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## The High-Pressure Synthesis and Structural Refinement of $\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$ , an Anhydrous Boron Chondrodite

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Single crystals of a synthetic anhydrous chondrodite,  $\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$ , have been prepared by hydrothermal synthesis under high pressure. This compound is a member of a large series of synthetic boron chondrodites,  $\text{M}_4^{3+}\text{M}_1^{2+}\text{M}_1^{2+}(\text{BO}_4)_2(\text{OH})_x\text{O}_{2-x}$  ( $\text{M}^{3+} = \text{Al, Ga, Fe}$  and  $\text{M}^{2+} = \text{Ni, Co, Mg, Fe}$ ). It is monoclinic, space group  $P2_1/c$  with two molecules in a cell of dimensions  $a = 7.221$  (3),  $b = 4.371$  (2),  $c = 9.534$  (5) Å, and  $\beta = 108.45^\circ$ . All crystals are twinned by reticular pseudomerohedry. The twinning is controlled by the orthorhombic pseudosymmetry of a superlattice obtained from the monoclinic cell by the matrix 401/010/001. The structure has been refined from single-crystal X-ray data. The least-squares refinement was carried out on 392 twinning-free reflexions which gave an  $R$  of 0.020. There are three independent octahedral sites in the chondrodite structure, two fourfold and one twofold. The cation distribution among the three sites was found to be  $(\text{Al}_{1.88}\text{Co}_{0.12})$  (1)  $\text{Al}_2$  (2)  $(\text{Co}_{0.89}\text{Al}_{0.11})$  (3)  $(\text{BO}_4)_2\text{O}_2$ . The average interatomic distances are:  $\text{Al}(1)\text{--O}$  1.944,  $\text{Al}(2)\text{--O}$  1.911,  $\text{Co--O}$  2.064,  $\text{B--O}$  1.493 Å.

### Introduction

The structure of the mineral chondrodite,  $\text{Mg}_5(\text{SiO}_4)_2(\text{OH})_{0.7}\text{F}_{1.3}$ , consists of a distorted close-packed network of oxygen and fluorine atoms where the Mg and Si cations occupy half of the octahedral and  $\frac{1}{10}$  of the tetrahedral sites, respectively. The structure is monoclinic, space group  $P2_1/c$  with two molecular formulae per unit cell of dimensions:  $a = 7.840$ ,  $b = 4.728$ ,  $c = 10.254$  Å and  $\beta = 109.06^\circ$  (Gibbs, Ribbe & Anderson, 1970).

It has been shown that one can synthesize chondrodite-type compounds in which the boron atoms substitute for the silicon atoms, a large percentage of the divalent atoms are replaced by trivalent ones and consequently all or part of the hydroxyls and fluorine atoms are replaced by oxygen atoms (Capponi, Chenavas & Joubert, 1975). The general formula of this series of compounds should probably be written as  $\text{M}_4^{3+}\text{M}_1^{2+}\text{M}_1^{2+}(\text{BO}_4)_2(\text{OH})_x\text{O}_{2-x}$ . Since all the boron atoms have a fourfold coordination, these compounds should be synthesized under high pressure.

This paper reports the single-crystal synthesis and the structural refinement of one member of the series, the anhydrous chondrodite  $\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$ .

### Experimental

Single crystals of  $\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$  were obtained by hydrothermal synthesis under high pressure. A mixture

of  $2\text{Al}_2\text{O}_3 + \text{CoO} + 3\text{H}_3\text{BO}_3$  and a few drops of water were subjected to 20 kbar and  $1100^\circ\text{C}$  in a 20 mm Belt-X apparatus. An excess of  $\text{H}_3\text{BO}_3$  with respect to the stoichiometric proportion was used to compensate for the  $\text{H}_3\text{BO}_3$  dissolved by the water. After one hour at 20 kbar and  $1100^\circ\text{C}$ , the temperature was lowered slowly ( $50^\circ\text{h}^{-1}$ ) to  $1050^\circ\text{C}$  and then the furnace power was turned off. The assembly was allowed to cool to room temperature and the pressure was released. The sample container was broken open, immersed in water, and transparent orange needle-like crystals were obtained. In general they were about 0.5 mm long and 0.1 mm in diameter.

