

## Electron Population Analysis of Accurate Diffraction Data. V. Structure and One-Center Charge Refinement of the Light-Atom Mineral Kernite, $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$

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### Abstract

The structure of the mineral kernite has been reinvestigated, using a new set of accurate X-ray diffractometer data. The conventional least-squares refinement leads to a final value of  $R_w(F)$  of 3.6 percent ( $R(F) = 3.4\%$ ). Determination of the net atomic charges with the Extended L-shell (ELS) method gives partial positive charges for the sodium (0.4–0.5 units) and boron (0.4–0.7 units) and negative charges (0.4–0.5 units) for the oxygen atoms. No difference in charge was detected between trigonal and tetrahedral boron and between bridging and hydroxylic oxygen atoms.

The value of the least-squares scale factor is quite sensitive to the nature of the atomic scattering factors used. The result of an experimental measurement of the scale factor shows that the atomic densities in kernite are described better by contracted Slater-type orbitals than by isolated atom Hartree-Fock orbitals.

Difference density maps based on high-order refinements ( $\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$ ) show more density in the B-O than Na-O bonds, supporting the covalent nature of the bonds between boron and oxygen atoms.

### Introduction

The mineral kernite belongs to the sodium borate series  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  whose known members are  $n = 0, 1, 2$  (metakernite), 3 (kernite), 5 (tincalconite) and 10 (borax). The structure of borax was solved by Morimoto (1956) and attempts have been made to determine the structures of kernite and tincalconite. Christ and Garrels (1959) suggested that tincalconite contains the same  $(\text{B}_4\text{O}_5(\text{OH}_4))^{-2}$  anion as borax, and that kernite consists of infinite chains, and is therefore fundamentally different from these borates. Other reports have also suggested some sort of infinite chain polyanion in view of kernite's fibrous cleavage (Edwards and Ross, 1960; Christ, 1960). An initial report of the correct structure was reported by Giese (1966) and an independent determination was reported shortly thereafter by Cialdi *et al.* (1967).

Although it is well known that X-ray diffraction experiments determine the electron distribution rather than the positions of the atoms in a crystal, it is only with the recent availability of automatic diffractometers and new data-processing techniques that electron-density studies have become feasible. In an earlier paper of this series the application of one-center formalisms to some organic and inorganic molecules

was described (Coppens, Pautler and Griffin, 1971). More sophisticated two-center formalisms, in which the overlap density in the bonds is explicitly allowed for, have been developed (Stewart, 1969; Coppens, Willoughby and Csonka, 1971), but they generally require complementary information from neutron diffraction to eliminate the correlation between thermal motion and bonding anisotropy in the least-squares refinement.

The one-center formalisms lead to a measurement of net atomic charges, defined in terms of the atomic wave functions used for the calculation of atomic scattering factors. Since many calculations of bonding energy in crystals are based on the ionic model it is of interest to investigate to what extent the charge distribution in a mineral actually conforms to this model. The mineral kernite,  $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  was selected, because good crystals were available and because it contains no atoms heavier than sodium. Thus, bonding effects will be less masked by strong scattering from unperturbed inner electron shells. In addition, as earlier structure analyses (Giese, 1966; Cialdi *et al.*, 1967) have shown, the mineral contains both trigonal and tetrahedral boron atoms, as well as ring, hydroxyl and water oxygen atoms. This variety of chemical bonding offers an

excellent opportunity to study the effect of chemical environment on the atomic charges in a crystal.

## Experimental

### Cell dimensions and data collection

Cell dimensions were determined by least squares from the settings of 20 carefully centered high-order  $\text{CuK}\alpha$  reflections. Crystallographic data are:

space group  $P2_1/c$   
 $a = 7.0172 \pm .0002 \text{ \AA}$   
 $b = 9.1582 \pm .0002$   
 $c = 15.6774 \pm .0005$   
 $\beta = 108.861 \pm .002^\circ$   
 $Z = 4$   
 $\mu = 2.746 \text{ cm}^{-1}$  for  $\text{MoK}\alpha$

A small fragment ( $.013 \times .015 \times .049 \text{ cm}$ ) of a large kernite crystal was used for a remeasurement of the diffraction data. The low impurity content was confirmed by a microprobe analysis (done by Dr. W. McLean at McGill University). Two symmetry related sets of three-dimensional intensities were collected on a Picker automatic diffractometer using  $\text{MoK}\alpha$  radiation and a  $3\text{--}3.5^\circ$  scan length on  $2\theta$ . The unweighted and weighted internal consistencies on  $F^2$  (defined respectively as  $\Sigma(F^2 - \langle F^2 \rangle) / \Sigma F^2$  and the corresponding weighted expression) were 2.9 percent and 2.2 percent respectively. Symmetry equivalent reflections were averaged to a unique set of 3604 reflections [ $(\sin\theta/\lambda)_{\text{max}} = 0.72 \text{ \AA}^{-1}$ ], of which 2499 were larger than three times the standard deviation. All the data were corrected for absorption by Gaussian integration over the volume of the crystal.

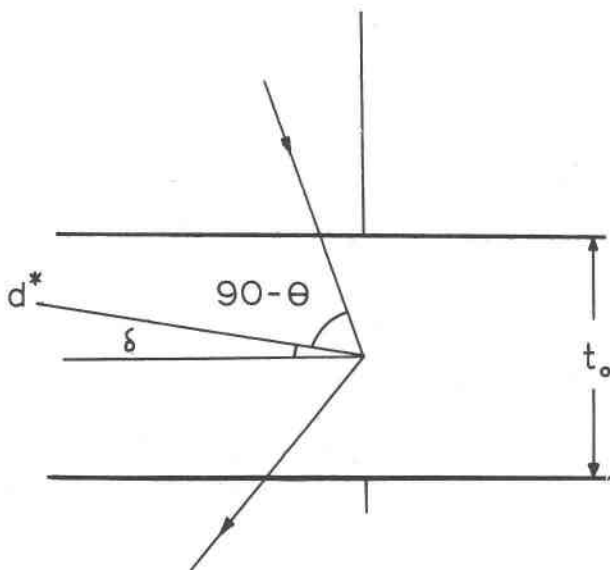


FIG. 1. Experimental arrangement for the scale factor measurement.

