

## KALIBORITE: AN EXAMPLE OF A CRYSTALLOGRAPHICALLY SYMMETRICAL HYDROGEN BOND

PETER C. BURNS\* AND FRANK C. HAWTHORNE

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2*

### ABSTRACT

The crystal structure of kaliborite,  $\text{KMg}_2\text{H}[\text{B}_6\text{O}_8(\text{OH})_5]_2(\text{H}_2\text{O})_4$ , monoclinic,  $a$  18.572(6),  $b$  8.466(3),  $c$  14.689(5) Å,  $\beta$  100.02(3)°,  $V$  2274(1) Å<sup>3</sup>,  $Z = 4$ , space group  $C2/c$ , has been refined by full-matrix least-squares methods to an  $R$  index of 4.4% and a  $wR$  index of 4.7% for 2403 unique observed [ $F \geq 5\sigma(F)$ ] reflections measured with  $\text{MoK}\alpha$  X-radiation. The kaliborite structure contains a  $6:(2\Delta + 3T) + \Delta$  fundamental building block (FBB). Each FBB contains a pentaborate ( $2\Delta + 3T$ ) unit composed of two three-membered ( $1\Delta + 2T$ ) rings and an additional triangle that is attached to the pentaborate unit. The borate FBBs polymerize, forming zigzag chains along  $b$ . The Mg cation is in octahedral coordination, and linked to an adjacent borate chain. The heteropolyhedral chains are joined through the K atoms, which are in a distorted cubic coordination, and *via* hydrogen bonds. Nine of the ten hydrogen atoms provide bonding between the heteropolyhedral chains, the other hydrogen atom links anions of the same heteropolyhedral chain. Kaliborite is one of two borate minerals that are known to contain a crystallographically symmetrical hydrogen bond.

*Keywords:* hydrogen bonding, kaliborite, borate, crystal structure.

### SOMMAIRE

La structure cristalline de la kaliborite,  $\text{KMg}_2\text{H}[\text{B}_6\text{O}_8(\text{OH})_5]_2(\text{H}_2\text{O})_4$ , monoclinique,  $a$  18.572(6),  $b$  8.466(3),  $c$  14.689(5) Å,  $\beta$  100.02(3)°,  $V$  2274(1) Å<sup>3</sup>,  $Z = 4$ , groupe spatial  $C2/c$ , a été affiné par moindres carrés à matrice entière jusqu'à un résidu  $R$  de 4.4% ( $wR = 4.7\%$ ) en utilisant 2403 réflexions uniques observées [ $F \geq 5\sigma(F)$ ] et mesurées avec rayonnement  $\text{MoK}\alpha$ . La structure contient un bloc structural fondamental  $6:(2\Delta + 3T) + \Delta$ . Chacun de ces blocs contient une unité à cinq atomes de bore ( $2\Delta + 3T$ ) composée de deux anneaux à trois membres ( $1\Delta + 2T$ ) et un triangle additionnel rattaché à l'unité pentaboratée. Ces blocs structuraux fondamentaux sont polymérisés en chaînes en zigzag le long de  $b$ . Le cation Mg a une coordinence octaédrique, et est lié à une chaîne de borate adjacente. Les chaînes hétéropolyédriques sont articulées par les atomes de K, qui possèdent une coordinence cubique difforme, et par des liaisons hydrogène. Neuf des dix atomes d'hydrogène contribuent à la liaison entre chaînes hétéropolyédriques, et l'autre atome d'hydrogène lie les anions au sein d'une même chaîne hétéropolyédrique. La kaliborite est un de deux borates connus ayant une liaison hydrogène cristallographiquement symétrique.

(Traduit par la Rédaction)

*Mots-clés:* liaison hydrogène, kaliborite, borate, structure cristalline.

### INTRODUCTION

Kaliborite,  $\text{KMg}_2\text{H}[\text{B}_6\text{O}_8(\text{OH})_5]_2(\text{H}_2\text{O})_4$ , occurs in a number of localities, including the salt deposits at Leopoldshall, at Neustrassfurt, and near Aschersleben, Saxony, Germany; in the salt deposits at Mte. Sambuco, Calascibetta, Sicily; at Sallent, Spain; and in the Inder Lake deposits, Kazakhstan. Corazza & Sabelli (1966) determined the structure of kaliborite

using X-ray data recorded on photographic plates, and they refined the structure to an  $R$  index of 9.5%.

Clark & Christ (1977) noted that there are apparently unusual (*i.e.*, crystallographically symmetrical) hydrogen bonds in the structures of preobrazhenskite and kaliborite, although the precision of the X-ray data collected for these minerals by Rumanova *et al.* (1972) and Corazza & Sabelli (1966) precluded the location of these hydrogen atoms. We have recently verified that there is a crystallographically symmetrical hydrogen bond in preobrazhenskite (Burns & Hawthorne 1994a), and here we report a refinement of the structure of kaliborite, including a discussion of the hydrogen bonds.

\* Present address: Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

## EXPERIMENTAL

## STRUCTURE REFINEMENT

*Collection of X-ray data*

A sample of kaliborite from Kazakhstan was obtained from the Canadian Museum of Nature (sample number 53372). A small cleavage fragment was mounted on a Nicolet R3m automated four-circle diffractometer. Twenty-two reflections over the range  $11^\circ \leq 2\theta \leq 27^\circ$  were centered using graphite-mo-chromated MoK $\alpha$  X-radiation. The unit-cell dimensions (Table 1) were derived from the setting angles of the twenty-two automatically aligned reflections by least-squares techniques. Data were collected using the  $\theta$ - $2\theta$  scan method with a  $2.2^\circ$   $2\theta$  scan range and a variable scan-rate ranging from 4 to  $29.3^\circ$   $2\theta$ /min. A total of 3642 reflections was measured; the index ranges  $0 \leq h \leq 26$ ,  $0 \leq k \leq 11$ ,  $-20 \leq l \leq 20$  were covered, and reflections forbidden by the C-centering were omitted. Two standard reflections were measured every fifty reflections; no significant change in their intensities occurred during data collection. An empirical absorption-correction based on 36 psi-scans for each of 10 reflections over the range  $11^\circ \leq 2\theta \leq 56^\circ$  was applied, reducing  $R$ (azimuthal) from 2.55 to 2.04%. The data were corrected for Lorentz, polarization, and background effects; of the 3642 reflections measured, there were 2403 classed as observed [ $F \geq 5\sigma(F)$ ].

*Infrared spectroscopy*

A powdered sample was prepared by grinding about 20 mg of kaliborite in an alumina mortar until the grain size was generally less than 2  $\mu$ m. About 2 mg of sample was mixed with 150 mg of KBr by grinding in an alumina mortar. The resulting mixture was pressed in an evacuated die into a 13-mm pellet. A high-resolution infrared spectrum was recorded on a Bomen Michelson 100 Fourier-transform interferometric infrared spectrometer. Frequency measurements were calibrated internally against a He-Ne laser and are accurate to  $0.01 \text{ cm}^{-1}$ , according to the manufacturer.

