position n'est plus stériquement possible. Deux possibilités peuvent alors être envisagées:

– la rangée du plan densifié se place et reste en position notée 1 à la Fig. 6(b) et alors le phénomène de densification ne peut plus se poursuivre.

– la rangée du plan densifié vient en position notée 2, créant des tensions intolérables avec les anions voisins du même plan. Cette dernière difficulté peut cependant être levée par glissement de c/2 le long de Oz de la moitié droite de la structure, comme indiqué par les flèches de la Fig. 6(b), c'est à-dire par la création d'une paroi d'antiphase A. La densification peut alors se poursuivre sans problème comme le montre la Fig. 6(c). Ce glissement se reproduira évidemment périodiquement toutes les sept rangées fluorine. Il conduit aux phases de la famille (II).

Conclusions

UZr$_6$FO$_{14}$ constitue un nouvel et important exemple de structure vernier de type fluorine excédentaire en anions.

En application de l'élégant concept développé par Hyde et al. (1974) nous pouvons, s'en servant de base, construire l'ensemble des superstructures orthorhombiques observées dans le système.

Le comparaison avec les autres structures du même type connues, a permis de justifier quelques phénomènes apparemment surprenants, mais les explications fort simples fournies ne doivent, en raison de la rareté des données expérimentales, être considérées que comme de simples hypothèses. On peut cependant s'étonner, compte tenu de l'extrême souplesse du processus de densification mis en œuvre pour l'édification structurale de ces phases, qu'un aussi petit nombre d'entre elles aient été actuellement isolées. Nos efforts pour en synthétiser de nouvelles à base essentiellement de zirconium, élément s'adaptant particulièrement bien aux coordinences requises, se sont avérés jusqu'ici assez vains.

Nous tenons à remercier le Professeur R. Chevalier de l'Université de Clermont-Ferrand II pour l'aide précieuse qu'il nous a apportée lors de l'enregistrement et des corrections des intensités diffractées.

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Deformation Refinement of Sodium Perchlorate Monohydrate

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Abstract

The crystal structure of NaClO$_4$.H$_2$O has been refined with a deformation model. X-ray data were from Berglund, Thomas & Tellgren [*Acta Cryst.* (1975), B31, 1842–1846]. The deformation refinement with Hirshfeld-type deformation density functions gave $R_w(F^2) = 0.0325$ compared to 0.0642 for a conven-

tional refinement. The bias introduced by the bonding density is demonstrated by a shift (~0·02 Å) in the refined perchlorate O atom positions towards the Cl atom in the conventional refinement and by a shift (0·01 Å) in the water O position into the lone-pair region. The shifts in the positional parameters were up to 7σ. No significant changes were found for the thermal parameters. The results from the deformation refinements are compared with a neutron diffraction data refinement [Berglund, Tellgren & Thomas (1976). *Acta Cryst.* B**32**, 2444–2449].

Introduction

In a previous X-ray study of ammonium perchlorate (Lundgren, 1979*b*) the bias introduced by the bonding density in a conventional refinement was demonstrated by a shift in the refined O atom positions towards the Cl atom, *i.e.* the Cl—O distances were lengthened ~0·01 Å in a deformation refinement. The aim of the present study is to investigate whether the changes in the perchlorate-ion geometry observed for NH_4ClO_4 could also be observed in a deformation refinement of $NaClO_4.H_2O$. Good quality X-ray data for this compound were already available at this Institute (Berglund, Thomas & Tellgren, 1975; hereafter BTTX). Furthermore, a previous neutron diffraction study of the compound (Berglund, Tellgren & Thomas, 1976; hereafter BTTN) presented the possibility of comparing the geometries of the perchlorate ion derived from a deformation refinement and a neutron data refinement.

Structure refinement

All refinements were made by full-matrix least-squares techniques in space group $C2/c$ with *UPALS* and intensity data from BTTX. The function minimized was $\sum w(F_o^2 - k^2 F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$ was estimated from Poisson counting statistics and other random errors $[\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0·01F_o^2)^2]$. All reflexions were included in the calculations. Of the 1280 independent reflexions, 130 had $F_o^2 < 3\sigma(F_o^2)$; none of the F_o^2 were negative. Reflexions had been collected out to $\sin\theta/\lambda = 0·704$ Å^{-1}. Scattering factors for Cl^0, O^0, Na$^+$ and H^0 with anomalous-dispersion correction terms were taken from Ibers & Hamilton (1974). The programs used for all calculations with IBM 370/155, IBM 1800 and NORD-10 computers have been described by Lundgren (1979*a*).