Refinement	number of reflections	number of parameters	parameters per reflection	$R(F)^a$	$R_w(F)^b$	$R(F^2)^c$	$R_w(F^2)^c$
Conventional Least Squares (A)	2499	187	13.3	.034	.036	.043	.070
High Order Refinement STO <sup>c</sup> Scattering Factors (B)	1068	154	6.9	.046	.040	.065	.075
High Order Refinement HF <sup>d</sup> Scattering Factors (C)	1069	154	6.9	.046	.040	.065	.073
Extended L-Shell STO Valence and HF Core Scattering Factors (D) 2493	212	212	11.8	.030	.029	.035	.056
Extended L-Shell STO Valence and HF Core Scattering Factors (E)	2501	212	11.8	.032	.032	.037	.062
Extended L-Shell HF Valence and Core Scattering Factors (F)	2501	212	11.8	.031	.031	.037	.060

a  $R(F) = \Sigma |F_o| - k |F_c| / \Sigma F_o^2$   
b  $R_w(F) = \{ \Sigma_w (F_o - k|F_c|)^2 / \Sigma_w F_o^2 \}^{1/2}$   
c STO = Slater type orbital  
d HF = Hartree Fock orbitals

### Scale factor

Since measurement of the absolute scale is highly desirable in quantitative studies of electron density, an experimental scale factor was determined following a method similar to that of Burbank (1965). In order for the measurement to be independent of the distribution of intensity across the incident beam, a thin crystal larger than the incident beam was used. Only the thickness of the crystal plate enters the expression

$$\frac{E_s \omega}{I_o} = \frac{N^2 \lambda^3}{\sin 2\theta} |F|^2 \left( \frac{e^2}{mc^2} \right)^2 \frac{t_0}{\cos(\theta - \delta)} P$$

where the geometry is defined in Figure 1 and the symbols have the following meaning:

- $E_s$  is the total diffracted energy when the crystal passes the reflection range with velocity  $\omega$  in radians/sec.
- $I_o$  is the total energy in the direct beam per second
- $P$  is the polarization factor
- $N$  is the number of unit cells per unit volume
- $t_0$  is the thickness of the crystal
- $F$  is the absolute structure amplitude in electron units
- $\lambda$  is the X-ray wavelength and
- $e^2/mc^2$  is the classical scattering amplitude of a point electron.

Thus only the values of  $E_s$ ,  $I_o$  and  $t_0$  need be measured to calculate the absolute structure factor  $F$ . Carefully calibrated attenuators are needed for the measurement of the direct beam intensity  $I_o$ . The use of monochromatized radiation eliminates problems resulting from wavelength-dependent absorption in the attenuators. The effect of absorption can be minimized for reflections with  $d^*$  parallel to the crystal slab by recording  $I_o$  with the crystal interposed between the incident beam and counter in a non-reflecting position, but with the angle  $\theta - \delta$  between the face normal and the beam. A calculation showed that for all reflections measured in this experiment absorption effects are within 0.05 percent of the intensity. The problem of extinction in the crystal was avoided by examining reflections of only moderate intensity.

Measurement of the thickness of the crystal proved quite difficult. The most reproducible results were obtained by

TABLE 2. FINAL X-RAY ATOMIC COORDINATES FOR THREE OF THE REFINEMENTS

	Conventional Least Squares Refinement			Extended L-Shell Refinement			High Order Refinement			Conventional Least Squares Refinement			Extended L-Shell Refinement			High Order Refinement		
	A			D			B			A			D			B		
Na(1)	x	.31928(9)	.31940(7)	.31955(18)	O(8)	x	.77580(19)	.77557(16)	.77571(42)	H(2)	x	.0934(32)	.1039(29)					
	y	.46486(6)	.46486(5)	.46475(12)		y	.03282(15)	.03310(13)	.03319(27)		y	.2134(23)	.1971(26)					
	z	.31089(4)	.31097(3)	.31101(8)		z	.06828(8)	.06811(7)	.06818(16)		z	.2498(15)	.2509(13)					
Na(2)	x	.18557(10)	.18559(8)	.18630(24)	O(9)	x	.56568(14)	.56538(12)	.56505(26)	H(3)	x	.9720(32)	.9571(38)					
	y	.36637(7)	.36636(5)	.36643(15)		y	.27262(9)	.27256(7)	.27295(15)		y	.1114(25)	.1113(26)					
	z	.07245(5)	.07246(4)	.07250(11)		z	.36309(6)	.36302(5)	.36308(11)		z	.3818(15)	.3781(18)					
O(1)	x	.51273(14)	.51259(12)	.51303(28)	O(10)	x	.03920(19)	.03886(18)	.03858(37)	H(4)	x	.5666(30)	.5652(26)					
	y	.02504(9)	.02511(8)	.02489(17)		y	.06215(14)	.06227(12)	.06198(27)		y	.3580(21)	.3675(22)					
	z	.39728(6)	.39723(5)	.39723(10)		z	.41534(8)	.41516(7)	.41477(15)		z	.0360(13)	.0404(13)					
O(2)	x	.44023(13)	.44033(11)	.44005(25)	O(11)	x	.16711(19)	.16732(16)	.16766(36)	H(5)	x	.1086(35)	.1066(33)					
	y	.09882(9)	.09885(7)	.09874(15)		y	.11744(12)	.11727(10)	.11746(24)		y	.0233(26)	.0241(24)					
	z	.24094(6)	.24093(5)	.24093(10)		z	.07617(8)	.07639(7)	.07650(14)		z	.3802(16)	.3817(16)					
O(3)	x	.76727(13)	.76728(11)	.76703(24)	B(1)	x	.55313(22)	.55295(18)	.55273(35)	H(6)	x	.7212(30)	.7115(30)					
	y	.20590(10)	.20593(8)	.20541(16)		y	.16779(16)	.16774(13)	.16795(23)		y	.1005(24)	.1129(26)					
	z	.26849(6)	.26852(5)	.26847(12)		z	.42154(10)	.42155(8)	.42167(15)		z	.0512(14)	.0474(14)					
O(4)	x	.46493(12)	.46498(10)	.46474(21)	B(2)	x	.55340(21)	.55325(17)	.55343(29)	H(7)	x	.2233(55)	.2243(53)					
	y	.35087(9)	.35091(7)	.35118(14)		y	.23267(14)	.23269(11)	.23234(20)		y	.4689(36)	.4679(38)					
	z	.20889(6)	.20892(5)	.20878(10)		z	.26884(9)	.26884(7)	.26876(13)		z	.4882(27)	.4925(28)					
O(5)	x	.79170(14)	.79154(11)	.79135(25)	B(3)	x	.57414(20)	.57400(16)	.57436(29)	H(8)	x	.0314(45)	.0211(46)					
	y	.44864(10)	.44846(8)	.44849(17)		y	.48048(14)	.48041(12)	.48043(19)		y	.0928(31)	.0822(30)					
	z	.21540(7)	.21539(5)	.21502(13)		z	.19969(9)	.19969(7)	.19985(12)		z	.0812(19)	.0773(18)					
O(6)	x	.06216(16)	.06226(12)	.06237(29)	B(4)	x	.86829(22)	.86821(18)	.86821(32)									
	y	.29094(12)	.29059(11)	.29048(23)		y	.31396(16)	.31393(13)	.31364(24)									
	z	.24052(9)	.24056(7)	.23979(19)		z	.24180(10)	.24181(8)	.24187(16)									
O(7)	x	.58479(19)	.58495(15)	.58424(47)	H(1)	x	.2506(35)	.2637(34)										
	y	.29347(12)	.29393(10)	.29343(21)		y	.1008(23)	.1008(21)										
	z	.00999(7)	.01012(6)	.01027(13)		z	.1206(16)	.1315(16)										

measuring the degree of absorption of  $TiK\alpha$  X-rays passing through the crystal. This result was confirmed by calculating  $t_0$  from the measured surface area, weight and density of the specimen. Direct optical measurements of the thickness are, in our experience, less reliable.

