The crystal structures of K$_2$Al$_2$B$_2$O$_7$, and SrAl$_2$B$_2$O$_7$ have been solved ab initio by applying 'traditional' single crystal techniques to structure factors extracted from X-ray powder patterns. K$_2$Al$_2$B$_2$O$_7$ crystallizes in the trigonal space group P321, with a=8.55802(2), c=8.45576(3) Å, V=536.328 Å$^3$, and Z=3. The structure consists of a 3-dimensional network composed of corner-sharing BO$_3$ triangles and Al$_2$O$_7$ units. The BO$_3$ groups lie approximately parallel to the $ab$ plane, and the planes containing them are joined by Al$_2$O$_7$ “pillars” parallel to the $c$ axis. The K cations reside in channels parallel to the $c$ axis. SrAl$_2$B$_2$O$_7$ crystallizes in the rhombohedral space group R3$\bar{2}$, with a=4.90363(9), c=23.9346(6) Å, V=498.416 Å$^3$, and Z=3. In this structure, SrAl$_2$B$_2$O$_7$ act as “pillars” between planes containing BO$_3$ units. The structure is, however, layered, as the Al$_2$O$_7$ join pairs of BO$_3$ planes. An ABC stacking sequence of these double layers creates trigonal prismatic cavities, in which the Sr reside.

The average structure of Cu$_2$Al$_2$B$_2$O$_7$ has been confirmed to higher accuracy and precision by a resonant scattering study. This compound crystallizes in the tetragonal space group I4/m, with a=10.57945(1), c=5.67357(6) Å, V=635.013 Å$^3$, and Z=2. A new model for the local structure is proposed. Cu$^{2+}$ and Al$^{3+}$ equally occupy a trigonal bipyramidal site. The Cu occur as “cis” pairs around a “4-ring” of these 5-coordinate sites. A square planar oxygen is displaced from the center of this “4-ring” toward the pair of Al and away from the pair of Cu cations. The Cu$^{2+}$ and Al$^{3+}$ apparently occupy different locations in the coordination sphere at low temperatures, only moving to a common site as the calcination temperature is raised. Both the crystallinity and average crystallite size of this material can be controlled by controlling the calcination temperature.

### Introduction

Metal aluminum borates represent a fascinating class of materials. Depending on the composition, they can be useful as catalytic, laser, or nonlinear optical materials. In the early stages of research and development, it can often be difficult to grow the single crystals “necessary” for detailed structural characterization. Because knowledge of the crystal structures of such materials is necessary for the development of structure/property correlations, we are sometimes forced to obtain detailed structural information using only powder diffraction data. In addition, real catalysts are always polycrystalline, “forcing” the use of powder diffraction techniques to study such materials. Recent advances in hardware and software, especially the availability of synchrotron radiation, make it possible to answer many structural questions using only powder diffraction data. In this paper, we provide examples of ab initio structure solution, and the use of powder diffraction techniques to obtain information about the non-structural properties of a material.

### POTASSIUM ALUMINUM BORATE, K$_2$Al$_2$B$_2$O$_7$

Only one ternary phase, KAlB$_3$O$_7$ [1] in the K$_2$O-Al$_2$O$_3$-B$_2$O$_3$ system has been characterized structurally. During exploration of this ternary system, we discovered a black amorphous semiconducting phase of the approximate composition 1K$_2$O:1Al$_2$O$_3$:2B$_2$O$_3$. From preparations having compositions near 1K20:1Al$_2$O$_3$:1B$_2$O$_3$, a phase having the X-ray powder diffraction pattern of K$_2$Al$_2$B$_2$O$_7$ [2] was produced.

The powder pattern of K$_2$Al$_2$B$_2$O$_7$ can be indexed on a very high quality trigonal/hexagonal unit cell having a=8.5597(4) and c=8.4597(4) Å. Magic angle spinning NMR indicated that the Al coordination is tetrahedral, and that the borons are trigonal. The observed density indicated that the cell contents were K$_6$Al$_6$B$_6$O$_21$. Because K$_2$Al$_2$B$_2$O$_7$ is formed near the semiconducting phase in the phase diagram, we believed that knowledge of the crystal structure, and comparison of the structure to those of nearby crystalline phases, would give some insight into the
structure of the amorphous phase and the mechanisms of conductivity.

Experimental

The sample was mixed with 4.87 wt% NIST 640b Si internal standard, and ground in a McCrone micronising mill using ethanol as the milling liquid. The X-ray powder diffraction pattern was measured on beamline X3BL at the National Synchrotron Light Source at Brookhaven National Laboratory, using a wavelength of 0.89978 Å. The pattern was measured from 6-74° 2θ in 0.004° steps, counting for 4 sec/step. The sample was rocked from T-1 to T+1° during each data point. An 0-2θ scan of the (112) peak at 17.206° 2θ indicated significant granularity. The degree of powder averaging obtained by a 2θ rocking would not be expected to affect solution of the structure, but may affect the agreement of the observed and calculated patterns.