Conventional refinement

A conventional refinement was made, starting with parameter values from BTTX. The refined parameters changed by <3σ compared with the BTTX refinement, except for the scale factor which changed by 7σ (2·2%). This may be attributed to the fact that the 12 reflexions which had earlier been rejected due to poor agreement with the corresponding F_c^2 values all had a positive $F_o^2 - F_c^2$ value. Some data concerning the refinement are given in Table 1 (series *A*); atomic parameters are given in Table 2. A δR plot of the data (Abrahams & Keve, 1971) is shown in Fig. 1(*a*).

Table 1. *Some data on the refinements*

A Conventional refinement.
B Deformation refinement, positional and thermal parameters (from ND) not varied.
C Deformation refinement, positional parameters (from ND) not varied.
D Deformation refinement.
E Deformation refinement, simple model.
$\Delta = (F_o^2 - F_c^2)$, $\sigma = \sigma(F_o^2)$.

	A	B	C	D	E
k (scale factor $\times F_c$)	1·0000 (24)*	0·9267 (20)	0·9898 (13)	0·9960 (30)	0·9886 (22)
g (isotropic extinction coefficient)	1·48 (20) × 10³	0·0	1·21 (12) × 10³	1·32 (12) × 10³	1·65 (16) × 10³
M (number of reflexions)	1280	1280	1280	1280	1280
N (number of refined parameters)	75	101	147	166	76
$s = [\sum w\Delta^2/(M - N)]^{1/2}$	3·722	3·982	2·510	1·963	2·762
$R = \sum|\Delta|/\sum F_o^2$	0·0333	0·0452	0·0224	0·0192	0·0284
$R_w = (\sum w\Delta^2/\sum wF_o^4)^{1/2}$	0·0642	0·0677	0·0419	0·0325	0·0475
Number of reflexions with $|\Delta/\sigma| > 4·0$	239	333	114	37	156
Maximum $|\Delta/\sigma|$	26·9	20·1	11·6	9·1	14·9
Charge ⎰ Na	+1·00	+0·32 (5)	+0·98 (3)	+1·00 (2)	+1·03 (3)
⎱ ClO_4	0·00	−1·03 (9)	−1·01 (7)	−1·02 (5)	−0·61 (4)
⎱ H_2O	0·00	+0·60 (9)	+0·04 (6)	+0·02 (5)	−0·40 (6)

* This scale factor is given the arbitrary value of 1·0. The scale factors for the deformation refinements are given in relation to this value.

Table 2. *Atomic coordinates* $(\times 10^5)$ *and anisotropic thermal parameters* $(\times 10^5 \text{ Å}^2)$

The form of the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]$. Parameters from the conventional refinement are given above parameters from the deformation refinement. The third line gives the difference between the parameters: $(p_1 - p_2)/|\sigma(p_1)^2 + \sigma(p_2)^2|^{1/2}$. The asphericity shift is the distance between the conventional and deformation refinement positions. The H parameters are from the neutron diffraction study.

