Charge Distribution in the Light-Atom Mineral Kernite

Abstract. *A charge density analysis of accurate x-ray data for the mineral kernite $Na_2B_4O_6(OH)_2 \cdot 3H_2O$ indicates that the sodium and boron atoms have partial positive charges of 0.4 to 0.5 unit and 0.4 to 0.7 unit, respectively, whereas the oxygen atoms have negative charges of about 0.4 to 0.5 unit. The best agreement with the intensities and with the experimental scale factor is obtained with contracted molecule–optimized atomic orbitals. Difference density maps based on high-order parameters show more density in B–O than in Na–O bonds, thus supporting the covalent nature of the bonds between boron and oxygen atoms.*

Information on the electronic charge distribution is of considerable importance for an understanding of the stability and atomic arrangement of a great variety of mineral structures. Some discussions on the structure of minerals have been based on completely ionic models, in which, for example, an oxygen atom would bear a negative charge of two electrons (*1*). Investigators have made calculations on the orientation of hydroxyl groups or water molecules, using full (*2*) or partial (*3*) ionic charges. But, in the frameworks which exist in many silicates and borates, interatomic distances are short and typical for bonds between covalently bonded atoms. Accepted chemical concepts would exclude large ionic charges for the atoms in such a framework. To provide further information we decided to study a number of minerals, using recently developed techniques for charge refinement of accurate x-ray diffraction data (*4*).

Because of the absence of heavy atoms (in which the many core electrons are unaffected by bonding), the absence of crystallographic disorder (*5–7*), and because thermal motion is usually small in minerals, kernite [$Na_2B_4O_6(OH)_2 \cdot 3H_2O$] is suitable for a charge density analysis. Its structure is of especial interest, since, as shown by Giese (*5*) and by Cialdi *et al.* (*6*), it contains boron atoms in both tetrahedral and trigonal positions, and bridging as well as hydroxylic oxygen atoms (Fig. 1).

Two symmetry-related sets of three-dimensional diffraction data were collected on an automated Picker diffractometer. Symmetry-equivalent reflections were averaged to a unique set of 3604 reflections [$(\sin \theta/\lambda)_{\max} = 0.72$ Å^{-1}, where θ is the Bragg angle and λ is the wavelength], of which 2499 were larger than three times the standard deviation. The parameters determined by Giese (*5*) were used as input in the conventional least-squares refinement, which led to a final agreement factor $R(F)$ of 3.4 and a weighted agreement factor $R_w(F)$ of 3.6 percent, where F is the x-ray structure factor and $R(F)$ and $R_w(F)$ are specified in Table 1. Giese's positional parameters were reconfirmed, although the results presented here are somewhat more accurate than those obtained previously.

The extended L-shell method was used, in which the occupancies of spherical valence shells are varied together with the positional, thermal, and extinction parameters (*4*). The more sophisticated aspherical treatments generally require complementary information from neutron diffraction (*8*), which could only have been obtained if synthetic, ^{11}B-enriched crystals of kernite had been available. The net atomic charges are constrained so that the crystal remains neutral during the refinement.

The results of the charge refinement depend, to a certain extent, on the nature of the atomic orbitals used for a description of the valence electrons (*4*). In previous work isolated atom self-consistent field Hartree-Fock orbitals (HF) as well as molecule-optimized standard Slater orbitals (*9*) have been used in a description of the valence electrons, whereas the cores of the atoms in the first row of the periodic table were assumed to be unperturbed by bonding. In the present study an additional refinement with a molecule-optimized core (*10*) for the sodium atom was included. Resulting agreement factors, net atomic charges, and scale factors relating observed and experimental structure factors are given in Table 1. The agreement between observation and calculation, as expressed in the agreement factors, is somewhat better for the Slater type orbital (STO) valence and sodium core set (Table 1, column 4) than for the other sets of results. However, it is gratifying that

Table 1. Experimental atomic charges; HF, Hartree-Fock orbitals; STO, Slater type orbital. Parenthetical values in columns 2, 3, and 4 are standard deviations.