Table 3. Interatomic Distances (Å) From The Conventional Least Squares Refinement (A)

Sodium-Oxygen Distances			
Na(1)-O(2)	2.429(1)	Na(2)-O(1)	2.484(1)
O(3)	2.510(1)	O(4)	2.393(1)
O(4)	2.398(1)	O(6)	3.106(1)
O(6)	2.392(1)	O(10)	2.432(1)
O(8)	2.289(1)	O(10)	2.436(1)
O(9)	2.417(1)	O(11)	2.285(1)
Boron-Oxygen Distances			
B(1)-O(1)	1.365(2)	B(2)-O(2)	1.449(2)
O(7)	1.378(2)	O(3)	1.523(2)
O(9)	1.350(2)	O(4)	1.436(2)
		O(9)	1.498(2)
B(3)-O(1)	1.500(2)	B(4)-O(3)	1.360(2)
O(2)	1.453(2)	O(5)	1.356(2)
O(4)	1.445(2)	O(6)	1.383(2)
O(5)	1.494(2)		
Hydrogen-Oxygen Distances			
H(1)-O(2)	1.92(2)	H(2)-O(6)	.74(2)
O(11)	.77(2)		
H(3)-O(3)	2.08(2)	H(4)-O(1)	2.03(2)
O(10)	.74(2)	O(7)	.75(2)
H(5)-O(5)	1.97(2)	H(6)-O(7)	2.01(2)
O(10)	.92(2)	O(8)	.73(2)
H(7)-O(8)	1.06(4)	H(8)-O(8)	1.82(3)
O(11)	1.74(4)	O(11)	1.00(3)
Oxygen-Oxygen Distances			
O(6)-O(5)	3.301(2)	O(7)-O(1)	2.779(1)
O(8)-O(7)	2.745(2)	O(10)-O(3)	2.799(2)
		O(5)	2.875(2)
O(11)-O(2)	2.678(1)	O(11)-O(8)	2.817(2)
O(8)	2.787(2)		

The energy of the direct beam and the integrated intensity of 33  $hk0$  and  $0k0$  reflections were measured on a crystal slab. A comparison of the values of the structure factor  $F$  with those of the complete data set yielded a value of  $1.231 \pm 0.015$  for  $k$ , defined by  $F_{obs} = kF_{absolute}$ , when the thickness from the Ti absorption ( $t_0 = 0.0121$  cm) was used. The value obtained with the thickness based on surface area and weight ( $t_0 = 0.0130$  cm) was  $1.28 \pm 0.04$ , which is within the error limits of the first result. The first value was adopted, as the underlying thickness measurements were considered more reliable.

### Conventional Least-Squares Refinement and Discussion of the Structure

The original set of X-ray measurements (Giese, 1966) had been refined to  $R = 0.042$  and the refinement provided positional parameters for all atoms including hydrogens. These parameters were used as input into a full matrix least-squares refinement minimizing  $\sum w\Delta^2$  where  $\Delta = F_{obs}^2 - F_{calc}^2$ . Reflections which  $F_{obs}^2 < 3\sigma(F_{obs}^2)$  only were included in the refinement whenever  $F_{calc}^2 > 3\sigma(F_{obs}^2)$ ; in this case the discrepancy  $\Delta$  was taken as  $3\sigma(F_{obs}^2) - F_{calc}^2$ .

<sup>1</sup> A table listing the observed and calculated structure amplitudes may be ordered as NAPS Document #01981 from Microfiche Publications, Division of Microfiche Systems Corporation, 305 East 46th Street, New York, N.Y. 10017. Please remit in advance \$1.50 for microfiche or \$5.00 for photocopies. Please check the most recent issue of this journal for the current address and price.

TABLE 4. BOND ANGLES ( $^{\circ}$ ) FROM THE CONVENTIONAL LEAST SQUARES REFINEMENT (A)

O(3)-B(2)-O(4)	109.70 (10)	H(7)-O(8)-H(6)	107.7 (2.5)
O(2)-B(2)-O(9)	110.82 (10)	H(7)-O(8)-H(8)	111.0 (2.0)
O(2)-B(2)-O(3)	107.90 (10)		
O(3)-B(2)-O(9)	107.52 (10)	H(3)-O(10)-H(5)	103.8 (1.4)
O(4)-B(2)-O(9)	109.65 (10)	H(8)-O(11)-H(1)	110.4 (2.2)
O(4)-B(2)-O(2)	111.78 (10)	H(8)-O(11)-H(7)	115.0 (1.9)
O(4)-B(3)-O(5)	111.71 (10)	H(1)-O(11)-H(7)	109.1 (2.0)
O(4)-B(3)-O(1)	105.66 (10)	O(2)-H(1)-O(11)	167.2 (2.3)
O(1)-B(3)-O(5)	106.18 (10)	O(3)-H(3)-O(10)	166.4 (2.4)
O(1)-B(3)-O(2)	110.89 (10)	O(1)-H(4)-O(7)	174.1 (2.1)
O(2)-B(3)-O(5)	108.59 (10)	O(6)-H(2)-O(5)	178.1 (2.1)
O(2)-B(3)-O(4)	113.55 (10)	O(5)-H(5)-O(10)	168.5 (2.1)
O(9)-B(1)-O(1)	123.04 (12)	O(7)-H(6)-O(8)	176.4 (2.2)
O(9)-B(1)-O(7)	118.39 (12)	O(8)-H(7)-O(11)	166.7 (3.0)
O(1)-B(1)-O(7)	118.57 (12)	O(8)-H(8)-O(11)	168.7 (2.5)
O(5)-B(4)-O(3)	124.15 (12)	B(1)-O(7)-H(4)	110.1 (1.5)
O(6)-B(4)-O(5)	115.40 (12)	B(4)-O(6)-H(2)	111.8 (1.5)
O(6)-B(4)-O(3)	120.45 (12)		
B(4)-O(3)-B(2)	119.78 (10)		
B(4)-O(5)-B(3)	120.72 (10)		
B(2)-O(9)-B(1)	120.04 (10)		
B(2)-O(4)-B(3)	123.60 (10)		
B(2)-O(2)-B(3)	125.61 (10)		
B(3)-O(1)-B(1)	121.51 (10)		

Extinction for kernite was quite small, and could be adequately described by a single isotropic parameter in the least squares refinement (Zachariassen, 1967). The number of reflections, number of parameters, the parameter/reflection ratio and the  $R$  values for a number of refinements are shown in Table 7. As can be seen, the full-data conventional least squares refinement (hereafter, called  $A$ ) is overdetermined by a factor of 13.3, and leads to a final  $R(F)$  of 0.034. The positional parameters are listed in Table 2; the bond distances and bond angles are shown in Tables 3 and 4 respectively.

Kernite consists of infinite borate polyanion chains of composition  $(B_4O_6(OH)_2)_n^{-2n}$ , two per unit cell, parallel to the  $b$ -axis. One triangular  $BO_2OH$  group and two tetrahedral  $BO_4$  groups share corner oxygens to form six membered rings. Three rings form the chains by sharing two corner oxygen atoms of both tetrahedra in each ring. Figure 2 is a projection onto (100) showing one of the chains. The thermal motion is anisotropic but generally small (except for the water molecules), as is often the case in mineral structures. The thermal parameters are listed in Table 5. The isotropic thermal parameters of H(7) and H(8) are unusually large, but no obvious anom-

alies are observed in difference maps in which all but these hydrogen atoms are subtracted.

The angles between the least squares planes of two adjacent B-O rings are  $93.4^{\circ}$  and  $80.0^{\circ}$ . It is of interest to note that the chains possess the pseudo-symmetry  $4_1$  and  $4_3$  because of the closeness of these angles to  $90^{\circ}$ .