	x	y	z	Aspherity shift (Å)	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	25000	25000	50000	—	3492 (44)	3285 (46)	3306 (42)	−83 (34)	822 (34)	−155 (33)
	25000	25000	50000		3435 (29)	3294 (28)	3256 (27)	−81 (18)	848 (19)	−166 (17)
				1·1	−0·2	1·0	−0·1	−0·6	0·3	
Na(2)	0	46611 (16)	25000	0·000 (1)	3873 (48)	3728 (48)	3476 (44)	0	1306 (37)	0
	0	46620 (9)	25000		3778 (30)	3684 (30)	3470 (28)	0	1314 (21)	0
		−0·5			1·7	0·8	0·1		−0·2	
Cl	12542 (2)	−2263 (6)	19333 (3)	0·000 (1)	3683 (20)	2577 (19)	2809 (19)	−184 (13)	1556 (14)	−348 (12)
	12538 (4)	−2268 (3)	19330 (3)		3703 (17)	2613 (17)	2839 (16)	−182 (8)	1565 (10)	−345 (7)
	0·7	0·6	0·7		−0·8	−1·4	−1·2	−0·1	−0·5	−0·2
O(1)	16772 (10)	−1612 (21)	33140 (11)	0·021 (3)	7438 (94)	4750 (79)	3019 (58)	−1256 (61)	535 (62)	−723 (48)
	16688 (21)	−1688 (42)	33245 (20)		7526 (98)	4702 (67)	3004 (60)	−1271 (60)	552 (58)	−724 (43)
	3·5	1·6	−4·5		−0·6	0·5	0·2	0·2	−0·2	0·0
O(2)	19364 (11)	−1157 (22)	13520 (17)	0·015 (4)	6739 (91)	5401 (85)	8336 (109)	−1159 (65)	5683 (88)	−1542 (67)
	19451 (24)	−1095 (50)	13505 (37)		7159 (95)	5523 (79)	8702 (116)	−1396 (68)	6047 (98)	−1829 (71)
	−3·3	−1·1	0·4		−3·2	−1·1	−2·3	2·5	−2·8	2·9
O(3)	6580 (10)	17928 (27)	15072 (13)	0·024 (4)	8278 (100)	5473 (86)	5916 (82)	3464 (78)	3187 (76)	1164 (66)
	6626 (26)	18312 (57)	15005 (30)		8270 (116)	5410 (87)	5993 (83)	3443 (87)	3177 (80)	1233 (67)
	−1·7	−6·1	2·0		0·0	0·5	−0·7	0·2	0·1	−0·7
O(4)	7517 (9)	−24329 (22)	15700 (11)	0·020 (3)	6524 (80)	4774 (78)	3981 (60)	−2799 (63)	2005 (59)	−1023 (52)
	7576 (19)	−24655 (45)	15713 (21)		6527 (85)	4619 (72)	4052 (55)	−2720 (65)	2043 (56)	−1042 (47)
	−2·8	6·5	−0·6		−0·0	1·5	−0·9	−0·9	−0·5	0·3
O(w)	37478 (8)	2313 (21)	5122 (10)	0·011 (2)	4418 (66)	4582 (72)	3726 (63)	−970 (50)	1000 (54)	311 (46)
	37485 (5)	2449 (30)	5058 (12)		4339 (49)	4577 (51)	3674 (41)	−1034 (33)	824 (39)	486 (37)
	−0·7	−3·7	4·1		1·0	0·1	0·7	1·1	2·7	−3·0
H(1)	32917	3269	−1963	−	8614	25320	5319	−5971	2718	2671
H(2)	35617	18245	6118	−	8689	4720	14150	−151	−1766	2059

Deformation refinements

The deformation functions suggested by Harel & Hirshfeld (1975) and Hirshfeld (1977) were used to describe the bonding density. The refinement procedure was the same as for NH_4ClO_4 (Lundgren, 1979b). Coordinates and anisotropic thermal parameters for the H atoms were, in all refinements, taken from BTTN, and were not varied. The large thermal ellipsoids for the H atoms, as obtained in BTTN, were later interpreted in terms of a dynamically disordered water molecule jumping between two distinct positions (Berglund & Tegenfeldt, 1977, 1979). However, the average positions, as determined in the diffraction experiment, were used for the present work. Gaussian-type deformation functions up to octupole terms were used. A single parameter $\gamma = 3 \cdot 5 \text{ Å}^{-2}$ governing the breadth of the deformation function was used for all atoms. This had earlier been found to be the best value for NH_4ClO_4. Symmetry constraints were introduced for functions centred on Na^+ (spherical), Cl and O(w) (*mm*) and H (cylindrical). Identical deformation functions were centred on the two independent Na^+ ions and on the two H atoms, respectively. The total number of refined deformation parameters was 99.

A neutron diffraction study should give the correct values for the positions of the atomic nuclei and for the thermal parameters, provided all systematic effects in the data set (extinction, thermal diffuse scattering, multiple scattering, *etc.*) have been taken care of in the data reduction, or have been included in the refined model. These neutron parameters can then be used in combination with X-ray data to produce $X–N$ deformation electron density maps of the structure (*e.g.* Fig. 2*f*). A deformation refinement would then be equivalent to finding the coefficients for the functions used to expand the densities observed in the $X–N$ maps.