Atom	HF core, HF valence	HF core, STO valence	HF core (B, O), STO core (Na), STO valence
Na(1)	+ 0.43(16)	+ 0.41(4)	+ 0.57(4)
Na(2)	+ .54(18)	+ .29(5)	+ .45(5)
O(1)	− .40(3)	− .33(3)	− .51(3)
O(2)	− .37(3)	− .29(3)	− .45(2)
O(3)	− .34(3)	− .29(3)	− .43(2)
O(4)	− .41(3)	− .34(2)	− .52(2)
O(5)	− .34(3)	− .35(3)	− .46(2)
O(6)	− .42(4)	− .32(4)	− .47(3)
O(7)	− .34(4)	− .20(4)	− .39(4)
O(8)	− .39(5)	− .28(5)	− .43(4)
O(9)	− .37(3)	− .33(3)	− .48(3)
O(10)	− .33(6)	− .02(6)	− .30(6)
O(11)	− .45(5)	− .32(4)	− .48(4)
B (1)	+ .28(6)	+ .40(4)	+ .50(4)
B (2)	+ .13(6)	+ .41(4)	+ .44(4)
B (3)	+ .22(5)	+ .54(4)	+ .55(4)
B (4)	+ .32(6)	+ .56(4)	+ .64(4)
H (1)	+ .32(6)	+ .22(5)	+ .35(4)
H (2)	+ .30(5)	+ .28(5)	+ .41(4)
H (3)	+ .40(5)	+ .02(6)	+ .23(6)
H (4)	+ .28(6)	− .03(6)	+ .13(5)
H (5)	+ .24(5)	+ .09(6)	+ .23(6)
H (6)	+ .27(6)	+ .01(6)	+ .16(5)
H (7)	+ .22(7)	− .14(8)	+ .08(8)
H (8)	+ .30(6)	+ .02(7)	+ .17(6)
		Scale factor k	
	1.32(2)	$1.27_5(2)$	1.24(2)
		$R(F)$*	
	0.031	0.032	0.030
		$R_w(F)$†	
	0.031	0.032	0.029

* $R(F) = \dfrac{\Sigma \lvert \lvert F_{\text{obs}} \rvert - k \lvert F_{\text{calc}} \rvert \rvert}{\Sigma F_{\text{obs}}}$ † $R_w(F) = \left[\dfrac{\Sigma\, w(F_{\text{obs}} - k \lvert F_{\text{calc}} \rvert)^2}{\Sigma\, w F_{\text{obs}}{}^2} \right]^{1/2}$

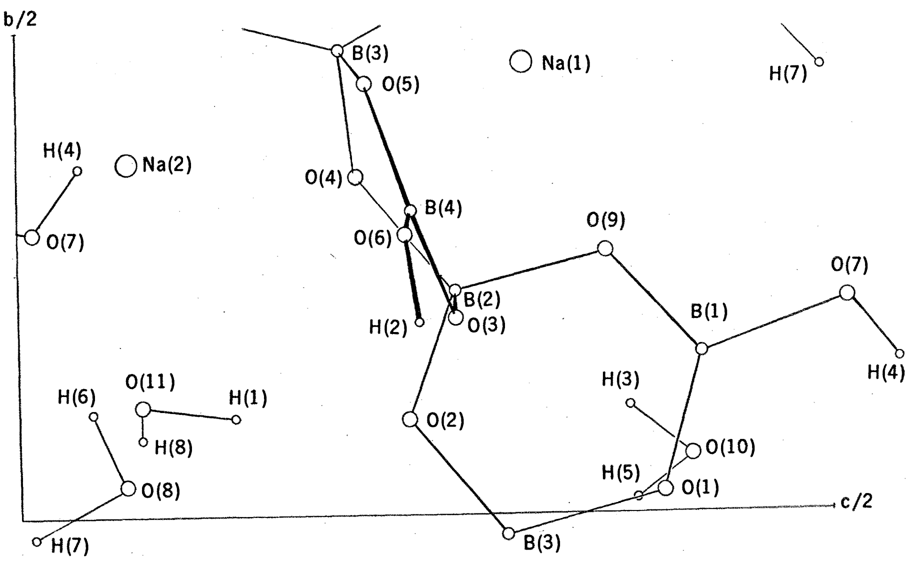

Fig. 1. Projection of the structure on the *bc* plane.