Weissenberg photographs taken with Cu  $K\alpha$  radiation confirmed the space group  $P2_1/c$  as systematic absences were observed among the  $h0l$  reflexions for  $l = 2n + 1$  and among the  $0k0$  for  $k = 2n + 1$ . The lattice parameters reported in Table 1 were obtained from a powder pattern taken with a Guinier focusing camera and Fe  $K\alpha$  radiation. The value of the normalized cell volume  $V' = c \times b \times d_{100}/N = V/n = 57.1$  Å<sup>3</sup> ( $n$  being the period of the octahedral chains which is 5 for the chondrodite compounds) led us to the formula

Table 1. Cell constants

$a = 7.221$ (3) Å	$Z = 2$
$b = 4.371$ (2)	$V = 285.45$ Å <sup>3</sup>
$c = 9.534$ (5)	$V' = V/5 = 57.09$ Å <sup>3</sup>
$\beta = 108.45^\circ$	

$\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$ , which was confirmed by the structural refinement (Capponi *et al.*, 1975; Ribbe, Gibbs & Jones, 1968).

The crystal lattice of the boron chondrodites is consistent with a pseudo-orthorhombic superlattice which can be obtained from the monoclinic cell by the transformation matrix 401/010/001. For the compound reported in this paper the angle between [401] and [001] is  $89.18^\circ$ . Under these conditions twinning by reticular pseudomerohedry (Friedel, 1964) controlled by the pseudosymmetry of the orthorhombic superlattice has to be expected. The twin laws predicted by the theory are  $(100)=[001]_{180^\circ}$  and  $(\bar{1}04)\equiv[401]_{180^\circ}$ . The twin laws  $(010)\equiv[010]_{180^\circ}$  are symmetry operations of the monoclinic lattice and therefore they will not give rise to twinning. Since the operations of the twofold axes are indistinguishable from the operations of the corresponding equivalent planes, only the latter ones need to be considered. A similar twin has been found in the silicon chondrodites (Jones, 1969).

Precession photographs taken on single crystals of  $\text{Al}_4\text{Co}(\text{BO}_4)_2\text{O}_2$  confirmed the presence of twinning. A typical diffraction pattern for upper layers perpendicular to the  $b$  axis is illustrated schematically in Fig. 1.

The twin laws (100) and  $(\bar{1}04)$  are characterized by a small value of the obliquity ( $0.82^\circ$ ). Therefore, the

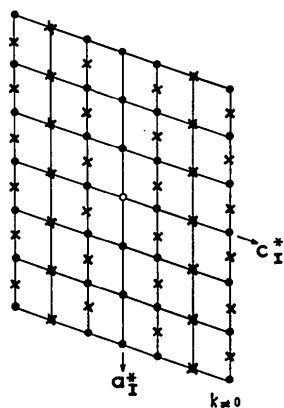


Fig. 1. The precession diffraction pattern for upper layers perpendicular to the  $b$  axis. The black dots represent the reciprocal nodes of the individual with the strongest reflexions (individual I). The crosses represent the nodes repeated by the planes (100) and  $(\bar{1}04)$  (individuals II and III).

three twinned individuals give reflexions almost exactly superposed on each other when  $l=2n$  and at  $n'a^*/2$  ( $n'$  odd) when  $l=2n+1$ . In the former case a spot with film coordinates  $hkl$  (referred to the reciprocal axes of one of the twinned individuals, for instance individual I having the most intense diffraction effects) is formed by the superposition of three reflexions, one from each individual of the twin, having indices:  $(hkl)_I + (h + \frac{1}{2}, k, l)_{II} + (\bar{h} + \frac{1}{2}, k, l)_{III}$ . For  $l=2n+1$  a reflexion  $hkl$  (referred to the reciprocal axes of individual I) is produced only by individual I. The spots inconsistent with the  $a$  lattice parameter are produced by individuals II and III. From the spots with  $l=2n+1$  one can calculate the total volume of the crystal which belongs to each individual. It was visually estimated for the crystal used for the intensity data collection that only 10% of the total volume belonged to individuals II and III.