TABLE 1. MISCELLANEOUS INFORMATION FOR KALIBORITE

Space group	C2/c	Crystal Size (mm)	0.12 x 0.16 x 0.24
<i>a</i> (Å)	18.572(6)	Total ref.	3642
<i>b</i> (Å)	8.466(3)	[ $F > 5\sigma(F)$ ]	2403
<i>c</i> (Å)	14.689(5)	Final <i>R</i>	4.4
$\beta$ (°)	100.02(3)	Final <i>wR</i>	4.7
<i>V</i> (Å <sup>3</sup> )	2274(1)	GOF*	2.5
Unit-cell contents 4{KMg <sub>2</sub> HB <sub>3</sub> O <sub>6</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> }			
$R = \sum( F_o  -  F_c ) / \sum  F_o $			
$wR = [\sum w( F_o  -  F_c )^2]^{1/2} / \sum w F_o^2$ , $w = 1/\sigma^2(F)$			

\* GOF = Goodness of fit

Scattering curves for neutral atoms, together with anomalous-dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively. The Siemens SHELXTL PLUS (PC version) system of programs was used throughout this study. The *R* indices are of the form given in Table 1 and are expressed as percentages.

Refinement of the structure was done in the space group C2/c using the atomic parameters of Corazza & Sabelli (1966) as the starting model. Refinement of the atomic positional parameters and isotropic displacement parameters gave an *R* index of 8.2%. Conversion to an anisotropic displacement model, together with refinement of all parameters, gave an *R* index of 5.3%. At this stage of the refinement, a three-dimensional difference-Fourier map was calculated, and the position of ten hydrogen atoms was determined. Subsequent cycles of refinement showed that the hydrogen positions were not well-behaved, as indicated by anomalously short O-H bond lengths, a common feature of hydrogen positions refined using X-ray data. The "soft" constraint that O-H distances should be  $\sim 0.96$  Å was imposed by adding extra weighted observational equations to the least-squares matrix. Only the O-H distance is constrained, and each H position is free to refine around the oxygen atom. Neutron-diffraction studies (*i.e.*, Hamilton & Ibers 1968) of structures containing hydrogen bonds have shown that donor-hydrogen bond lengths do vary somewhat with the hydrogen-acceptor bond length. However, the donor-hydrogen bond lengths obtained *via* unconstrained refinement of X-ray data normally fall well outside the range found using neutron data, and this makes the hydrogen bonding in the structure difficult or impossible to interpret. Neutron-diffraction studies of borate minerals are limited owing to extreme absorption effects. Therefore, the most appropriate way to obtain information on hydrogen bonding is *via* constrained refinement of X-ray data, and we have found (Burns & Hawthorne 1993a, b, 1994b) that this approach gives realistic hydrogen-bonding schemes for various borate minerals. Refinement of all parameters gave a final *R* index of 4.4% and a *wR* index of 4.7%. Models including a refinable weighting scheme of structure factors and an isotropic extinction correction were tried, but did not improve the results. Final atomic positional and equivalent isotropic displacement parameters are given in Table 2, anisotropic displacement parameters in Table 3, selected interatomic distances and angles in Table 4, and a bond-valence analysis is given in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR KALIBORITE

	x	y	z	$^{\circ}U_{eq}$
K	0	0.1187(1)	1/4	262(3)
Mg	0.13784(5)	0.4234(1)	0.16721(6)	97(3)
B(1)	0.5005(1)	0.1473(4)	0.1077(2)	107(7)
B(2)	0.0891(2)	0.8378(4)	0.0256(2)	143(8)
B(3)	0.1109(1)	0.7955(3)	0.1964(2)	94(7)
B(4)	0.2628(1)	0.2025(3)	0.2548(2)	107(7)
B(5)	0.3047(1)	0.4591(3)	0.1928(2)	89(7)
B(6)	0.2399(2)	0.4974(4)	0.0236(2)	173(8)
O(1)	0.0134(1)	0.7310(2)	0.0241(1)	153(5)
OH(2)	0.0361(1)	0.7340(2)	0.1889(1)	111(5)
O(3)	0.1171(1)	0.8722(2)	0.1054(1)	130(5)
O(4)	0.37643(9)	0.3994(2)	0.2268(1)	112(5)
O(5)	0.1658(1)	0.6612(2)	0.2088(1)	116(5)
O(6)	0.2946(1)	0.6096(2)	0.2380(1)	176(6)
O(7)	0.2466(1)	0.3481(2)	0.2104(1)	117(5)
O(8)	0.2991(1)	0.4863(3)	0.0914(1)	176(6)
OH(9)	0.4214(1)	0.1352(2)	0.1073(1)	145(5)
OH(10)	0.4278(1)	0.5920(3)	0.0568(1)	270(7)
OH(11)	0.0321(1)	0.4888(2)	0.1126(1)	152(5)
OH(12)	0.2557(1)	0.9580(4)	0.0647(1)	327(8)
OH(13)	0.1710(1)	0.4636(3)	0.0411(1)	200(6)
OW(14)	0.0988(1)	0.2048(3)	0.1204(2)	230(6)
OW(15)	0.3892(1)	0.8757(3)	0.2046(1)	204(6)
H(1)	0	0.257(8)	3/4	564(48)**
H(2)	0.408(3)	0.235(3)	0.130(3)	564(48)
H(3)	0.383(1)	0.546(6)	0.067(3)	564(48)
H(4)	0.003(2)	0.422(5)	0.068(2)	564(48)
H(5)	0.207(1)	0.839(6)	0.076(3)	564(48)
H(6)	0.148(2)	0.439(6)	-0.020(1)	564(48)
H(7)	0.120(2)	0.101(3)	0.123(3)	564(48)
H(8)	0.077(2)	0.196(6)	0.057(1)	564(48)
H(9)	0.404(3)	0.964(4)	0.172(3)	564(48)
H(10)	0.341(1)	0.851(6)	0.173(3)	564(48)

\*  $U_{eq} = U_{eq} \times 10^4$ \*\* A single  $U_{eq}$  was refined for all H.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR KALIBORITE