No systematic absences were observed in the powder pattern. Together with the trigonal/hexagonal unit cell (no evidence was observed for lower, especially orthorhombic, symmetry), this “limits” the possible space groups to: P3, P312, P31m, P6, P61m, P622, P6mm, P62m, P6m2 and P6/mmm. In all of the Laue classes but 6/m/m, there are inequivalent reflections which overlap exactly. This overlap makes the extraction of accurate structure factors from the powder pattern more difficult. Many reflections, which would be absent for a rhombohedral cell, are absent or very weak in the observed pattern. These weak reflections suggested the likely presence of pseudosymmetry, and that the structure solution would be difficult.

Consideration of the coordination requirements of the cations and the approximate number of atoms in the unit cell suggested that the presence of a 6-fold rotation axis was unlikely. Attempts to solve the structure from laboratory powder data in P3, P312, P3m1, P31m, P321, P31m, P311, P3m1, P6, P6, P61m, P622, P6mm, P62m, P6m2 and P6/mmm. In all of the Laue classes but 6/m/m, there are inequivalent reflections which overlap exactly. This overlap makes the extraction of accurate structure factors from the powder pattern more difficult. Many reflections, which would be absent for a rhombohedral cell, are absent or very weak in the observed pattern. These weak reflections suggested the likely presence of pseudosymmetry, and that the structure solution would be difficult.

Initial powder data processing was carried out using GSAS [3]. A 3-term cosine Fourier series background function, scale factors for each of the four phases, the lattice parameters, and profile terms were refined. The structure model used the six K atoms at the above coordinates. The LeBail extraction procedure incorporated into GSAS was used to extract 426 individual structure factors for 2θ < 56° (d > 0.96 Å).

These structure factors were used to create a SHELXTL Plus [4] data file. Attempts to solve the structure using direct methods were unsuccessful. A Patterson synthesis suggested the presence of a K atom at the origin, and a second K at a, b, 0.5148. The z coordinate of the first atom was fixed to define the origin. Successive cycles of refinement and difference Fourier synthesis yielded the positions of some other reasonable atoms, but not the complete structure. The second-best heavy atom position suggested by the Patterson was a, a, 0 -- a general position in P3. Successive cycles of least squares refinement and difference Fourier maps yielded another K on a general position, and six Al positions on the 3-fold axes. Further refinement of this model gradually yielded the positions of the O and B atoms. The B and Al were distinguished by the coordination number and the M-O distances.

Final refinement of the structure was carried out using GSAS. The atom coordinates were refined subject to soft constraints of 1.74(l) Å on the Al-O bonds and 1.37(l) Å on the O-O bonds. The weight of these constraints was gradually decreased through the course of refinement. The atoms were refined with a common isotropic displacement coefficient for each atom type. Included in the final refinements were scale factors for each phase, and the lattice parameters for K₂Al₂B₄O₇ and an Al₂O₃ impurity. The size broadening terms X and ptec were refined for K₂Al₂B₄O₇. The profiles for the other phases were described using fixed X and Y terms determined early in the refinement. The background indicated the presence of an amorphous component, and was described by a 6-term real space pair correlation function, using two fixed distances of 2.80 and 0.50 Å.

The final refinement in P3 of 56 variables using 17029 observations yielded the residuals Rp=0.1467 and wRp=0.1821. The final reduced R² was 6.388. The Bragg R(F) was 0.1489. At this point, the asymmetric unit contained two independent K, six Al on 3-fold axes, two B on general positions, and nine O.
(six on general positions, and three on 3-fold axes). One of the boron atoms was decidedly nonplanar (the sum of the O-B-O angles was 330°). The Al-O-Al angles of the Al₂O₇ units were 180°, this large angle is uncommon (but not unprecedented), and larger than the usual 130-160° Al-O-Al angle. Although the framework topology was almost certainly correct, these structural features, and the difficulty of convergence, pointed to a space group error.

The structure was examined for the presence of additional symmetry elements by application of the MISSYM program of the NRCVAX software system [5]. A number of additional symmetry elements were found to relate the K, Al, and B atoms, but when the default tolerances were applied to all atoms, no additional symmetry was detected. When the tolerances were increased slightly, additional 2-fold axes parallel to [010], [100], and [110] were suggested. Space group P321 (#150) therefore seemed likely. The 2-fold axes intersected at a b 0. A coordinate transformation was therefore applied to the P3 atom coordinates, and the unique atoms in P321 remained. The new asymmetric unit contained two K atoms on 2-fold axes, three Al on 3-fold axes, one B at a general position, three O at general positions, one O on a 3-fold axis, and one O at the origin, a position of 32 symmetry. Other coordinate transformations lead to wrong combinations of atoms on special positions, which led to the wrong stoichiometry.