A deformation refinement where positional and thermal parameters were taken from BTTN and kept fixed showed poor convergence (Table 1, series *B*). The extinction parameter refined to a negative value which was reset to zero in the program. As will be discussed later, the neutron thermal parameters differ from the X-ray thermal parameters from the conventional refinement. A deformation refinement where the thermal parameters were varied converged smoothly
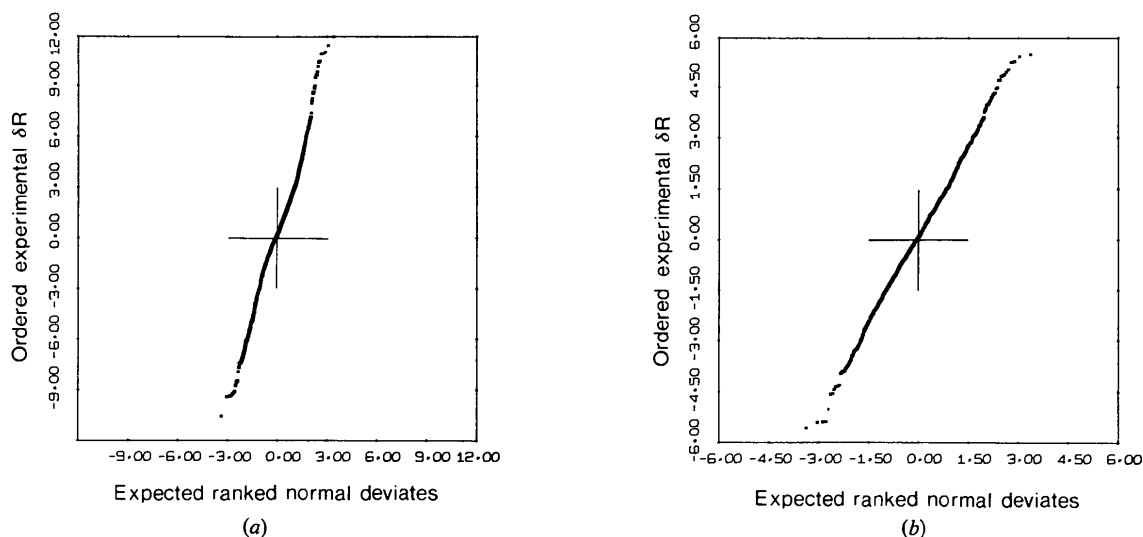
Fig. 1. Normal probability plots. (a) δR plot of the data following the conventional refinement. The slope of the least-squares line through the points is 3·18 and the y intercept is 0·25. The points for fourteen reflexions fall outside the plot range. (b) δR plot following the deformation refinement. The slope of the least-squares line through the points is 1·74 and the y intercept is 0·11. The points for seven reflexions fall outside the plot range. Note the different plot ranges used in (a) and (b).
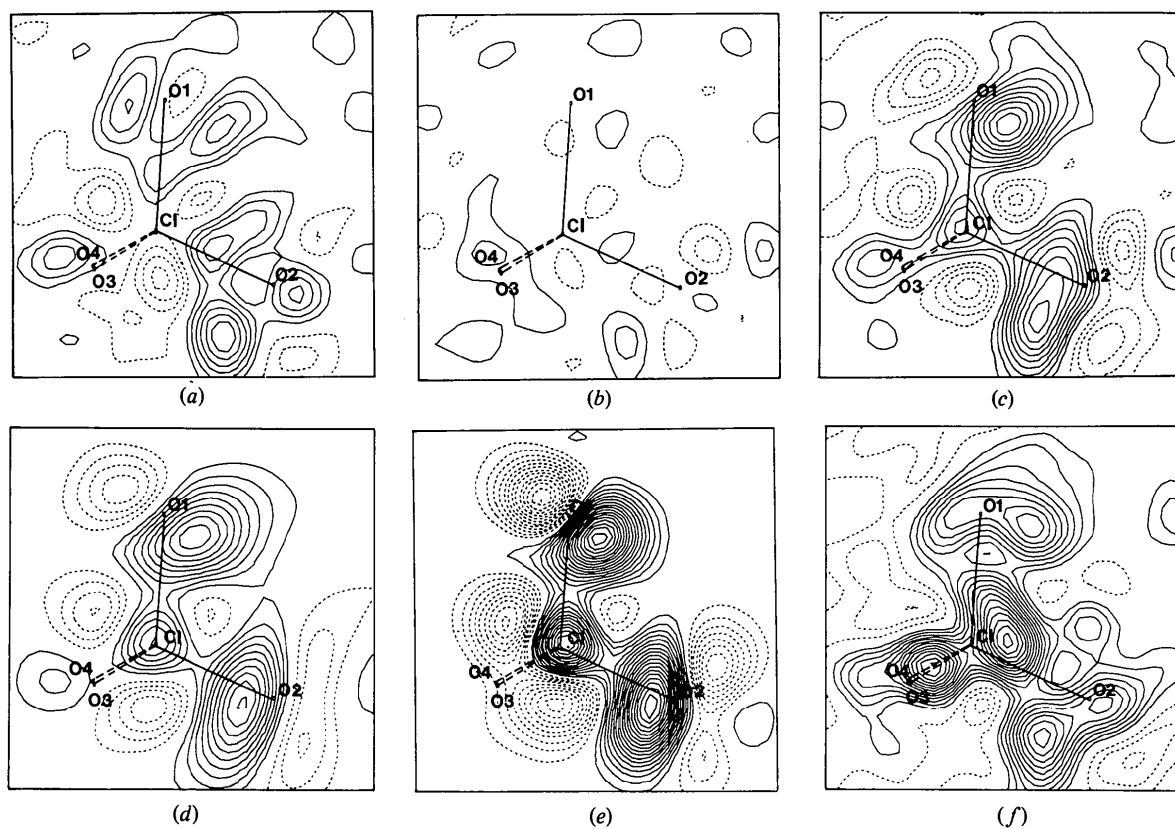