	$^{\circ}U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
K	241(5)	292(6)	254(5)	0	50(4)	0
Mg	87(4)	90(4)	104(4)	-2(3)	-8(3)	-7(3)
B(1)	89(11)	130(13)	93(11)	-19(10)	-8(9)	-9(10)
B(2)	127(12)	161(14)	130(13)	-6(11)	-3(10)	-20(11)
B(3)	100(12)	87(12)	94(11)	-9(10)	14(9)	0(10)
B(4)	116(13)	99(13)	103(12)	-4(10)	13(10)	12(10)
B(5)	79(11)	82(12)	97(11)	7(9)	-6(9)	-16(9)
B(6)	150(13)	253(17)	106(13)	6(12)	-8(11)	-14(12)
O(1)	167(9)	177(9)	103(8)	7(7)	-6(7)	-58(8)
OH(2)	90(8)	151(9)	88(8)	-28(7)	4(6)	-32(7)
O(3)	123(8)	151(9)	110(8)	19(7)	5(7)	-38(7)
O(4)	87(8)	107(8)	136(8)	35(7)	-1(6)	11(6)
O(5)	91(8)	82(8)	159(9)	-18(7)	-21(7)	12(7)
O(6)	115(8)	114(9)	281(11)	-69(8)	-16(8)	2(7)
O(7)	97(8)	91(8)	157(9)	25(7)	4(6)	3(6)
O(8)	119(8)	278(11)	114(8)	63(8)	-23(7)	-30(8)
OH(9)	84(8)	182(10)	159(9)	-28(8)	-8(7)	-20(7)
OH(10)	251(11)	403(14)	137(9)	98(10)	-19(8)	-146(10)
OH(11)	132(9)	114(9)	188(9)	-30(8)	-36(7)	10(7)
OH(12)	162(10)	676(19)	131(10)	120(11)	-5(8)	-43(12)
OH(13)	123(9)	348(13)	117(9)	11(9)	-16(7)	-46(8)
OW(14)	244(11)	119(10)	278(11)	-17(9)	-96(9)	17(8)
OW(15)	228(10)	203(11)	181(10)	-15(8)	33(8)	-46(9)

\*  $U_{ij} = U_{ij} \times 10^4$ 

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR KALIBORITE

K-O(4) <sub>a,b</sub>	2.825(2) x2	B(3)-OH(2)	1.470(3)
K-OH(10) <sub>a,b</sub>	2.829(2) x2	B(3)-O(3)	1.508(3)
K-OW(14) <sub>c</sub>	2.855(3) x2	B(3)-O(4) <sub>g</sub>	1.418(3)
K-OW(15) <sub>a,b</sub>	2.889(2) x2	B(3)-O(5)	1.518(3)
<K-O>	2.849	<B(3)-O>	1.478
Mg-O(8)	2.141(2)	B(4)-O(5) <sub>b</sub>	1.388(3)
Mg-O(7)	2.113(2)	B(4)-O(8) <sub>b</sub>	1.343(4)
Mg-OH(11)	2.064(2)	B(4)-O(7)	1.386(3)
Mg-OH(13)	2.079(2)	<B(4)-O>	1.372
Mg-OW(14)	2.062(2)	B(5)-O(4)	1.431(3)
Mg-OW(15) <sub>b</sub>	2.071(3)	B(5)-O(6)	1.464(4)
<Mg-O>	2.088	B(5)-O(7)	1.499(3)
B(1)-O(1) <sub>d</sub>	1.473(4)	B(5)-O(8)	1.492(3)
B(1)-OH(2) <sub>d</sub>	1.458(3)	<B(5)-O>	1.471
B(1)-OH(9)	1.472(3)	B(6)-O(8)	1.382(3)
B(1)-OH(11) <sub>e</sub>	1.461(4)	B(6)-OH(12) <sub>f</sub>	1.367(4)
<B(1)-O>	1.466	B(6)-OH(13)	1.379(4)
B(2)-O(1)	1.372(4)	<B(6)-O>	1.366
B(2)-O(3)	1.376(3)		
B(2)-OH(10) <sub>f</sub>	1.358(4)		
<B(2)-O>	1.369		
Hydrogen bonding			
OH(2) <sub>h</sub> -H(1)	1.212(7)	H(1)-OH(2) <sub>h</sub>	1.212(7)
OH(2) <sub>h</sub> -OH(2) <sub>h</sub>	2.421(4)	OH(2) <sub>h</sub> -H(1)-OH(2) <sub>h</sub>	173(7)
OH(9) <sub>i</sub> -H(2)	0.95(3)	H(2)-O(4)	2.14(4)
OH(9) <sub>i</sub> -O(4)	3.049(3)	OH(9) <sub>i</sub> -H(2)-O(4)	158(4)
OH(10) <sub>j</sub> -H(3)	0.96(3)	H(3)-O(8)	1.73(3)
OH(10) <sub>j</sub> -O(8)	2.684(3)	OH(10) <sub>j</sub> -H(3)-O(8)	173(5)
OH(11) <sub>k</sub> -H(4)	0.96(4)	H(4)-O(11)	1.86(4)
OH(11) <sub>k</sub> -O(11)	2.760(3)	OH(11) <sub>k</sub> -H(4)-O(11)	156(4)
OH(12) <sub>l</sub> -H(5)	0.95(3)	H(5)-O(3)	1.89(3)
OH(12) <sub>l</sub> -O(3)	2.836(3)	OH(12) <sub>l</sub> -H(5)-O(3)	171(4)
OH(13) <sub>m</sub> -H(6)	0.95(3)	H(6)-OH(9) <sub>k</sub>	1.75(3)
OH(13) <sub>m</sub> -OH(9) <sub>k</sub>	2.683(3)	OH(13) <sub>m</sub> -H(6)-OH(9) <sub>k</sub>	159(3)
OW(14) <sub>n</sub> -H(7)	0.96(3)	H(7)-O(3)	1.96(2)
OW(14) <sub>n</sub> -O(3)	2.849(3)	OW(14) <sub>n</sub> -H(7)-O(3) <sub>h</sub>	155(4)
OW(14) <sub>n</sub> -H(8)	0.96(2)	H(8)-O(11)	1.98(4)
OW(14) <sub>n</sub> -O(11)	2.787(3)	OW(14) <sub>n</sub> -H(8)-O(11)	137(4)
H(7)-H(8)	1.39(5)	H(7)-OW(14) <sub>n</sub> -H(8)	94(4)
OW(15) <sub>o</sub> -H(9)	0.96(4)	H(9)-OH(9) <sub>m</sub>	1.79(4)
OW(15) <sub>o</sub> -OH(9) <sub>m</sub>	2.743(3)	OW(15) <sub>o</sub> -H(9)-OH(9) <sub>m</sub>	174(4)
OW(15) <sub>o</sub> -H(10)	0.98(3)	H(10)-OH(12)	2.23(3)
OW(15) <sub>o</sub> -OH(12)	3.014(3)	OW(15) <sub>o</sub> -H(10)-OH(12)	139(4)
H(9)-H(10)	1.51(6)	H(9)-OW(15) <sub>o</sub> -H(10)	104(4)
K polyhedron			
O(4) <sub>a,b</sub> -K-OH(10) <sub>a,b</sub>	3.261(3) x2	O(4) <sub>a,b</sub> -K-OH(10) <sub>a,b</sub>	67.7(1) x2
O(4) <sub>a,b</sub> -K-OW(14) <sub>a</sub>	3.402(3) x2	O(4) <sub>a,b</sub> -K-OW(14) <sub>a</sub>	70.7(1) x2
O(4) <sub>a,b</sub> -K-OW(15) <sub>a,b</sub>	4.056(3) x2	O(4) <sub>a,b</sub> -K-OW(15) <sub>a,b</sub>	86.6(1) x2
OH(10) <sub>a,b</sub> -K-OW(14) <sub>a</sub>	3.291(3) x2	OH(10) <sub>a,b</sub> -K-OW(14) <sub>a</sub>	68.0(1) x2
OH(10) <sub>a,b</sub> -K-OW(15) <sub>a,b</sub>	3.397(3) x2	OH(10) <sub>a,b</sub> -K-OW(15) <sub>a,b</sub>	70.1(1) x2
OW(14) <sub>a</sub> -K-OW(15) <sub>a,b</sub>	2.924(3) x2	OW(14) <sub>a</sub> -K-OW(15) <sub>a,b</sub>	68.9(1) x2
OW(15) <sub>a</sub> -K-OW(15) <sub>b</sub>	4.098(3)	OW(15) <sub>a</sub> -K-OW(15) <sub>b</sub>	86.8(1)
<O-K-O>	3.443	<O-K-O>	71.6
Mg octahedron			
O(5)-O(7)	3.059(3)	O(5)-Mg-O(7)	92.0(1)
O(5)-OH(11)	3.011(3)	O(5)-Mg-OH(11)	91.5(1)
O(5)-OH(13)	2.991(3)	O(5)-Mg-OH(13)	90.3(1)
O(5)-OW(15) <sub>b</sub>	2.994(3)	O(5)-Mg-OW(15) <sub>b</sub>	90.6(1)
O(7)-OH(13)	2.816(3)	O(7)-Mg-OH(13)	84.4(1)
O(7)-OW(14)	3.074(3)	O(7)-Mg-OW(14)	84.8(1)
O(7)-OW(15) <sub>b</sub>	3.013(3)	O(7)-Mg-OW(15) <sub>b</sub>	82.1(1)
OH(11)-OH(13)	2.857(3)	OH(11)-Mg-OH(13)	91.1(1)
OH(11)-OW(14)	2.698(3)	OH(11)-Mg-OW(14)	81.7(1)
OH(11)-OW(15) <sub>b</sub>	2.982(3)	OH(11)-Mg-OW(15) <sub>b</sub>	92.3(1)
OH(13)-OW(14)	2.915(3)	OH(13)-Mg-OW(14)	89.5(1)
OW(14)-OW(15) <sub>b</sub>	2.924(3)	OW(14)-Mg-OW(15) <sub>b</sub>	90.1(1)
<O-O>	2.993	<O-Mg-O>	90.0
B(1) tetrahedron			
O(1) <sub>d</sub> -OH(2) <sub>d</sub>	2.384(3)	O(1) <sub>d</sub> -B(1)-OH(2) <sub>d</sub>	106.9(2)
O(1) <sub>d</sub> -OH(9)	2.407(3)	O(1) <sub>d</sub> -B(1)-OH(9)	109.7(2)
O(1)-OH(11) <sub>e</sub>	2.421(3)	O(1) <sub>d</sub> -B(1)-OH(11) <sub>e</sub>	112.2(2)
OH(2) <sub>d</sub> -OH(9)	2.405(3)	OH(2) <sub>d</sub> -B(1)-OH(9)	110.3(2)
OH(2) <sub>d</sub> -OH(11) <sub>e</sub>	2.354(3)	OH(2) <sub>d</sub> -B(1)-OH(11) <sub>e</sub>	107.6(2)
OH(9)-OH(11) <sub>e</sub>	2.399(3)	OH(9)-B(1)-OH(11) <sub>e</sub>	109.1(2)
<O-O>	2.393	<O-B(1)-O>	109.6