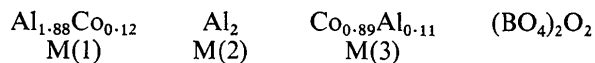
All intensity measurements were made with an automatic four-circle Hilger and Watts diffractometer with Zr-filtered  $\text{Mo K}\alpha$  radiation. The procedure for the collection of the intensity data has been described in detail elsewhere (Bassi, 1973). The specimen was an almost regular hexagonal prism (0.2 mm long and 0.1 mm in diameter), which was oriented with the [010] direction along the  $\varphi$  axis of the diffractometer. All reflexions between  $\theta=3$  and  $\theta=35^\circ$  were measured. This resulted in 1408 independent reflexions. Because of the twinning, all reflexions with  $l=2n$  for which  $I_{hkl} < 2I_{h+1/2, k, l}$  were discarded. With this criterion the maximum error in the intensity of the strong reflexions was 5%. Also, those reflexions for which the peak-height was not ten times the background were considered as unobserved. The total number of observed reflexions used in the refinement was then 392. The intensities were converted into structure factors by applying the Lorentz and polarization corrections. No correction for absorption was applied as the linear absorption coefficient was  $38 \text{ cm}^{-1}$ .

The refinement was carried out with the least-squares program written by C. T. Prewitt. In this program the atomic scattering factor for each atomic position is  $GQf_n + GRf_m$ , where  $GQ$  and  $GR$  can be varied. The atomic scattering factors (for neutral atoms) were those reported by Cromer & Waber (1965). Each reflexion was weighted by  $w = 1/\sigma^2$  where  $\sigma = 0.5\sqrt{1/pF^2 + \alpha^2F^2}$ ,  $p$  being the statistical weight of the intensity measurement and  $\alpha$  an empirical

Table 2. Positional and thermal parameters ( $\times 10^4$ )

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Al(1)	2984 (1)	195 (2)	1692 (1)	32 (2)	44 (4)	16 (1)	-6 (2)	9 (1)	1 (2)
Al(2)	758 (1)	54 (2)	3908 (1)	24 (1)	42 (4)	14 (1)	5 (2)	4 (1)	0 (2)
Co	5000	0	5000	22 (1)	37 (3)	14 (1)	-2 (2)	2 (1)	0 (1)
B	2909 (4)	5711 (7)	3510 (4)	14 (5)	11 (14)	16 (4)	9 (6)	3 (3)	-2 (5)
O(1)	2871 (4)	7025 (6)	4964 (3)	23 (7)	29 (3)	19 (3)	-6 (6)	5 (3)	-3 (5)
O(2)	1188 (5)	7414 (4)	2422 (3)	27 (7)	47 (15)	15 (4)	4 (4)	7 (4)	3 (3)
O(3)	4590 (5)	7087 (6)	3161 (3)	29 (5)	55 (8)	13 (3)	-7 (6)	4 (3)	0 (4)
O(4)	2816 (5)	2411 (4)	3450 (3)	31 (7)	12 (13)	14 (3)	5 (3)	2 (4)	-2 (3)
O(5)	1124 (5)	2812 (6)	610 (3)	30 (6)	59 (9)	11 (3)	2 (6)	9 (3)	3 (4)

parameter taken as 0.05. The starting values for the positional parameters and the isotropic temperature factors were those reported for the mineral alleghanyite,  $\text{Mn}_5(\text{SiO}_4)_2(\text{OH})_2$  (Rentzeperis, 1970). There are three independent positions for the manganese cations: Mn(1), Mn(2), and Mn(3). The first two are fourfold while the last is twofold. A random cation distribution was assumed at the beginning and appropriate starting values taken for  $GQ_1$ ,  $GR_1$ ,  $GQ_2$ ,  $GR_2$ ,  $GQ_3$  and  $GR_3$ . After six cycles of refinement convergence was attained and almost all the cobalt cations were ordered on the twofold positions.  $R$  had decreased to 0.029 and the cation distribution was:



In the last stage of the refinement anisotropic temperature factors were introduced for all atoms, while the site occupancy parameters were kept constant. The final  $R$  and  $wR$  were 0.020 and 0.030,

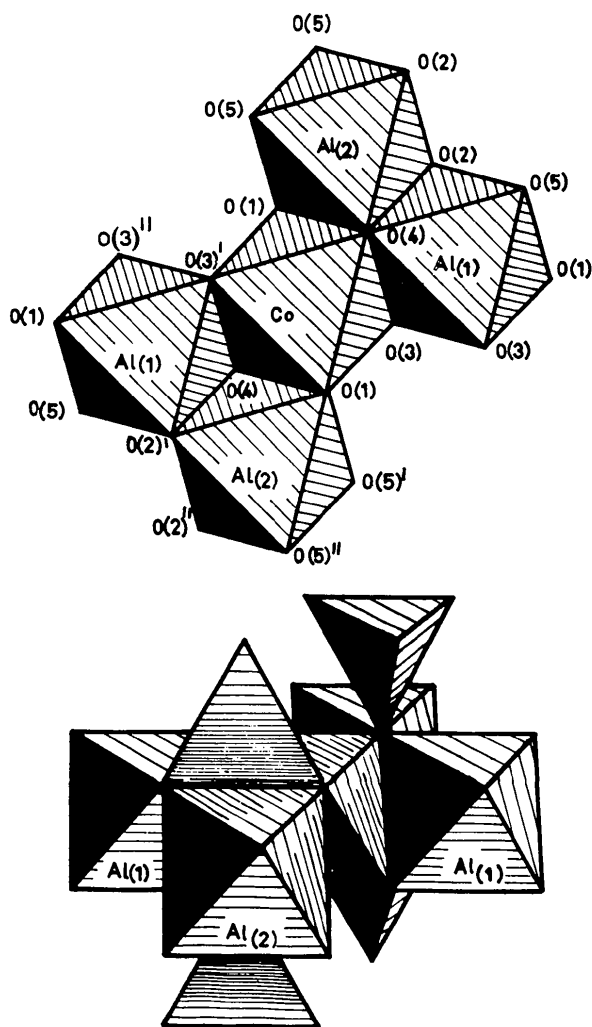


Fig. 2. (a) Basic unit of octahedra in the chondrodite structure. (b) The octahedral unit, together with the boron tetrahedra.

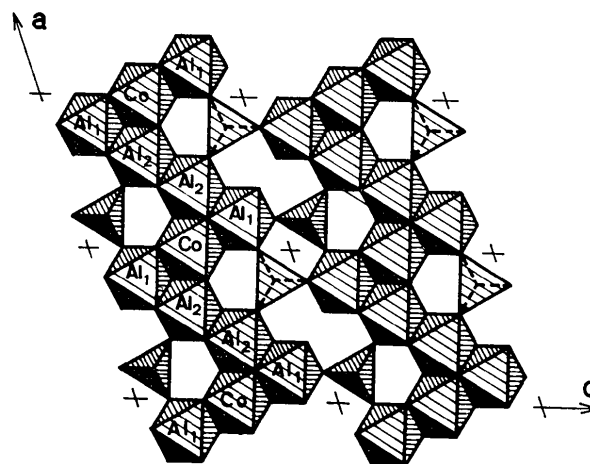


Fig. 3. Zigzag octahedral chains joined together by the boron tetrahedra. The layer is parallel to the (010) plane.