Fig. 2. ClO_4^-: residual and model maps. The maps are calculated in the plane through Cl, O(1) and O(2). Sections through Cl and other O atoms are very similar. Contours are drawn at intervals of 0·05 e Å^{-3}. Negative contours are dashed; the zero-level contour is omitted. All 1280 reflexions are included in the calculations. (a) Residual density: parameters from conventional refinement. (b) Residual density: parameters from deformation refinement. (c) Residual density: scale factor, positional and thermal parameters from deformation refinement. Deformation functions were not included in the structure factor calculation. (d) Dynamic model map, i.e. an F_c synthesis calculated with parameters from the deformation refinement but omitting the spherical free-atom form factors. (e) Static model map, i.e. a plot of the deformation functions. (f) X-N map.

Table 3. *Bond distances* (Å) *and angles* (°) *in the* ClO_4^- *ion*

A   X-ray data, conventional refinement.
D   X-ray data, deformation refinement.
E   X-ray data, deformation refinement (simple model).
N   Neutron data.

	A	D	E	N
Cl—O(1)	1·432 (1) [1·458]*	1·442 (2) [1·468]	1·435 (1) [1·462]	1·430 (2) [1·456]
—O(2)	1·422 (2) [1·444]	1·436 (4) [1·459]	1·427 (1) [1·450]	1·422 (2) [1·445]
—O(3)	1·423 (2) [1·453]	1·436 (3) [1·467]	1·428 (1) [1·460]	1·419 (2) [1·450]
—O(4)	1·430 (1) [1·448]	1·441 (3) [1·459]	1·433 (1) [1·452]	1·428 (2) [1·446]
O(1)—Cl—O(2)	110·15 (9)	110·65 (20)	110·48 (7)	110·15 (18)
O(1)—Cl—O(3)	109·46 (8)	109·26 (16)	109·25 (6)	109·59 (15)
O(1)—Cl—O(4)	108·69 (7)	108·01 (13)	108·66 (5)	108·59 (12)
O(2)—Cl—O(3)	108·62 (8)	107·89 (18)	108·36 (6)	108·35 (16)
O(2)—Cl—O(4)	109·31 (8)	109·07 (16)	109·29 (6)	109·13 (13)
O(3)—Cl—O(4)	110·61 (8)	111·97 (13)	110·80 (7)	111·02 (17)

* Distances corrected for thermal riding motion are given in square brackets.
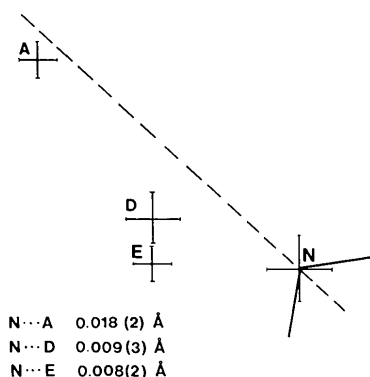

N···A 0.018 (2) Å
N···D 0.009 (3) Å
N···E 0.008 (2) Å

Fig. 3. The water O positions as obtained in the different refinements. N neutron data; A X-ray data, conventional refinement; D X-ray data, deformation refinement; E X-ray data, simple deformation model. The figure is drawn in the plane of the H_2O molecule as determined from the neutron data. The points A, D and E deviate by <0·003 (1) Å from this plane. The bisector of the H—O—H angle is indicated. The size of the cross represents the uncertainty of the position ($\pm 1\sigma$).