The chains are linked together by hydrogen bonds in the  $c$ -axis direction (Fig. 3) involving half of the hydroxyl groups on the triangular boron atoms. The remaining hydroxyl groups, pointing in the  $a$ -axis direction, do not form hydrogen bonds. For example, the O(6)-O(5) distance equals 3.301 Å, which is longer than the usually observed 2.7-2.8 Å oxygen-oxygen distance associated with hydrogen bonding.

All other hydrogen atoms are involved in hydrogen bonding. An interesting ring of four hydrogen bonds around the center at the origin is formed by the water molecules containing O(8) and O(11) and their symmetry equivalents. The sequence in this ring is O(11)-H(8)-O(8)-H(7)-O'(11)-H'(8)-O'(8)-H'(7)-O(11). Kernite has two perfect cleavages  $\{(001) \text{ and } (100)\}$  and both of these involve breaking of hydrogen bonds and sodium water-molecule bonds.

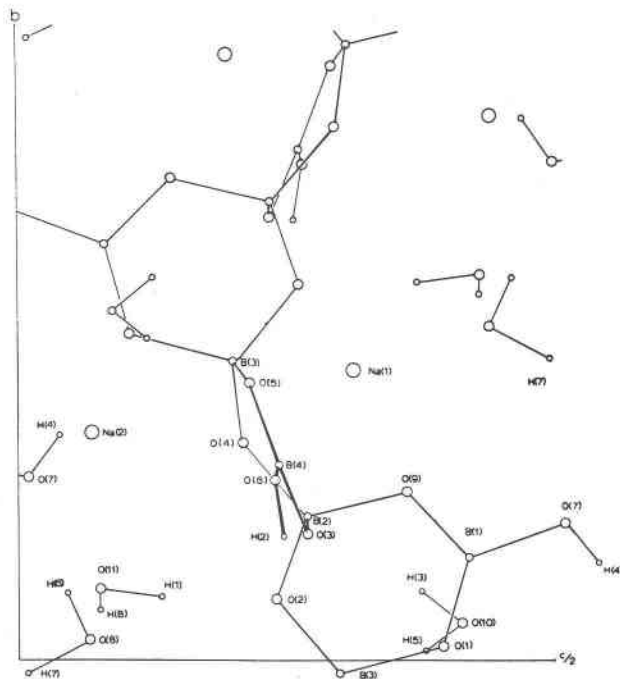


FIG. 2. Projecting of the structure on the  $bc$  plane, showing the infinite chains extending in the  $b$  direction.

TABLE 5. FINAL THERMAL PARAMETERS ( $\beta_{ij}$ ) FOR KERNITE\*

Refine- ment		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Refine- ment		B
Na (1)	A	.01180 (14)	.00377 (6)	.00251 (3)	.00037 (7)	.00332 (5)	.00011 (3)	H (1)	A	3.9 (5)
	B	.01072 (24)	.00354 (12)	.00228 (5)	.00043 (10)	.00308 (8)	.00017 (5)		B	3.9 (5)
	D	.01103 (11)	.00344 (5)	.00234 (2)	.00036 (6)	.00317 (4)	.00012 (3)		D	0.6 (6)
Na (2)	A	.01409 (16)	.00501 (8)	.00309 (3)	-.00047 (8)	-.00086 (6)	.00013 (4)	H (2)	A	4.3 (6)
	B	.01355 (30)	.00471 (13)	.00284 (6)	-.00044 (13)	-.00094 (10)	.00019 (6)		B	4.3 (6)
	D	.01323 (13)	.00466 (6)	.00290 (3)	-.00042 (7)	-.00091 (4)	.00014 (3)		D	0.0 (6)
O (1)	A	.01255 (22)	.00220 (9)	.00101 (4)	-.00040 (12)	.00163 (7)	-.00006 (5)	H (3)	A	4.6 (6)
	B	.01180 (35)	.00155 (13)	.00084 (6)	-.00053 (15)	.00146 (10)	-.00007 (5)		B	4.6 (6)
	D	.01115 (19)	.00133 (8)	.00070 (3)	-.00053 (9)	.00143 (6)	-.00008 (4)		D	1.9 (7)
O (2)	A	.00860 (20)	.00173 (9)	.00104 (4)	-.00077 (11)	.00083 (7)	.00004 (5)	H (4)	A	3.3 (5)
	B	.00771 (28)	.00125 (13)	.00079 (5)	-.00099 (13)	.00073 (9)	-.00001 (5)		B	3.3 (5)
	D	.00700 (17)	.00088 (7)	.00072 (3)	-.00076 (9)	.00063 (6)	.00003 (4)		D	1.8 (6)
O (3)	A	.00601 (19)	.00308 (10)	.00215 (4)	.00121 (11)	.00140 (7)	.00072 (5)	H (5)	A	5.4 (6)
	B	.00498 (25)	.00246 (14)	.00199 (6)	.00121 (14)	.00126 (9)	.00080 (7)		B	5.4 (6)
	D	.00445 (16)	.00219 (8)	.00183 (4)	.00125 (9)	.00115 (6)	.00072 (4)		D	2.1 (7)
O (4)	A	.00527 (18)	.00168 (9)	.00134 (4)	.00003 (10)	.00089 (7)	.00030 (5)	H (6)	A	3.3 (5)
	B	.00406 (25)	.00116 (12)	.00110 (5)	-.00007 (12)	.00058 (8)	.00034 (6)		B	3.3 (5)
	D	.00359 (15)	.00089 (7)	.00102 (3)	.00002 (8)	.00061 (5)	.00028 (4)		D	2.1 (6)
O (5)	A	.00644 (20)	.00301 (10)	.00248 (5)	.00018 (11)	.00214 (8)	.00034 (5)	H (7)	A	12.6 (1.2)
	B	.00524 (27)	.00245 (15)	.00229 (7)	.00021 (13)	.00197 (10)	.00042 (6)		B	12.6 (1.2)
	D	.00494 (17)	.00210 (9)	.00215 (4)	.00015 (9)	.00191 (6)	.00032 (4)		D	11.0 (1.7)
O (6)	A	.00683 (22)	.00502 (13)	.00432 (6)	.00100 (14)	.00290 (9)	.00024 (7)	H (8)	A	7.9 (8)
	B	.00528 (28)	.00475 (18)	.00408 (10)	.00079 (17)	.00279 (13)	.00010 (10)		B	7.9 (8)
	D	.00494 (18)	.00437 (12)	.00392 (5)	.00085 (11)	.00259 (8)	.00015 (6)		D	6.1 (1.1)
O (7)	A	.02726 (36)	.00359 (12)	.00119 (4)	.00335 (16)	.00289 (10)	.00038 (6)			
	B	.02526 (62)	.00342 (16)	.00088 (6)	.00303 (23)	.00249 (14)	.00048 (7)			
	D	.02527 (29)	.00275 (10)	.00085 (4)	.00334 (13)	.00262 (8)	.00043 (5)			
O (8)	A	.01854 (32)	.00669 (15)	.00265 (6)	.00329 (18)	.00335 (11)	.00125 (8)			
	B	.01656 (48)	.00620 (21)	.00230 (8)	.00262 (26)	.00309 (16)	.00103 (10)			
	D	.01665 (26)	.00604 (13)	.00226 (5)	.00309 (14)	.00306 (9)	.00123 (6)			
O (9)	A	.01193 (23)	.00229 (10)	.00108 (4)	-.00099 (11)	.00136 (7)	-.00018 (5)			
	B	.01103 (33)	.00174 (13)	.00089 (5)	-.00121 (14)	.00137 (10)	-.00019 (6)			
	D	.01036 (19)	.00143 (8)	.00078 (3)	-.00102 (9)	.00116 (6)	-.00019 (4)			
O (10)	A	.01360 (28)	.00796 (15)	.00197 (5)	.00303 (16)	.00157 (10)	.00073 (7)			
	B	.01258 (40)	.00708 (22)	.00179 (7)	.00252 (22)	.00169 (13)	.00057 (9)			
	D	.01164 (24)	.00701 (13)	.00156 (4)	.00289 (13)	.00133 (8)	.00064 (6)			
O (11)	A	.01219 (28)	.00616 (13)	.00194 (5)	-.00022 (15)	.00025 (10)	-.00015 (6)			
	B	.01146 (38)	.00536 (19)	.00170 (7)	-.00030 (19)	.00036 (13)	-.00016 (8)			
	D	.01103 (24)	.00519 (11)	.00160 (4)	-.00031 (12)	.00018 (8)	-.00023 (5)			
B (1)	A	.00849 (30)	.00290 (15)	.00123 (6)	-.00026 (17)	.00117 (11)	-.00022 (7)			
	B	.00902 (39)	.00209 (17)	.00103 (7)	-.00053 (18)	.00129 (13)	-.00032 (8)			
	D	.00707 (25)	.00202 (12)	.00091 (5)	-.00021 (13)	.00097 (9)	-.00031 (6)			
B (2)	A	.00599 (27)	.00192 (13)	.00113 (5)	-.00001 (15)	.00088 (10)	.00008 (7)			
	B	.00534 (30)	.00145 (15)	.00094 (6)	-.00002 (16)	.00084 (10)	.00020 (7)			
	D	.00451 (22)	.00111 (10)	.00086 (4)	.00006 (12)	.00093 (8)	.00010 (5)			
B (3)	A	.00593 (27)	.00201 (13)	.00116 (5)	.00012 (15)	.00114 (10)	.00012 (7)			
	B	.00546 (33)	.00127 (15)	.00086 (6)	.00008 (16)	.00083 (11)	.00010 (7)			
	D	.00451 (22)	.00111 (10)	.00085 (4)	.00006 (12)	.00093 (8)	.00010 (5)			
B (4)	A	.00563 (28)	.00370 (15)	.00177 (6)	.00026 (17)	.00113 (11)	-.00017 (8)			
	B	.00445 (33)	.00315 (18)	.00177 (8)	.00042 (18)	.00116 (12)	.00007 (9)			
	D	.00402 (22)	.00278 (12)	.00146 (5)	.00025 (14)	.00089 (9)	-.00015 (6)			