TABLE 4 — (Continued)

## DESCRIPTION OF THE STRUCTURE

<b>B(2) triangle</b>			
O(1)–O(3)	2.402(3)	O(1)–B(2)–O(3)	121.8(3)
O(1)–OH(10)f	2.302(3)	O(1)–B(2)–OH(10)f	115.0(2)
O(3)–OH(10)f	2.403(3)	O(3)–B(2)–OH(10)f	123.1(3)
<O–O>	2.368	<O–B(2)–O>	120.0
<b>B(3) tetrahedron</b>			
OH(2)–O(3)	2.404(3)	OH(2)–B(3)–O(3)	107.8(2)
OH(2)–O(4)g	2.331(3)	OH(2)–B(3)–O(4)g	107.8(2)
OH(2)–O(5)	2.485(3)	OH(2)–B(3)–O(5)	110.5(2)
O(3)–O(4)g	2.485(3)	O(3)–B(3)–O(4)g	114.2(2)
O(3)–O(5)	2.414(3)	O(3)–B(3)–O(5)	105.8(2)
O(4)g–O(5)	2.417(3)	O(4)g–B(3)–O(5)	110.9(2)
<O–O>	2.413	<O–B(3)–O>	108.4
<b>B(4) triangle</b>			
O(5)b–O(6)b	2.398(3)	O(5)b–B(4)–O(6)b	122.6(2)
O(5)b–O(7)	2.416(3)	O(5)b–B(4)–O(7)	121.2(2)
O(6)b–O(7)	2.317(3)	O(6)b–B(4)–O(7)	116.2(2)
<O–O>	2.376	<O–B(4)–O>	120.0
<b>B(5) tetrahedron</b>			
O(4)–O(6)	2.365(3)	O(4)–B(5)–O(6)	109.5(2)
O(4)–O(7)	2.424(3)	O(4)–B(5)–O(7)	111.7(2)
O(4)–O(8)	2.359(3)	O(4)–B(5)–O(8)	107.6(2)
O(6)–O(7)	2.410(3)	O(6)–B(5)–O(7)	108.8(2)
O(6)–O(8)	2.407(3)	O(6)–B(5)–O(8)	109.0(2)
O(7)–O(8)	2.451(3)	O(7)–B(5)–O(8)	110.0(2)
<O–O>	2.403	<O–B(5)–O>	108.5
<b>B(6) triangle</b>			
O(8)–OH(12)f	2.388(3)	O(8)–B(6)–OH(12)f	122.9(3)
O(8)–OH(13)	2.373(3)	O(8)–B(6)–OH(13)	120.6(3)
OH(12)f–OH(13)	2.335(3)	OH(12)f–B(6)–OH(13)	116.5(2)
<O–O>	2.365	<O–B(6)–O>	120.0

$$a = x - \frac{1}{2}, y - \frac{1}{2}, z; b = \frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z; c = \bar{x}, y, \frac{1}{2} - z; d = x + \frac{1}{2}, y + \frac{1}{2}, z; e = x + \frac{1}{2}, y - \frac{1}{2}, z; f = \frac{1}{2} - x, \bar{y} + \frac{1}{2}, \bar{z}; g = \frac{1}{2} - x, y + \frac{1}{2}, \frac{1}{2} - z; h = \bar{x}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}; i = \bar{x}, \bar{y} + \frac{1}{2}, z + \frac{1}{2}; j = \bar{x}, \bar{y} + \frac{1}{2}, \bar{z}; k = \frac{1}{2} - x, \frac{1}{2} - y, \bar{z}; l = x, y - 1, z; m = x, y + 1, z.$$

*Fundamental building block*

The fundamental building block (*FBB*) in kaliborite contains six boron atoms (Fig. 1). There are three  $[B(O,OH)_4]$  tetrahedra and three  $[B(O,OH)_3]$  triangles in the *FBB*. The B(1)O(OH)<sub>3</sub>, B(3)O<sub>3</sub>(OH), and B(5)O<sub>4</sub> tetrahedra have <B–O> distances of 1.466, 1.478, and 1.471 Å, respectively, and the B(2)O<sub>2</sub>(OH), B(4)O<sub>3</sub>, and B(6)O(OH)<sub>2</sub> triangles have <B–O> distances of 1.369, 1.372, and 1.366 Å, respectively. These distances are within the ranges typical of  $<^{[4]}B-O>$  and  $<^{[3]}B-O>$  observed in minerals.