(Table 1, series C). However, a deformation refinement where the positional parameters were also varied resulted in a significant improvement in R_w (Table 1, series D). It is thus clear that the X-ray data fit better to a model where the positional and thermal parameters are different from those obtained from the neutron data, even if a full set of deformation functions is included in the refinement. The atomic coordinates and thermal parameters from the final cycle of series D are given in Table 2. A δR plot of the data is shown in Fig. 1(b). It may be noted that the deformation model completely accounts for the large $F_o^2 - F_c^2$ discrepancies which appeared for a number of low-order reflexions in the conventional refinement. It is thus a somewhat questionable procedure to remove any of them from a conventional refinement as was done in BTTX.

The deformation model used in the above three series of refinement was always the same. Since the refinement of redundant parameters should be avoided, a refinement with a simplified deformation model was also performed. In this, monopole functions were centred on each atom, in addition to dipole functions centred on Cl, O and H, and directed along the covalent bonds. The perchlorate O atoms were assumed to be identical. The refinement thus included only nine varied deformation parameters, but otherwise the same parameters as in series D. Data for the refinement are given in Table 1 (series E). The shifts of the perchlorate O atoms observed in refinement D (see below) were also observed here, and in the same directions but with smaller magnitudes (Table 3). The shift of the water O atom was almost the same as in series D (Fig. 3). The deformation model gave a neutral structure but the charges on the molecules were quite different from those found in series D. Although the more complete deformation model is obviously better than the simpler model (Table 1), this difference in charges suggests that the formal charges on the different molecules may also be model dependent when the deformation models are more similar than in the present case.

Results from the full deformation refinement (D) will be used in the following unless stated otherwise.

Results from the deformation refinement

The data given in Table 1, the δR plots (Fig. 1) and the residual maps (Fig. 2a,b) all indicate that the deformation model is more successful than the conventional spherical free-atom model in describing the observed structure factors. The inclusion of the deformation functions led to shifts in the atomic

parameters. Changes up to 6σ (0·02 Å) were observed in the positonal parameters for the O atoms; the changes in the thermal parametes were $\leq 3\sigma$ (0·0042 Å^2). For a detailed description of the bonding situation around Na$^+$ and ClO$_4^-$ see BTTX, and around H$_2$O see BTTN.

Na$^+$

The two independent Na$^+$ ions occupying special positions in the structure each have an approximately octahedral environment with Na$^+\cdots$O distances in the range 2·36–2·42 Å. No significant changes in the atomic parameters resulted from the deformation refinement as compared to the conventional refinement. The coefficient of the single spherical deformation function centred on these atoms was not significantly different from zero.

ClO$_4^-$

The bonding environment is rather similar for the four perchlorate O atoms. Each O atom is bonded to a Na$^+$ ion and is also weakly H bonded to a water molecule. All features exhibited by the perchlorate ion in the deformation refinement of NH$_4$ClO$_4$ (Lundgren, 1979b) are reproduced in the present case. The positional parameters obtained for the O atoms from the conventional refinement clearly show the bias introduced by the bonding density. Coordinates for O atoms from the deformation refinement give Cl–O distances ~0·01 Å longer than do coordinates from the conventional refinement. A difference map calculated with positional and thermal parameters from the deformation refinement (but not including the deformation functions) is shown in Fig. 2(c). This map should be compared with Fig. 2(a) where the O atoms have shifted towards Cl to give the best possible fit to the actual electron density distribution which is centred not exactly at the nuclear positions. The asphericity shifts of the atoms are given in Table 2. The angles Cl–O(conventional)–O(deformation) are 118 (8), 157 (15), 123 (9) and 122 (9)°.

As in NH$_4$ClO$_4$, no deformation density is observed in the lone-pair region of the O atoms (Fig. 2d,e).

As a check on the validity of the deformation refinement, a rigid-bond test (Hirshfeld, 1976) was applied to the Cl–O bonds (Table 4). This indicates that the relative vibrational motion of the Cl and O atoms is small in the direction of the bond and, even in the conventional refinement, not significantly different from zero. The same test applied to the neutron parameters indicates larger relative vibrational motion, both in absolute and relative magnitude.