\* A = Full-data least-squares (HF); B = High-order least-squares (STO); D = Full-data refinement (STO).

The two sodium atoms are irregularly coordinated by five oxygens and one water molecule around Na(1), and two oxygens and three water molecules around Na(2). These polyhedra share O(4) ring

oxygens and also O(10) water oxygens. In the *c*-axis direction there is sharing of two centrosymmetrically related water molecules, O(10), by Na(2) atoms which in turn are bonded to oxygens

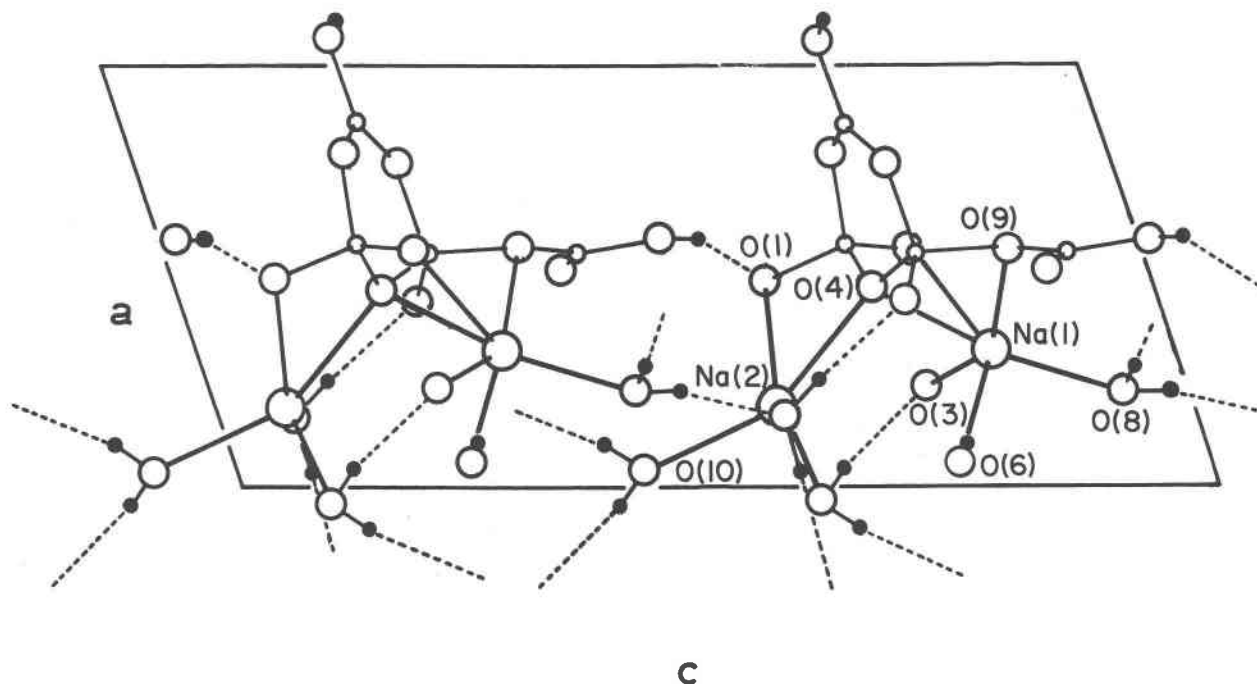


FIG. 3. Projection of the structure on the *ac* plane showing the hydrogen bonding and sodium coordination.

in two chains. The Na(1) atoms link neighboring chains in the *a*-axis direction by bonding hydroxyl O(6) of one chain to ring oxygens of another chain. The individual Na-O distances for Na(1) and Na(2) vary considerably but the average distances for both polyhedra are identical.

#### Extended L-Shell Refinement (ELS) and Net Atomic Charges

In an earlier paper in this series the application of one-center charge refinement formalisms to some organic and inorganic molecules was described (Coppens, Pautler, and Griffin, 1971). In the extended L-shell (ELS) refinement the occupancies of the spherical valence shells are refined together with the positional, thermal and extinction parameters. In Table 1 the *R* index for ELS refinements with differing atomic orbitals is compared with those of the conventional least-squares refinement (A). However, before the ELS results can be discussed, the significance of the improvement in the *R* factors for the ELS calculations must be verified. Using Hamilton's *R*-factor level of significance test (Hamilton, 1965; Pawley, 1970), we find that the improvement with the ELS method is highly significant at the conservative 0.005 percent confidence level ( $R_{212, 2279, 0.005} \approx$

1.06). Thus the discussion of the ELS method results is clearly justified.

