardation in a single-crystal of natron vs. temperature. The two curves result from two measurement cycles that were averaged and merged from at least four single curves, each. The melting point (Mp) of natron at 305 K and the temperatures of single-crystal X-ray refinements are also indicated

birefringence) decreases with a decreasing negative slope from 80 K towards a saddle point at around 220 K. Then it continues to decrease with an increasing negative slope until it dehydrates and becomes turbid. Nevertheless, it is evident that the retardation curve decreases further towards the melting point (305 K), above which, as a matter of fact, the birefringence must be zero. The observed saddle region in the curves may well indicate a temperature range where the dynamic behavior of the carbonate groups starts, but it does not indicate a definite transition of a thermodynamic first order, tricritical, or second order type. The paper of *Mehta* and *Adam* (1998) also confirms that the structure is still ordered at 173 K which is closely below the saddle region.

Analogous results were obtained from temperature-dependent molecular spectroscopy investigations. Infrared absorption overtone spectra of a natron single-crystal indicated only a smooth, linear change of band positions and peak widths with changing temperature. A similar temperature-dependent behavior was found in peak centers and half widths of Raman spectra of a natron single-crystal. Finally, a differential scanning calorimetry also resulted in a smooth curve without any indication of a phase transition.

Therefore, a continuous change without transition in space group symmetry from the ordered low-temperature form of natron to the partly disordered structure at ambient conditions is the most convenient description. Moreover, as the $[Na_2(H_2O)_{10}]^{2+}$ units and the CO_3^{2-} molecules are held together only by hydrogen bonds, and as these H bonds are successively distorted and broken with increasing dynamics of the carbonate groups, 100% disorder are equivalent with the melting point of natron at 305 K. It is assumed that the melt (equivalent to a concentrated aqueous solution in its own crystal water) contains hydrated sodium atoms and

carbonate groups, and thus, similar building units as the solid natron crystal. Because 40% disorder were observed at 270 K, and 54% at 295 K, the remaining 46% order must be abandoned within only 10 K. This increasing rate of disorder may well account for the exponential decrease of the birefringence curve above 270 K. From another point of view, the observed crystal structures of natron with disordered carbonate groups at 270 and 295 K represent just an intermediate state between the melt at 305 K and the perfectly ordered structure at low temperatures.

A conclusive answer to the question why the low-temperature structure of natron is ordered in a non-centrosymmetric way even though the surrounding structure is almost centrosymmetric cannot be given. A few arguments, however, may be obtained from an investigation of the hydrogen bond system as sketched in Fig. 4. This figure shows only the strong H bonds with donor–acceptor distances between 2.73 and 2.84 Å. The critical point is that 10 H_2O molecules, i.e. 5 O atoms and their (almost) centrosymmetric counterparts, have to form H bonds to 3 O atoms of the carbonate group. This cannot be achieved in a regular centrosymmetric way and must lead to distortion of the ideal centrosymmetric arrangement of the surrounding structure. The left part of Fig. 4 confirms the centrosymmetric donation of H bonds towards the carbonate group, whereas the right part (O7, O8, O9, O10 and H14, H16, H17, H18, H19, H20) shows a non-symmetric H bonding scheme. The most evident observation is that O9 forms a strong H bond towards the CO_3 group (via H17), whereas O10 (via H19) does not show an equivalent bond. Moreover, the mutual hydrogen bonding between the hydrated $Na_2(H_2O)_{10}$ units is centrosymmetric in the left part of Fig. 4 and not symmetric in the right part.

At higher temperatures the thermal motion of the carbonate groups and the surrounding lattice may lead to dynamic disorder, however, a regular distribution

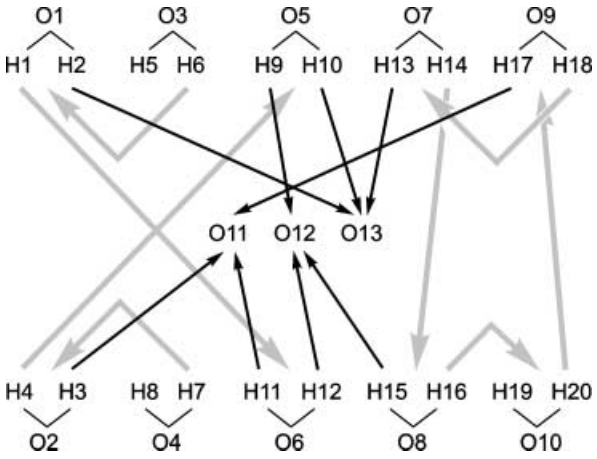

Fig. 4. Schematic drawing of the strong hydrogen bonds in natron with donor–acceptor distances of 2.73–2.84 Å. The bottom row sequence of H_2O molecules represents the centrosymmetric equivalents of the upper row (see the note of Table 2). The three O atoms of the CO_3 group in the center of the drawing accept each three strong H bonds (black arrows). H bonds between the hydrated Na polyhedra are represented by grey arrows. Note the break of centrosymmetry right from the line H13–H15

of 9 strong H bonds between 10 donors and 3 acceptors is still not possible (disorder over two centrosymmetrically equivalent CO_3 positions is observed to only $\sim 10\%$ – see above). The disorder of the anion groups at room temperature might suggest replacement of the CO_3 group by other, more spherical, 2-valent anion groups, such as sulphate tetrahedra, resulting in a similar structure. ''Glauber's salt'', mirabilite, $Na_2SO_4 \cdot 10H_2O$ also shows (librational) disorder of the anion groups at room temperature (*Levy* and *Lisensky*, 1978). The structure, however, is different from that of natron. It contains infinite chains of edge-sharing hydrated Na octahedra that are interconnected by sulphate groups and separate H_2O molecules. The difference in the structures may be caused by the considerably larger anion size of the SO_4 group compared to that of CO_3.

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