The *FBB* contains two three-membered rings that contain two tetrahedra and one triangle (Fig. 1). The (1Δ + 2T) rings form a pentaborate unit by sharing the B(3)O<sub>3</sub>(OH) tetrahedron. Using the notation of Christ & Clark (1977), this pentaborate unit may be written as (2Δ + 3T). The kaliborite *FBB* has an additional  $[B(O,OH)_3]$  triangle that is attached to the pentaborate unit *via* corner-sharing (Fig. 1); thus the *FBB* may be written as 6:(2Δ + 3T) + Δ. Such a *FBB* has not been observed in other borate minerals, but the (2Δ + 3T) pentaborate unit is quite common. It occurs as an isolated cluster in the structures of garrelsite and ulexite, and it polymerizes to form chains in the structures of larderellite and probertite, sheets in the structure of heidornite, and frameworks in the structures of the polymorphs of hilgardite.

TABLE 5. BOND-VALENCE\* ANALYSIS FOR KALIBORITE

	K	Mg	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)	Σ
O(1)			0.759	0.997								0.18				0.15			2.086
OH(2)			0.790		0.765				0.50 <sup>2</sup> ‡										2.055
O(3)				0.987	0.690								0.17		0.16				2.007
O(4)	0.117 <sup>2</sup> ‡				0.881		0.850			0.12									1.968
O(5)		0.298			0.676	0.955													1.929
O(6)						1.079	0.778												1.857
O(7)		0.321				0.980	0.708												1.989
O(8)							0.721	1.053			0.20								1.974
OH(9)			0.781							0.88				0.20		0.19			2.031
OH(10)	0.118 <sup>2</sup> ‡			1.036							0.80								1.952
OH(11)		0.367	0.784									0.82							1.971
OH(12)								1.011					0.83					0.10	1.941
OH(13)		0.352						0.979						0.80					2.131
OW(14)	0.108 <sup>2</sup> ‡	0.369													0.84	0.85			2.167
OW(15)	0.099 <sup>2</sup> ‡	0.360															0.81	0.80	2.169
Σ	0.880	2.067	3.084	3.020	3.012	2.994	3.067	3.043	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

\* parameters from Brown &amp; Altermatt (1985)

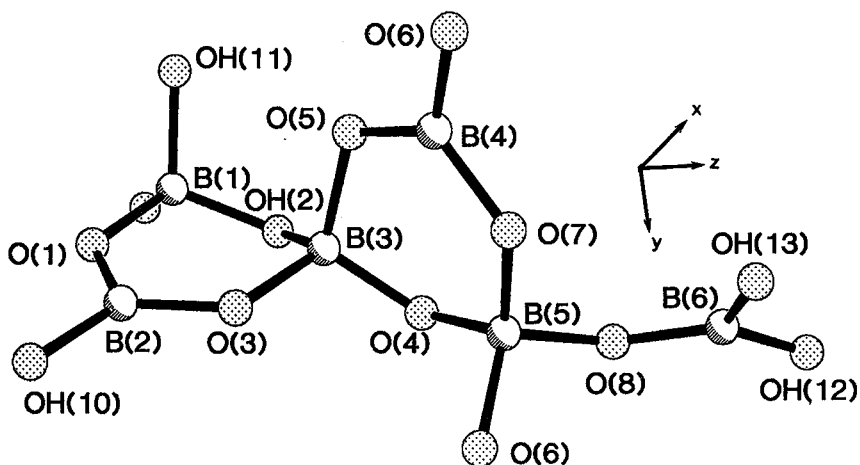


FIG. 1. The fundamental building block in kaliborite.

#### *Mg and K coordinations*

The kaliborite structure contains one Mg position. The Mg cation is coordinated by two oxygen anions, two hydroxyl groups, and two ( $\text{H}_2\text{O}$ ) groups in an octahedral arrangement. The  $\langle \text{Mg}-\text{O} \rangle$  distance is 2.088 Å, and individual Mg-O distances range from 2.062 to 2.141 Å. The single position occupied by K in the kaliborite structure is located on a center of symmetry. It is coordinated by two oxygen anions,

two hydroxyl groups and four ( $\text{H}_2\text{O}$ ) groups located at the corners of a distorted cube. The  $\langle \text{K}-\text{O} \rangle$  distance is 2.949 Å, and individual bond-lengths range from 2.925 to 2.989 Å.

#### *Structural connectivity*

The borate *FBBs* polymerize to form chains running along *b* (Fig. 2). The *FBBs* polymerize by sharing the O(6) anion, which links the B(5) tetrahedron of

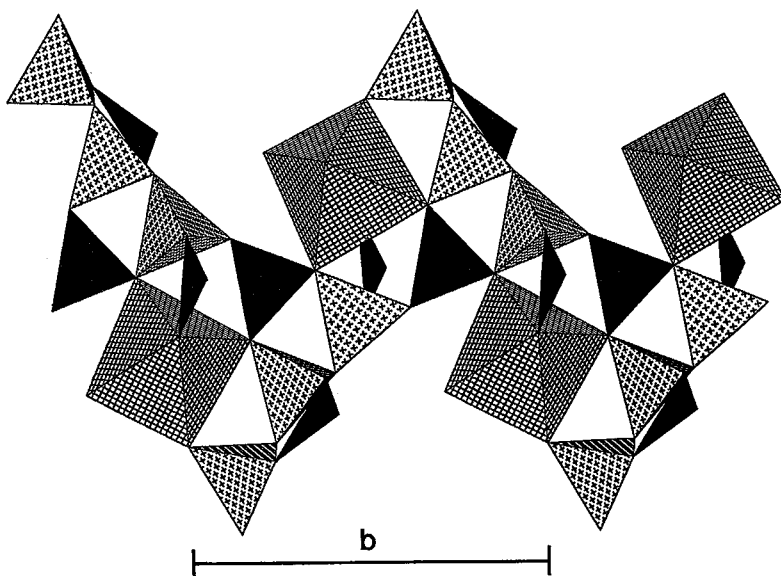


FIG. 2. The heteropolyhedral chains of kaliborite projected onto (001). Borate tetrahedra are shaded with crosses, borate triangles are given as solid triangles, and magnesium octahedra are cross-hatched.