It is puzzling that the deformation refinement, which should in principle give correct positional parameters for the atomic nuclei, does not give the same geometry

Table 4. *R.m.s. components* (Å) *of thermal motion of* Cl *and* O *along* Cl–O *bonds*

(a) Conventional refinement.
(b) Deformation refinement.
(c) Neutron data refinement.

$Z_{A,B}$ is the r.m.s. component of A in the direction of B.

		Cl–O(1)	Cl–O(2)	Cl–O(3)	Cl–O(4)
(a)	$Z_{Cl,O}$	0·1702 (6)	0·1673 (10)	0·1801 (5)	0·1638 (5)
	$Z_{O,Cl}$	0·1710 (17)	0·1670 (55)	0·1799 (26)	0·1656 (24)
	Δ	−0·0008 (18)	0·0003 (56)	0·0002 (26)	−0·0018 (25)
(b)	$Z_{Cl,O}$	0·1706 (5)	0·1681 (7)	0·1806 (4)	0·1645 (5)
	$Z_{O,Cl}$	0·1709 (17)	0·1690 (55)	0·1787 (29)	0·1646 (24)
	Δ	−0·0003 (18)	−0·0009 (55)	0·0019 (29)	−0·0001 (25)
(c)	$Z_{Cl,O}$	0·1648 (14)	0·1602 (25)	0·1681 (13)	0·1492 (15)
	$Z_{O,Cl}$	0·1733 (24)	0·1625 (81)	0·1685 (42)	0·1572 (37)
	Δ	−0·0085 (28)	−0·0023 (85)	−0·0004 (44)	−0·0080 (40)

for the ClO$_4^-$ ion as the neutron data refinement; the neutron-determined geometry agrees with the geometry from the conventional refinement (Table 3). It cannot be decided from the present data alone whether the disagreement between the deformation positions and the neutron positions is an artefact introduced by the deformation model or by systematic errors in the neutron model. The deformation-refinement geometry agrees well, however, with the deformation-refinement geometry of the perchlorate ion in NH$_4$ClO$_4$ (Lundgren, 1979b). The average Cl–O distances are 1·439 (3) and 1·445 (10) Å, respectively. The averages of distances corrected for thermal riding motion are 1·463 (5) and 1·463 (3) Å, respectively.

H$_2$O

Apart from the large bias in the H positions, the conventional refinement also seems to introduce a bias in the water O position. The O position as determined in the conventional refinement lies on the H–O(w,neutron)–H bisector, and 0·018 (2) Å from the neutron-determined position. It is gratifying to note that, in this case, the deformation refinement shifts the O position towards the O(w,neutron) position (Fig. 3). NMR studies have shown, however, that the DMR and PMR spectra of single crystals of NaClO$_4$.D$_2$O and NaClO$_4$.H$_2$O, respectively, can be interpreted in terms of a dynamically disordered water molecule jumping between two distinct positions (Berglund & Tegenfeldt, 1977, 1979). In the light of these results, any interpretation of the deformation density maps for the water molecule and of the observed shift in the O position is necessarily somewhat dubious.