ELS calculations were done with three different sets of scattering factors (in all calculations, the hydrogen scattering factors of Stewart, Davidson, and Simpson, 1965, were used): 1) molecule optimized Slater type orbital (STO) scattering factors for the valence and Na *L*-shell electrons, and Hartree-Fock (HF) scattering factors of the Na, O and B *K*-shell electrons (referred to as D); 2) molecule-optimized Slater-type scattering factors for the valence electrons and isolated atom HF scattering factors for all core electrons including those in the Na *L*-shell (E); and 3) isolated atom self-consistent Hartree-Fock scattering factors (referred to as F). Orbital coefficients defining the scattering factors are listed in Table 6. The agreement of the positional parameters with the conventional refinement is everywhere within  $3\sigma$  (see Table 2 for results of refinement D). Experimental charges are shown in Table 8. As would be expected, they depend to a certain extent on the nature of the atomic orbitals used for description of the valence shell. However, the general features of the charge distribution are common to the three sets of results. The sodium ions bear partial positive charges of 0.4–0.5 units, while the boron and hydro-

gen atoms are positive and the oxygen atoms negative. This is in agreement with the relative electronegativities of these atoms, but the charges are always several times smaller than those corresponding to a completely ionic model. Thus, the new experimental results strongly support Slater's conclusion, arrived at from the consideration of interatomic distances, that atoms tend to be much more nearly neutral in a crystal than a straight ionic interpretation would indicate (Slater, 1965). They are also in agreement with Pauling's postulate of approximate electroneutrality, which states that "the electronic structure of a stable crystal is such that the charge on each atom is close to zero and varies at most between about  $+1/2$  and  $-1/2$ " (Pauling, 1946).

The scale factors (Table 7) from refinements D and E are significantly smaller than the value from refinement F. The experimental value of the scale factor can therefore be used to select the set of scattering factors which is more appropriate for kernite. The experimental value of  $1.231 \pm .015$  for  $k$  is not compatible with refinement F for which  $k = 1.324(2)$ . Thus, it is apparent that the molecular optimized Slater type orbitals of Hehre, Stewart and Pople (1969) give a better description of the valence electron distribution in the crystal than the self-consistent field results obtained on isolated atoms. The experimental scale factor does not, within the experimental errors, distinguish clearly between the models D and E. However, since the  $R$  factor is the lowest for model D we will focus the following discussion on the results of this refinement.

TABLE 6. ORBITAL COEFFICIENTS (IN RECIPROCAL ATOMIC UNITS) DEFINING ATOMIC ORBITALS USED IN THE CALCULATION OF SCATTERING FACTORS

	HF* (refinements A,F,C)	STO (refinement E)	STO (refinements D,B)
Na K-shell	(10.626)	(10.626)	(10.626)
Na L	(3.286, 3.401**)	(3.286, 3.401)	3.48
Na M	(0.836)	1.75	1.75
O K	(7.658)	7.658	7.658
O L	(2.246, 2.227)	2.25	2.25
B K	(4.680)	4.68	4.68
B L	(1.288, 1.211)	1.45	1.45
H***			

\* Values in parentheses are best "single zeta" approximations to Hartree Fock atomic orbitals (Clementi and Raimondi, 1963), given only for comparison purposes.

\*\* First value 2s, second value 2p electrons.

\*\*\* Hydrogen scattering factors according to Stewart, Davidson and Simpson (1965) were used

TABLE 7. SCALE FACTORS OBTAINED FROM THE DIFFERENT REFINEMENTS

Refinement	
conventional least squares (A)	1.353(2)
high order refinement, STO valence and Na L-Shell, HF B and O scattering factors (B)	1.276(14)
high order refinement, HF valence and core scattering factors (C)	1.279(14)
ELS, STO valence and Na L-Shell, HF B and O scattering factor (D)	1.240(2)
ELS, STO valence, HF core scattering factors (E)	1.275(2)
ELS, HF valence and core scattering factors (F)	1.324(2)
Experimental	$1.231 \pm .015$

The experimental charges (Table 8) do not differ for identical atoms in chemically different environments. Thus, the sodium atom charges are equal within the experimental errors, even though they are differently coordinated. Similarly, the charges on the three types of oxygen atoms are identical within experimental errors. The averages over the charges are  $-0.43$  for the hydroxyl,  $-0.40$  for the water and  $-0.47_5$  units for the ring oxygen atoms, with a fairly large range of values in each group. A similar trend

TABLE 8. EXPERIMENTAL ATOMIC CHARGES

	HF = Hartree Fock orbitals		STO = Slater Type orbitals	
	F HF core HF valence	E HF core STO valence	D HF core (B,O) STO core (Na) STO valence	
Na (1)	+ 0.43 (16)	+ 0.41 (4)	+ 0.57 (4)	
Na (2)	+ 0.54 (18)	+ 0.29 (5)	+ 0.45 (5)	
O (1)	- 0.40 (3)	- 0.33 (3)	- 0.51 (3)	
O (2)	- 0.37 (3)	- 0.29 (3)	- 0.45 (2)	
O (3)	- 0.34 (3)	- 0.29 (3)	- 0.43 (2)	
O (4)	- 0.41 (3)	- 0.34 (2)	- 0.52 (2)	
O (5)	- 0.34 (3)	- 0.35 (3)	- 0.46 (2)	
O (6)	- 0.42 (4)	- 0.32 (4)	- 0.47 (3)	
O (7)	- 0.34 (4)	- 0.20 (4)	- 0.39 (4)	
O (8)	- 0.39 (5)	- 0.28 (5)	- 0.43 (4)	
O (9)	- 0.37 (3)	- 0.33 (3)	- 0.48 (3)	
O (10)	- 0.33 (6)	- 0.02 (6)	- 0.30 (6)	
O (11)	- 0.45 (5)	- 0.32 (4)	- 0.48 (4)	
B (1)	+ 0.28 (6)	+ 0.40 (4)	+ 0.50 (4)	
B (2)	+ 0.13 (6)	+ 0.41 (4)	+ 0.44 (4)	
B (3)	+ 0.22 (5)	+ 0.54 (4)	+ 0.55 (4)	
B (4)	+ 0.32 (6)	+ 0.56 (4)	+ 0.64 (4)	
H (1)	+ 0.32 (6)	+ 0.22 (5)	+ 0.35 (4)	
H (2)	+ 0.30 (5)	+ 0.28 (5)	+ 0.41 (4)	
H (3)	+ 0.40 (5)	+ 0.02 (6)	+ 0.23 (6)	
H (4)	+ 0.28 (6)	- 0.03 (6)	+ 0.13 (5)	
H (5)	+ 0.24 (5)	+ 0.09 (6)	+ 0.23 (6)	
H (6)	+ 0.27 (6)	+ 0.01 (6)	+ 0.16 (5)	
H (7)	+ 0.22 (7)	- 0.14 (8)	+ 0.08 (8)	
H (8)	+ 0.30 (6)	+ 0.02 (7)	+ 0.17 (6)	
scale factor	1.32(2)	$1.27_5(2)$	1.24(2)	
R (F)	0.031	0.032	0.030	
R <sub>w</sub> (F)	0.031	0.032	0.029	