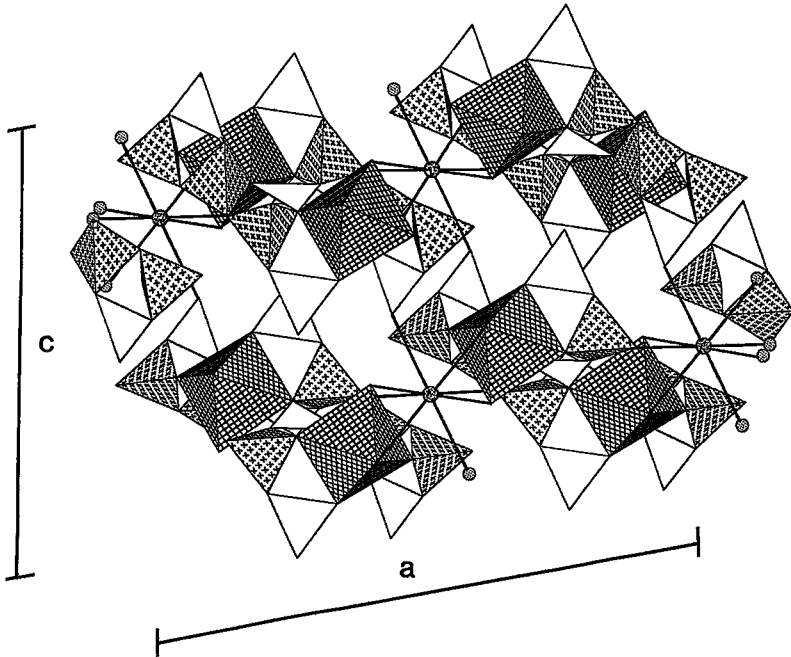


FIG. 3. The structure of kaliborite projected onto (010). Borate tetrahedra are shaded with crosses, borate triangles are given as open triangles, magnesium octahedra are cross-hatched, and potassium atoms are represented by circles shaded with a random-dot pattern.

one *FBB* and the B(4) triangle of the next *FBB* in the chain. The B(5) tetrahedra and B(4) triangles alternate along *b*, and the rest of the *FBB* is oriented such that its long direction is subperpendicular to the chain. This *FBB* linkage results in a zigzag chain (Fig. 2).

The  $Mg\phi_6$  ( $\phi$ : unspecified ligand) octahedra attach to the borate chains, forming heteropolyhedral chains (Fig. 2). The Mg cation bonds to four anions that are part of the borate chain and to two ( $H_2O$ ) groups. In a given Mg octahedron, there are two bonds to each of the adjacent borate *FBBs*, both of which are members of the same borate chain; Mg thus does not provide any interchain linkage.

The heteropolyhedral chains are linked through the K cation and *via* a network of hydrogen bonds (see below). The K cation bonds to four different adjacent chains (Fig. 3). The two heteropolyhedral chains closest to the K position attach through three bonds each; two involve ( $H_2O$ ) groups of the Mg octahedron, the third involves the O(4) anion, which bridges between the B(3) and B(5) tetrahedra of the same borate *FBB*. The K atom also has a bond to two more distant chains *via* the OH(10) anion, which bonds to the B(2) cation.

## HYDROGEN BONDING

The hydrogen positions obtained *via* constrained least-squares refinement of the X-ray data are realistic in terms of bond lengths and angles (Table 4), as well as in the bond-valence requirements of the donor and acceptor anions (Table 5). There are ten hydrogen positions in kaliborite (Table 2, Fig. 4), nine of which provide linkages between the heteropolyhedral chains. Of these, six positions provide linkages along [001], and three do so along [101]. The other hydrogen atom links anions of the same heteropolyhedral chain along [010].

### *Hydrogen bonds along [001]*

Six hydrogen atoms provide linkages along [001] between adjacent heteropolyhedral chains (Fig. 4). The OH(2) position is shared between the B(1) and B(3) tetrahedra, which contribute 1.55 v.u. toward the bond-valence requirements of the oxygen atom; thus the donor-hydrogen bond must be considerably weaker than is normally the case (*i.e.*,  $\ll 0.8$  v.u.). This requirement is met, as the H(1) position is on a 2-fold rotation axis, and it bonds to two symmetrically