Comparison of X-ray and neutron results

The only significant discrepancies between the *positional* parameters derived from the neutron and the X-ray conventional refinements occur for the water
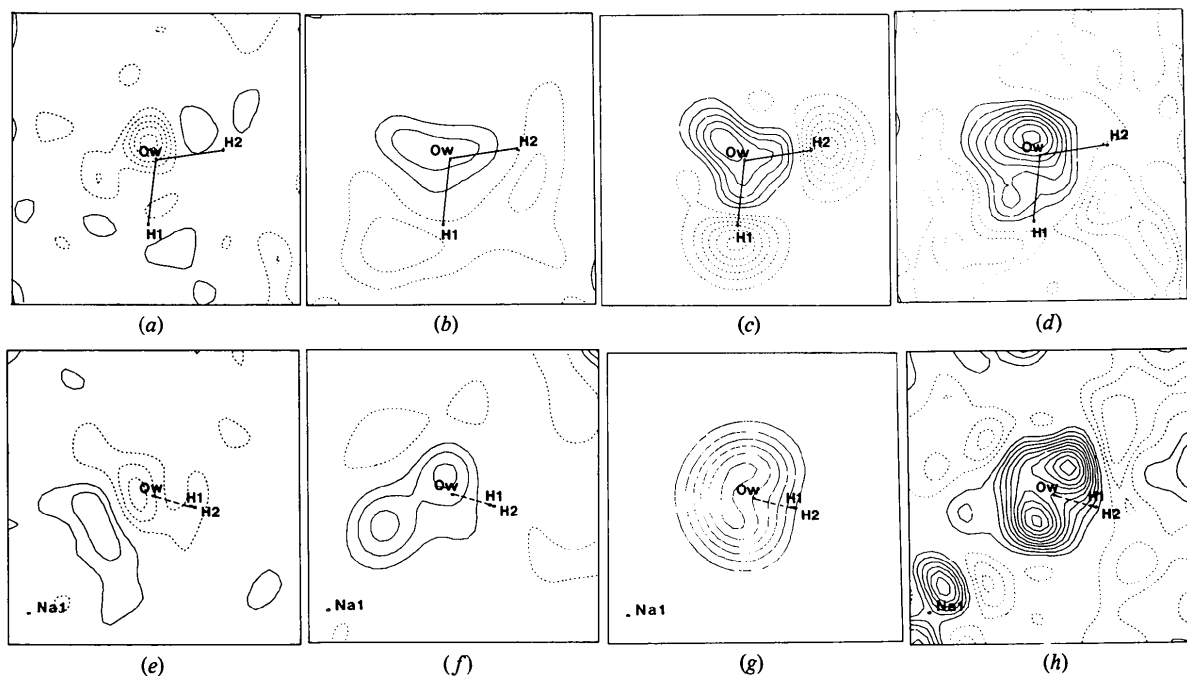
Fig. 4. H_2O: residual and model maps. Maps (a)–(d) are calculated in the plane of the molecule; maps (e)–(h) are calculated in the plane through the H—O—H bisector perpendicular to the plane of the molecule. Contour intervals etc. are as in Fig. 2. (a) and (e): residual densities (parameters from conventional refinement); (b) and (f): dynamic model maps; (c) and (g): static model maps; (d) and (h): X–N maps.

molecule. Apart from the familiar large disagreement between the H positions (0·2–0·3 Å), the O coordinates also differ by up to 6σ (0·015 Å). Positional parameters from the deformation refinement agree with the neutron-refinement parameters for the water O position, but discrepancies of up to 5σ are now found for the perchlorate O atoms.

An analysis of the *thermal* parameters, which are not significantly different in the conventional and deformation refinements of the X-ray data, shows that the mean of the average mean-square (m.s.) displacements from the X-ray refinement is higher than the value from the neutron refinement. Assuming a linear relationship between the m.s. amplitude and the temperature, the 8·5% difference in the average m.s. amplitudes in the present case would then lead to a temperature difference of 20–25 K. Such a large mismatch in temperature for the X-ray and neutron room-temperature experiments is unlikely; the reason for the systematic discrepancies in the thermal parameters must be sought (at least in part) elsewhere.

Differences in the thermal diffuse scattering and profile-analysis methods for the two experiments may explain some of the differences, although there were no high-angle data ($\sin \theta/\lambda > 0·7$ Å^{-1}) in the two data sets. On the other hand, the *absence* of high-angle data may affect the refinements differently. Furthermore, multiple scattering is expected to be a more serious

problem in the neutron study, where the thickness of the Ewald sphere is ~20 times larger than in the X-ray case.

The neutron data were severely affected by secondary extinction. One third of the data suffered an intensity loss exceeding 15%, with a maximum of 90%. A refinement with only reflexions with extinction corrections < 15% changed the scale factor 6%, doubled the isotropic extinction coefficient and shifted the thermal parameters towards the X-ray values. However, these changes were significant only for the Cl atom. No significant changes were observed for the positional parameters. The inadequacy of the extinction model may thus be added to the possible reasons for the discrepancies in the thermal parameters.

A difference in thermal parameters derived from neutron and X-ray data is often observed, even at low temperatures. This effect must then be considered in interpreting electron density results from a combination of X-ray and neutron data. A moderate change in the scale factor due to errors in thermal parameters can lead to large changes in an X–N map. An uncorrected systematic effect in the X-ray data can lead to the same effect. In the present case, the adjustment of the X-ray intensities to the neutron parameters led to a 6% decrease in the scale factor ($\times F_c$). The effect of this substantial scale-factor shift is demonstrated in the X–N maps (Figs. 2f and 4d,h), where the electron

densities at the atomic sites are considerably higher than in the deformation maps. This is particularly true for Na(1) (Fig. 4e–h), for which no residual density appears in the deformation maps.

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