Table 4. *Interatomic distances* ( $\text{\AA}$ ) *and angles* ( $^\circ$ )

<b>Al(1) octahedron</b>			
Al(1)—O(1)	1.892 (3)	O(1)—O(2)	2.972 (5)
—O(2)	2.053 (4)	O(1)—O(3')	2.930 (4)
—O(3')	2.031 (3)	O(1)—O(3'')	2.777 (4)
—O(3'')	1.902 (3)	O(1)—O(5)	2.633 (13)
—O(4)	1.972 (3)	O(4)—O(2)	2.529 (3)
—O(5)	1.817 (11)	O(4)—O(3')	2.713 (4)
Average	1.944	O(4)—O(3'')	2.776 (6)
		O(4)—O(5)	2.601 (29)
		O(3')—O(3'')	2.681 (4)
		O(3')—O(2)	2.336 (4)
		O(5)—O(3'')	2.960 (5)
		O(5)—O(2)	2.916 (19)
<b>Al(2) octahedron</b>			
Al(2)—O(1)	2.031 (3)	O(2'')—O(1)	2.349 (4)
—O(2')	1.927 (3)	O(2'')—O(2'')	2.811 (5)
—O(2'')	1.876 (3)	O(2'')—O(4)	2.527 (3)
—O(4)	1.968 (4)	O(2'')—O(5'')	2.884 (27)
—O(5')	1.817 (27)	O(5'')—O(1)	2.749 (12)
—O(5'')	1.848 (16)	O(5'')—O(2'')	2.846 (27)
Average	1.911	O(5'')—O(4)	2.709 (29)
		O(5'')—O(5'')	2.540 (17)
		O(2'')—O(4)	2.744 (5)
		O(2'')—O(5'')	2.642 (21)
		O(1)—O(4)	2.755 (4)
		O(1)—O(5'')	2.782 (6)
<b>Co octahedron</b>			
Co—O(1)	2.006 (3)	O(3)—O(1')	2.419 (5)
—O(3)	2.111 (3)	O(3)—O(1)	2.777 (4)
—O(4)	2.075 (3)	O(3'')—O(4)	2.713 (4)
Average	2.064	O(3)—O(4)	3.188 (4)
		O(1')—O(4)	2.744 (5)
		O(1)—O(4)	3.011 (4)
<b>B tetrahedron</b>			
B—O(1)	1.509	O(1)—O(2)	2.349
—O(2)	1.536	O(1)—O(3)	2.419
—O(3)	1.484	O(1)—O(4)	2.473
—O(4)	1.444	O(2)—O(3)	2.336
Average	1.493	O(2)—O(4)	2.529
		O(3)—O(4)	2.473
<b>Short cation-cation distances across shared edges</b>			
Al(1)—Al(2)	3.033 (2)	Al(2)—Co	2.907 (2)
Al(1)—Co	3.027 (1)	Al(2)—B	2.556 (4)
Al(1)—B	2.628 (4)	Co—B	2.541 (3)

respectively. These values correspond to the positional and thermal parameters reported in Table 2. The observed and calculated structure factors are listed in Table 3.\*

### Discussion

The interatomic distances and their standard deviations, calculated by the *ORFFE* program are reported in Table 4.

Fig. 2 represents the basic unit of the chondrodite structure. It consists of five edge-sharing octahedra, four of which are occupied by Al cations while the central one is occupied by Co. These units are linked to each other by shared edges so as to form infinite zigzag chains of edge-sharing octahedra which run parallel to the *a* axis. These chains are joined together by the boron tetrahedra. The resulting layers are parallel to the (010) plane (see Fig. 3). These layers are stacked on each other along the *b* axis. Each layer can be distinguished from the next by a double translation of  $\frac{1}{2}$  along *c* and *b*, followed by a rotation around the twofold screw axis. The octahedra of successive layers only share corners while they share one [Al(1) and Al(2)] or two edges (Co) with the boron tetrahedra of the next layers. The distortion of the hexagonal close-packed oxygen array is mainly due to this edge-sharing between octahedra and tetrahedra.