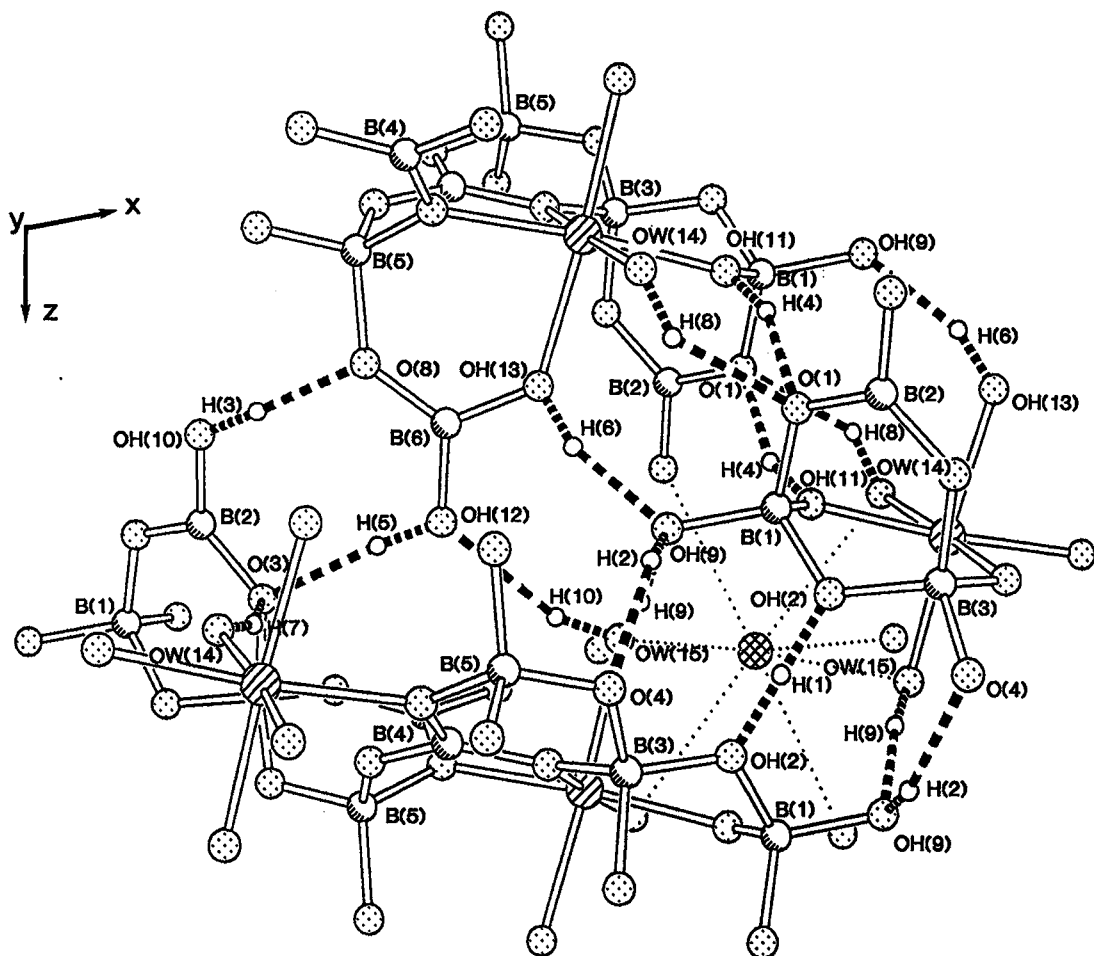


FIG. 4. The structure of kaliborite projected onto (010). Boron atoms are open circles with shading in the lower-left corners, magnesium atoms are shaded with parallel lines, potassium atoms are cross-hatched, oxygen atoms with a regular-dot pattern, and hydrogen atoms are given as small open circles. Hydrogen bonds are shown as heavy solid and dashed lines.

equivalent OH(2) positions, which occur in adjacent *FBBs*. The OH(2)–H(1) and H(1)–OH(2)<sub>i</sub> bond-lengths are 1.212(7) Å, indicating a very strong hydrogen bond. This crystallographically symmetrical hydrogen bond is considered further below.

The OH(10) and OH(12) anions are bonded to B(2) and B(6), respectively. The OH(10)–H(3)...O(8) and OH(12)–H(5)...O(3) bonds bridge along [001] between adjacent heteropolyhedral chains (Fig. 4). The O(8) and O(3) anions are bonded to B(6) and B(2), respectively, and thus these hydrogen bonds complete an eight-membered ring of B, O and H. The OH(10)–H(3)...O(8) and OH(12)–H(5)...O(3) bonds are quite strong, as indicated by the fairly short acceptor distances, 1.73(3) and 1.89(3) Å, respectively.

The OH(9)–H(2)...O(4) bond is of intermediate

strength, as indicated by an acceptor distance of 2.14(4) Å. The bond bridges adjacent heteropolyhedral chains along [001]; the OH(9) anion bonds to B(1), and the O(4) anion is shared between B(3) and B(5).

The OW(15) anion is the donor of two hydrogen bonds, each of which bridges between adjacent heteropolyhedral chains along [001] (Fig. 4). The OW(15) anion bonds to the K and Mg cations. The hydrogen-bond acceptor anions belong to different heteropolyhedral chains; OH(9) bonds to B(1), and OH(12) bonds to B(6). The OW(15)–H(9)...OH(9) bond is quite strong, as indicated by an acceptor anion at a distance of 1.79(4) Å. The OW(15)–H(10)...OH(12) bond is significantly weaker, with an acceptor anion at a distance of 2.23(3) Å.

### Hydrogen bonding along [101]

The OH(13)–H(6)...OH(9) bond bridges between adjacent heteropolyhedral chains along [101] (Fig. 4). The OH(13) anion bonds to B(6) and Mg. The OH(9) anion bonds to B(1), and acts as a donor for the H(2) atom and an acceptor for the H(9) atom. The OH(13)–H(6)...OH(9) bond is strong, as indicated by an acceptor distance of 1.75(3) Å.

The OW(14)–H(8)...O(1) and OH(11)–H(4)...O(1) bonds are oriented along [101], and bridge between anions of adjacent heteropolyhedral chains. The OW(14) anion bonds to Mg and K, and the OH(11) anion bonds to B(1) and Mg. The O(1) anion is an acceptor for both of these hydrogen bonds. The O(1) anion bonds to B(1) and B(2), which provide 1.756 v.u. toward its anion bond-valence requirements, and the remaining bond-valence requirement at O(1) is satisfied by accepting the hydrogen bonds. The OW(11)–H(4)...O(1) and OW(14)–H(8)...O(1) bonds are of intermediate strength, as indicated by acceptor anions at distances of 1.86(4) and 1.98(4) Å, respectively.

### Hydrogen bonding along [010]

The OW(14)–H(7)...O(3) bond links anions of the same heteropolyhedral chain (Fig. 4). The OW(14) anion bonds to Mg and K, and O(3) bonds to B(2) and B(3). The OW(14)–H(7)...O(3) bond is of intermediate strength, as indicated by an acceptor anion at a distance of 1.96(2) Å.

### Crystallographically symmetrical hydrogen bond

Crystallographically symmetrical hydrogen bonds are very rare in borate minerals; only two are known to date. Clark & Christ (1977) reported that such hydrogen bonds might occur in the structures of preobrazhenskite and kaliborite. Burns & Hawthorne (1994a) recently verified that a crystallographically symmetrical hydrogen bond does occur in the structure of preobrazhenskite. The situation in the preobrazhenskite structure is very similar to that reported here in the kaliborite structure; the hydrogen atom lies on a two-fold axis, and it bridges between symmetrically equivalent anions, each of which bonds to two tetrahedrally coordinated B atoms. The two B atoms contribute ~1.5 v.u. toward the bond-valence requirements of the anion; the rest is provided by the crystallographically symmetrical hydrogen bond.

The electron density associated with the symmetrical hydrogen bond in preobrazhenskite was examined in difference-Fourier maps calculated with the H position vacant. The peak in the electron density occurs on the two-fold axis, and there is only one peak in that vicinity, although the electron density is clearly anisotropic (see Fig. 4, Burns & Hawthorne 1994a).

A three-dimensional difference-Fourier map calculated around the vacant H(1) position in kaliborite shows the presence of the H(1) atom (Fig. 5), as there is a significant amount of electron density between the symmetrically equivalent OH(2) positions. However, the electron density shows two well-developed maxima, located slightly off the OH(2)–OH(2) join, and separated by about 0.7 Å. This feature indicates that the H(1) position may be disordered off the two-fold axis.

Several cycles of refinement were done with the H(1) atom displaced off the two-fold axis to account for the observed anisotropy of the electron density around the H(1) position. The refinement converged, but it did not lower the *R* values relative to the refinements done with the H(1) position fixed on the two-fold axis. The split H(1)' and H(1)'' positions refined to a separation of 0.7(2) Å. Only one of these H(1) positions will be locally occupied. The resulting local configuration has a donor at a distance of 0.88(12) Å and an acceptor at a distance of 1.56(12) Å, and the refined OH(2)h–H(1)...OH(2)i angle is 165(9)°.