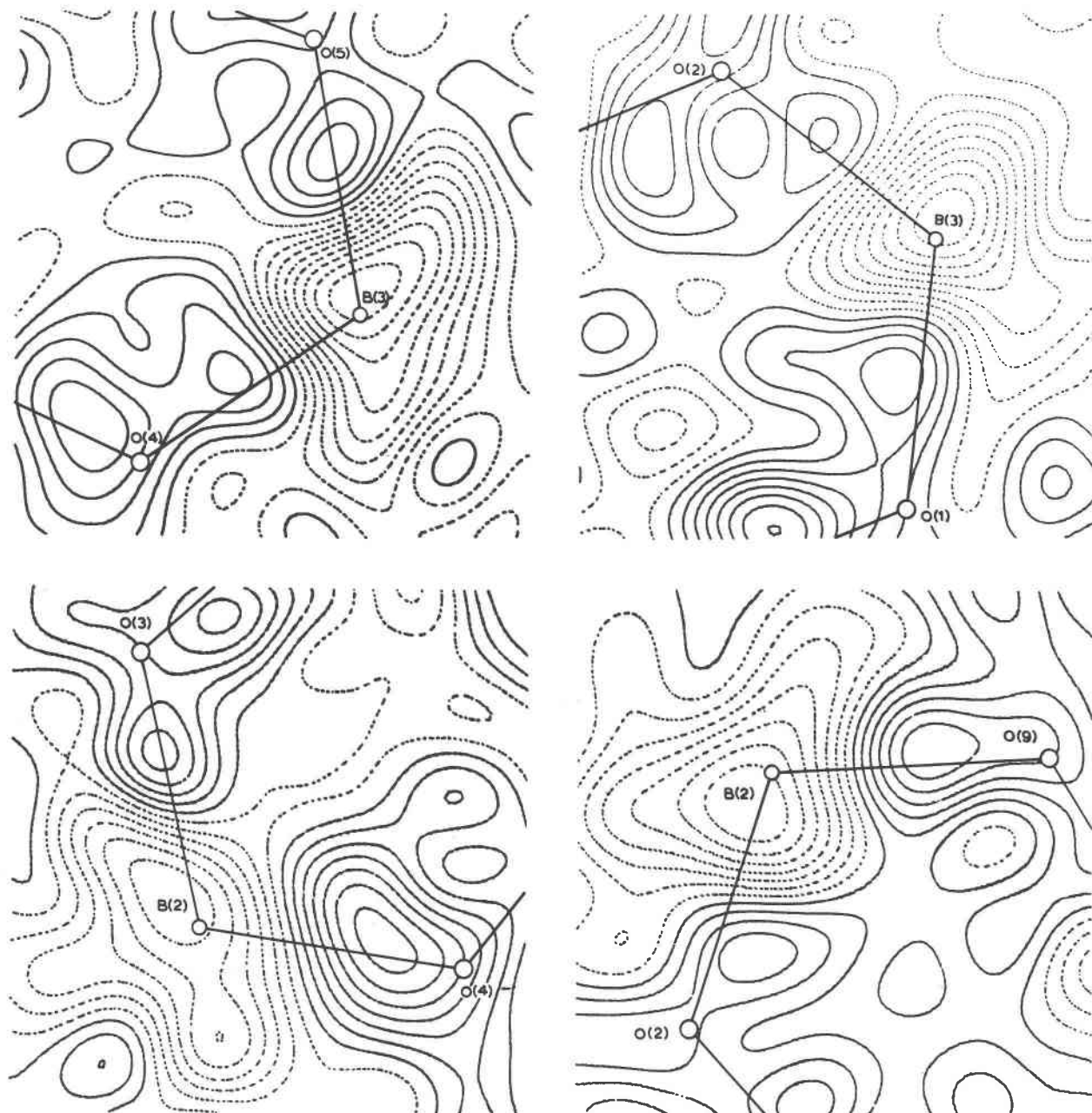


FIG. 4. Difference density maps. Contours at  $0.05 \text{ e}/\text{A}^3$ ; negative contours dotted. The sections shown lie in the plane of the boron and two oxygen atoms. The solid lines indicate bonds lying in the section.

is observed for the boron atoms where the tetrahedral and trigonal atoms show no clear differentiation according to charge. This contrasts with an idealized valence-bond diagram where the tetrahedrally-coordinated boron atom would bear a formal negative charge of one electron, while the trigonal boron atom could be neutral.

The net atomic charge obtained for the O(10)

water molecule is quite similar to the values obtained in previous studies (Coppens, Pautler and Griffin (1971)). The O(10) charge is  $-0.30$  while the hydrogens [H(3) and H(5)] have charges of  $+0.23$  units. Because of the unusually high thermal parameters for H(7) and H(8) the charges obtained for the other two water molecules are not nearly as well defined. The significance of the unusual nega-