The average cation-oxygen distances are 1.944, 1.911, 2.064, and 1.493 Å for Al(1)-O, Al(2)-O, Co-O and B-O, respectively. If one takes into account the disorder between the Al(1) and the Co cations the respective distances become 1.936 and 2.083 Å.† After this adjustment the Al(1)-O distance is still 1.3% larger than the Al(2)-O distance. This is probably because of the larger distortion of the oxygen octahedron around the Al(1) cation. If one defines an index of distortion of an octahedron as the standard deviation calculated from the average of the 12 O-O distances, this index decreases from 0.19 for Al(1) to 0.15 for Al(2). The feature that the M(1)-O distance is on the average larger than the M(2)-O distance has been found also in the well refined silicon chondrodites (Gibbs *et al.*, 1970; Rentzeperis, 1970).

The average Co-O distance (2.083 Å) is shorter than expected. The value calculated from the Shannon & Prewitt (1969) ionic radii is 2.12 Å. The index of distortion of the oxygen octahedron corresponding to this site is 0.26. As a consequence of this large distortion the observed value should be larger yet than the calculated one. On the contrary the average B-O

distance (1.493 Å) is larger than expected. In the high-pressure phases of LiBo<sub>2</sub> and CaB<sub>2</sub>O<sub>4</sub> where the boron cations are only tetrahedrally coordinated, a value of 1.480 Å was observed (Marezio, Remeika & Dernier, 1969; Marezio & Remeika, 1966). One could explain the shorter Co-O distance and the larger B-O distance by taking into consideration the fact that a Co octahedron shares two edges with two B tetrahedra. Therefore, the sizes of the two polyhedra are interrelated and in order to stabilize the structure it is conceivable that the larger polyhedron becomes smaller and the smaller larger.

The O(1), O(2), O(3), O(4) anions are bonded to three large cations and to one boron whereas the O(5) is bonded only to one Al(1) and to two Al(2). If one does not take into account the distortion of the structure, this oxygen is underbonded. In order to compensate for this deficiency the structure distorts in such a way that the three Al-O(5) distances become rather short. The overall average of the Al-O distances is 1.928 Å while the average of the three Al-O(5) distances is 1.827 Å. It is also because of this bonding deficiency that the less charged Co<sup>2+</sup> cations are mainly ordered on the M(3) sites which are not bonded to the O(5) atoms. In the hydroxyl chondrodites, this oxygen is not underbonded because it forms a short O-H bond; the M(1)-O(5) and the 2M(2)-O(5) distances do not need to be short and therefore the M(1) and M(2) sites can be occupied by divalent cations.

From the present refinement one can predict the cation distribution in hydroxyl boron chondrodites such as Al<sub>4-x</sub>M<sub>1+x</sub><sup>2+</sup>(BO<sub>4</sub>)<sub>2</sub>(OH)<sub>x</sub>O<sub>2-x</sub> (M = Co<sup>2+</sup>, Ni<sup>2+</sup>). When *x* is different from 0 the excess of divalent cation should occupy first the M(1) sites. In fact this site forms only one bond with the O(5) atom, whereas the M(2) site forms two bonds. The distance M(1)-O(5) does not need to shorten as the deficiency in bonding of O(5) is compensated for by the formation of hydrogen bonds.

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\* Table 3 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31060 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† Al(1)-O(corrected) =  $\begin{vmatrix} 1.944 & 0.06 \\ 2.064 & 0.88 \end{vmatrix} / \begin{vmatrix} 0.94 & 0.06 \\ 0.12 & 0.88 \end{vmatrix}$   
 Co-O(corrected) =  $\begin{vmatrix} 0.94 & 1.911 \\ 0.12 & 2.064 \end{vmatrix} / \begin{vmatrix} 0.94 & 0.06 \\ 0.11 & 0.89 \end{vmatrix}$