There are two possible explanations for the observed anisotropy in electron density at the H(1) site in kaliborite: (1) the H(1) atom is dynamically disordered between the H(1)' and H(1)'' positions; (2) there is a local static ordering of the H(1) atom at the H(1)' or the H(1)'' positions. In the latter case, the refined OH(2)–H(1) donor distance of 0.88(12) Å has a bond-valence of ~0.8 v.u. The OH(2) anion also receives a total of 1.55 v.u. from the B(1) and B(3) positions, and such a local configuration would result in an excess of bond valence at the donor OH(2) anion. In addition, a significant bond-valence deficiency will occur at the acceptor OH(2) anion of the same local configuration. These bonding arguments suggest that the anisotropy

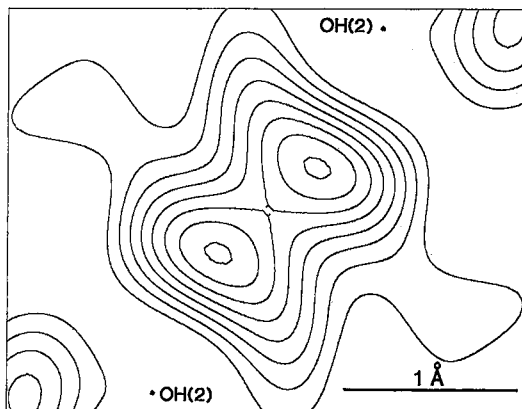


FIG. 5. Difference-Fourier map of the H(1) position calculated with the H(1) position vacant. Contour interval is 0.1  $e/\text{Å}^3$ .



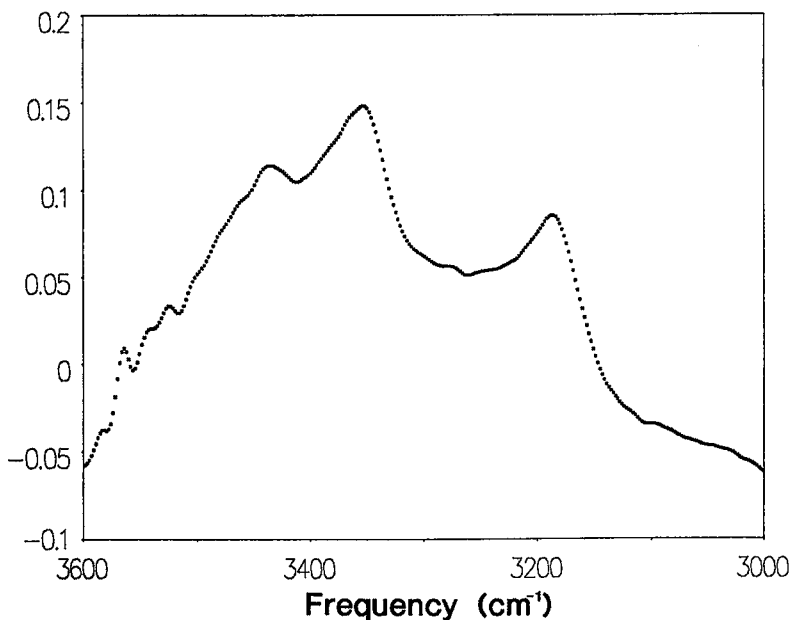


FIG. 6. The infrared spectrum of kaliborite in the principal OH-stretching region.

in electron density associated with the H(1) site is attributable to a dynamic disorder of the H atom, rather than local static ordering of the H(1) atom at the H(1)' or H(1)'' positions.

#### *Infrared spectrum*

The powder infrared spectrum of kaliborite (Fig. 6) in the principal OH-stretching region shows one prominent peak at  $\sim 3200\text{ cm}^{-1}$  and a broad, poorly resolved series of peaks centered at  $\sim 3400\text{ cm}^{-1}$ , with several prominent shoulders to the high-frequency side of the envelope. There are ten distinct hydrogen positions in kaliborite (Table 2), and the spectrum is too complex to lead to unambiguous identification of the positions of individual bands.

The powder infrared spectrum of preobrazhenskite (Burns & Hawthorne 1994a) is considerably simpler than that of kaliborite, and the band positions and intensities were obtained. The lowest-frequency band in the principal OH-stretching region in preobrazhenskite occurs at  $\sim 3200\text{ cm}^{-1}$ , and this was attributed to a crystallographically symmetrical hydrogen bond. The kaliborite spectrum also has an intense band at  $\sim 3200\text{ cm}^{-1}$  (Fig. 6), and this band also may be attributed to the crystallographically symmetrical hydrogen bond. The broad envelope in the kaliborite spectrum presumably contains contributions from the other nine H positions, and thus the band at  $\sim 3200\text{ cm}^{-1}$  is relatively very intense, in line with the

relationship of band intensities and band frequencies reported by Burns & Hawthorne (1994a).

#### ACKNOWLEDGEMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada via Operating, Equipment and Infrastructure grants to FCH. The University of Manitoba supported this work with a Postgraduate Fellowship to PCB. Reviews by two anonymous referees, and editorial work by Drs. R.F. Martin and R.C. Rouse improved the quality and clarity of the manuscript.

#### REFERENCES

- BROWN, I.D. & ALTERMATT, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.
- BURNS, P.C. & HAWTHORNE, F.C. (1993a): Hydrogen bonding in colemanite: an X-ray and structure-energy study. *Can. Mineral.* **31**, 297-304.
- \_\_\_\_\_ & \_\_\_\_\_ (1993b): Hydrogen bonding in meyerhofferite: an X-ray and structure energy study. *Can. Mineral.* **31**, 305-312.
- \_\_\_\_\_ & \_\_\_\_\_ (1994a): Structure and hydrogen bonding in preobrazhenskite, a complex heteropolyhedral borate. *Can. Mineral.* **32**, 387-396.

- \_\_\_\_\_ & \_\_\_\_\_ (1994b): Structure and hydrogen bonding in inderborite, a heteropolyhedral sheet structure. *Can. Mineral.* **32**, 533-539.
- CHRIST, C.L. & CLARK, J.R. (1977): A crystal-chemical classification of borate structures with emphasis on hydrated borates. *Phys. Chem. Minerals* **2**, 59-87.
- CLARK, J.R. & CHRIST, C.L. (1977): Unusual hydrogen bonding in some hydrated borate structures. *Acta Crystallogr.* **B33**, 3272-3273.
- CORAZZA, E. & SABELLI, C. (1966): The crystal structure of kaliborite. *Atti Accad. Naz. Lincei, R.C., Cl. Sci. Fis. Mat. Nat.* **41**, 527-552.
- CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.
- \_\_\_\_\_ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree-Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.
- HAMILTON, W.C. & IBERS, J.A. (1968): *Hydrogen Bonding in Solids*. W. A. Benjamin, Inc., New York.
- RUMANOVA, I.M., RAZMANOVA, Z.P. & BELOV, N.V. (1972): Crystal structure of preobrazhenskite  $3\text{MgO} \cdot 5.5\text{B}_2\text{O}_3 \cdot 4.5\text{H}_2\text{O} = \text{Mg}_3[\text{B}_{11}\text{O}_{14}(\text{OH})_8\text{HO}_2]$ . *Sov. Phys. Dokl.* **16**, 518-521.

Received January 12, 1994, revised manuscript accepted April 5, 1994.