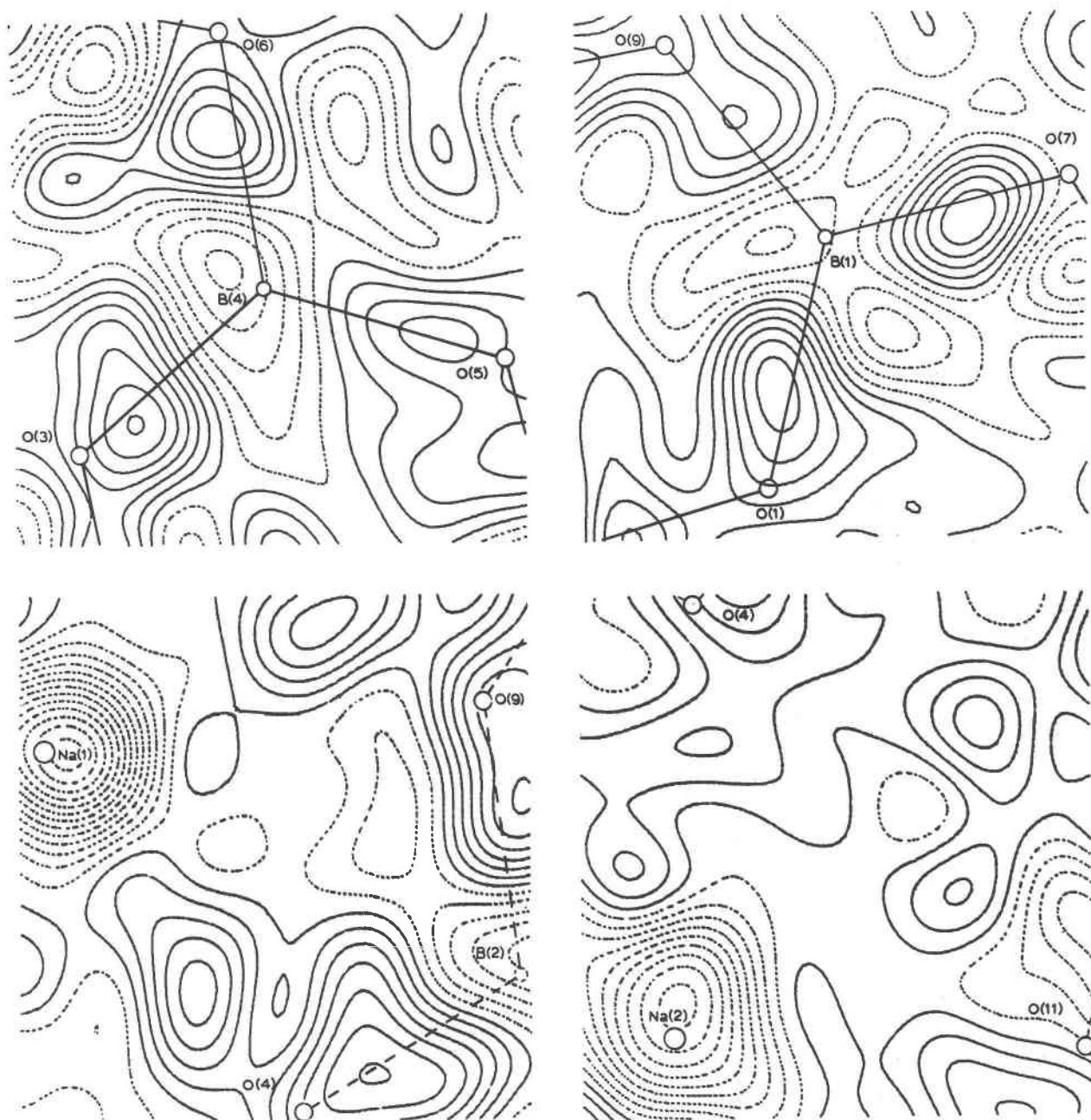


FIG. 5. Difference density maps. Contours at  $0.05 \text{ e}/\text{A}^3$ ; negative contours dotted. The sections in the upper half of the figure contain the three oxygen atoms, while those in the lower half are through one sodium and two oxygen atoms. The solid lines indicate bonds lying in the section; the dashed lines are projections of bonds to atoms not lying in the plane of the density map.

tive net charges on the O(8) and O(11) water molecules is therefore doubtful.

The value of the isotropic extinction parameter is somewhat different for the results of the ELS calculations [0.009(44)] as compared to that obtained for the conventional least squares refinement [0.108

(65)]; that is, the maximum reduction of intensity (for the strongest reflections) is approximately 1 percent in the ELS refinement as compared to a reduction of 10 percent in the conventional least squares refinement. This may indicate that the extinction parameter in the latter refinement is adjusted to al-

low for some of the errors in the model. To investigate how much the experimental charges are affected by such a change in the extinction parameter, the ELS calculations were repeated with the extinction parameter kept constant at the value obtained in the conventional least-squares refinement. The charges so obtained agree within  $1\sigma$  of those of the earlier ELS refinement, indicating that the uncertainty in the extinction parameter does not affect the experimental charges to any considerable extent.

In the ELS calculations, a constraint requiring the total number of electrons to be constant has been imposed so that the crystal will remain neutral during the refinement. If this constraint is not applied, a change in the scale factor may partially compensate for the apparent non-neutrality of the crystal. An alternate procedure is to fix the scale factor at an accurately determined experimental value, the deviation from neutrality of the crystal in such a refinement being a measure of the space-filling properties of the atomic orbitals used to describe the atomic valence shell. The ELS calculations were repeated with  $k$  fixed at 1.231 and using the molecular-optimized Slater-type orbitals for the valence shell and sodium  $L$ -shell (set D), but without the neutrality constraint. The charges obtained from this calculation agree generally within  $2\sigma$ , and always within  $3\sigma$ , with those from the earlier ELS refinement, while the change from neutrality of the crystal is 1.66 electron units, indicating a gain in negative density. It has been suggested (R. F. Stewart, private communication) that such a spherical charge refinement should lead to a deficiency in electrons, because the density in the bonds is not allowed for in the model. However a small shift within the error of the scale factor measurement would have affected the magnitude of the deviation from neutrality to a considerable extent. The relative deviation from neutrality is  $1.66/138 = 1.2$  percent, about equal to the relative standard deviation in the scale factor. Thus, a more accurate experimental value of the scale factor would be desirable, but it is difficult to see how the limiting factors in the experiment (such as extinction and lack of uniformity of crystal thickness) could be reduced further.

#### High-Order Refinement and Difference Density Maps

A number of studies on simple organic molecules have given evidence to support the validity of a high-order least-squares refinement as a method of ob-

taining parameters less affected by bonding (Stewart and Jensen, 1969; O'Connell, 1969; Coppens and Vos, 1971; Stevens and Hope, 1971). In the case of kernite, complementary neutron diffraction information could have been obtained only if  $^{11}\text{B}$  enriched crystals of kernite had been available. Therefore, bonding properties were further studied by the calculation of difference Fourier maps using a full-data X-ray set with the parameters obtained from a high-order X-ray refinement ( $\sin \theta/\lambda > 0.6\text{\AA}^{-1}$ ). The agreement factors, atomic coordinates and thermal parameters for the high-order calculation using an STO valence and Na  $L$ -shell and HF core scattering factors (B) are included in Tables 1, 2 and 5. In these calculations, the hydrogen positional and thermal parameters were not refined. Furthermore, when comparing the high-order and full-data refinements (Table 1), it should be remembered that the former is only over-determined by a factor of 6.9 whereas the ratio of observations to parameters is 13.3 for the latter refinement. From Table 2 it is noted that only slight changes in the atomic coordinates occur in the high-order refinement as compared to the full data set. As noticed in previous work (Coppens, 1971) the thermal parameters obtained in the refinements with STO form factors (B and D) are smaller than those from the HF full data refinement (A). Temperature parameters from a high-order refinement with HF scattering factors (C) are in much better agreement with the STO results, which can be understood in terms of a reduced accommodation of the valence structure of kernite by the anisotropic thermal parameters. It should be noted that for the oxygen and boron atoms STO high-order thermal parameters (B) are somewhat *larger* than the ELS-STO refinement based on all the data (D).

Difference maps are shown in Figures 4 and 5.<sup>1</sup> The central region of each B-O bond in both the tetrahedral and trigonal plane contains residual electron density, which supports the covalent nature of the B-O interaction. The oxygen atoms lie at the zero or slightly negative contour levels while the boron and sodium atoms are in regions of positive charge. In contrast to the B-O bonds, ten out of the eleven regions between sodium and oxygen atoms show very little density, indicating a more ionic nature of the bonds between these atoms. The excep-

<sup>1</sup> The spherical atoms subtracted are those defined in the last column of Table 6 (B, D).

tion is the area between O(4) and Na(1) (Fig. 5). However, there are no other indications, such as from bond lengths, that this bond is different from others in the crystal, so the significance of the density maximum is not clear. The inability to detect the oxygen lone pair electron density is in agreement with the results on sucrose by Hanson, Sieker and Jensen (1972), who observed that agreement between X-ray minus neutron ( $X-N$ ) and high order X-ray difference maps was good in the bonding region but quite different in the lone-pair regions of the oxygen atoms. Specifically, lone-pair electrons are not observed in the high-order difference maps, indicating scattering of the lone-pair electrons well beyond the lower limit cut-off of the high-angle refinement ( $\sin \theta/\lambda > 0.6 \text{ \AA}^{-1}$ ). Calculations on the scattering of a prepared state oxygen atom (Dawson, 1964; Coppens, 1969) fully support the persistence of lone-pair scattering into the high-order region.

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