the general features are common to all three sets of results. Thus, the sodium atoms bear partial positive charges of 0.4 to 0.5 unit, whereas the boron and hydrogen atoms are positively charged and the oxygen atoms are everywhere negatively charged. This charge distribution 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 a consideration of interatomic distances, that "atoms tend to be much more neutral in a crystal than a straight ionic interpretation would indicate" (*11*).

A choice from among the three sets of results is necessary for a more detailed discussion of the results. As noted earlier (*12*), the choice of atomic orbitals leads to differing values of the scale factor *k*, defined by

$$F_{obs} = kF_{calc}$$

the STO scale factors being considerably smaller than the scale factors obtained in the isolated atom Hartree-Fock treatment. The same effect is found in the present study (Table 1).

Thin, but extended sheets of kernite can be easily obtained because of the excellent cleavage of the crystals. By employing such a sheet larger than the x-ray beam (such that all the intensity in the beam is subject to diffraction) and measuring the direct and the reflected beams for a series of reflections, we have succeeded in obtaining an experimental value for *k* in our original data set. The experimental value of 1.23 ± 0.015 indicates *that the molecule-optimized Slater type orbitals of Hehre* et al. (*9*) *give a better description of the valence electron distribution in the crystal than the HF results obtained on isolated atoms.* This experimental value does not, within the experimental errors, distinguish clearly between the models represented by the last two columns of Table 1, although the *k* value obtained with the model of column 4 is in better agreement with that of the experiment than the other *k* values. Because this model also gives the lowest x-ray agreement factors, it will be used in the following discussion.

The most significant conclusion to be drawn from a detailed analysis of the net charges is the lack of distinction according to chemical environment. Thus, the charges on the sodium atoms are equal to within the experimental errors, even though the coordination is somewhat different, with Na(1) and Na(2) showing six- and fivefold coordination, respectively. Similarly, no difference is found between the bridging oxygen atoms O(1), O(2), O(3), O(4), O(5), and O(9); the hydroxylic oxygen atoms O(6) and O(7); and the water oxygen atoms O(8), O(10), and O(11). The averages over the charges in these three groups are -0.47_5, -0.43, and -0.40 positive units, respectively, with a fairly large range of values in each group. In earlier stages of the refinement it appeared that the tetrahedrally coordinated baron atoms B(2) and B(3) were less positively charged than the trigonally coordinated B(1) and B(4) atoms, but the final results show no clear differentiation. According to a valence bond diagram, a tetrahedrally coordinated boron atom bears a formal negative charge of one electron, but it appears that there is no relation between this idealized situation and the actual charge distribution.

Further information on the charge distribution is provided by difference density maps. Since the least-squares, curve-fitting procedure tends to produce difference maps in which bonding effects have been compensated for by adjustment of parameters, we have performed a second least-squares refinement, using only high-order data with $(\sin \theta/\lambda)_{min} > 0.6$ Å^{-1}. The resulting parameters are less affected by bonding, and they were used in the calculation of a number of maps showing the observed minus the calculated spherical atom density. In these maps (not shown here because of space limitations), density is observed between the boron and oxygen atoms, which further supports the covalent nature of these bonds. Corresponding maps through planes containing the sodium atoms show little density between the sodium and oxygen atoms, indicating that the bonds between these atoms are more ionic.

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13. We thank Drs. W. McLean and G. Donnay of McGill University for performing the microprobe analysis, Dr. R. F. Giese for supplying the crystals and discussing the results, Dr. C. Clemency for access to the x-ray fluorescence equipment used for crystal thickness measurements (which were part of the scale factor determination), and Dr. F. K. Ross for experimental assistance in the scale factor determination. Supported by funds from the National Science Foundation.

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