Refinement using common isotropic displacement coefficients by atom type proceeded smoothly. The Al-O-Al are still linear in this model. The constraints on Uiso for O4 and O5 were removed, to test the possibility of disorder off the 3-fold axes. The Uiso of O4 essentially did not change, but that of O5 increased greatly. (The largest hole in the ) F map was at this atom—the origin.) O5 was thus moved off the origin, to a position x00 on a 2-fold axis, and refined. The resulting Uiso is comparable to those of the other oxygens, and the A13-O5-Al3 angle is 151°—a more typical value. There is no evidence that O4 is displaced off the 3-fold axis, and thus that the A11-O4-Al2 angle is not 180°. The B is planar to within experimental error. In general, this structure is chemically more satisfactory.

The final refinement in P321 of 39 variables using 17014 observations yielded the residuals wRp = 0.1814 and Rp=0.1463. The final reduced R² was 5.800. The Bragg R(F) was 0.1451. The agreement of observed and calculated patterns is slightly better, with fewer variables, in P321, suggesting that it is the correct space group. Application of MISSYM suggested the presence of no additional symmetry elements, even with very large tolerances. The agreement between F₀ and Fc is poorest for the highest-angle reflections. The observed, calculated, and difference patterns are illustrated in Fig. 1. The largest differences occur at K₆Al₂B₄O₁₂ reflections, and probably indicate that a true powder average was not achieved. The largest peak in a difference Fourier map was 2.0 electrons, and the largest hole was -1.6 electrons. The slope of the final Wilson plot suggests that the standard uncertainties are underestimated by a factor of 2.1. The final structural parameters are reported in Table 1.

**Description of the Structure**

The crystal structure of K₂Al₂B₄O₁₂ consists of a 3-dimensional network composed of corner-sharing BO₄ triangles and Al₂O₇ units. The K cations reside in channels parallel to the c-axis formed by this framework. The cation coordination spheres and the atom numbering scheme are illustrated in Fig. 2. The boron coordination is trigonal and very nearly planar; the sum of the O-B-O angles is 359°. The B atom is +0.05D, and the oxygens are -0.01-0.02E from the mean BO₃ plane.

There are two independent Al₂O₇ units. Both of them occupy 3-fold axes, and consequently the average Al-O-Al angles are 180°. Although this configuration is uncommon in high-quality structures, it is not unprecedented. The Al-O bond distances and angles fall within the normal ranges. The deviations from ideal tetrahedral geometry are small. The configurations of the two Al₂O₇ units are different. A convenient measure is the O-Al-Al-O “torsion angle”. For the Al₁-Al₂ group, this angle is 39°, indicating that the tetrahedra are nearly in the staggered configuration (60°). For the Al₁3-Al₁3A group, the angle is 20°, indicating that this unit is closer to the eclipsed configuration.

The occurrence of two distinct Al₂O₇ units, both with imposed 3-fold symmetry, reflects a subtle feature of space group P321. There are two different types of 3-fold axes in this space group. One type, passing through the origin and occupied by the Al₁3-Al₁3A units, is intersected by the 2-fold axes in the ab plane. The other type, of which there are 2/cell, pass through a b 0 and a a 0, and do not intersect the perpendicular 2-fold axes. These axes are occupied by the Al₁1-Al₁2 units. A consequence of the symmetry is...
that there are two Al1-Al2 units for every Al3-Al3A unit. The central oxygens also have different site symmetries. The oxygen O4 of the Al1-Al2 unit has site symmetry 3, but the O5 of the Al3-Al3A unit has the higher symmetry 32 at its average position.

There are two independent K ions, each residing on a site of 2-fold symmetry. Considering only K-O distances < 3.2 \( \text{\AA} \), K1 is 5-coordinate, and the coordination trigonal bipyramidal. Two O2 and one O5 make up the equatorial plane, and two O3 are the axial ligands. Two additional O1 are 3.32 \( \text{\AA} \) from K1. If O5 is located at its average position (the origin), the K1-O5 distance is 3.07 \( \text{\AA} \). Threefold disorder of O5 off the origin leads to shorter distances to two different K1 (2.88 \( \text{\AA} \)). Because K1 is relatively coordinatively unsaturated, such distortion seems to be reasonable to meet the bonding requirements of K1. It is most reasonable to consider K2 to be 8-
The coordination of the B, Al, and K atoms in $K_2\text{Al}_2\text{B}_2\text{O}_7$, with the atom numbering scheme. K-O distances $<3.2\ \text{Å}$ are illustrated by thin solid lines, and those $>3.2\ \text{Å}$ by dashed lines. 50% probability ellipsoids. Only one of the three disordered O5 positions is shown.

The geometry is irregular. Two additional O1 are 3.23 \(\text{Å}\) from K2.

A convenient way of assessing the strength and reasonableness of a K-O bond is to calculate the bond valence [6]. Considering the nearest oxygens, K1 is only 5-coordinate, and all the bonds are relatively short. The sum of these bond valences is 1.09 close to the expected K valence of $+1$. The K2-O bonds are in general longer than those to K1. The K2 valence derived from the 8 shortest distances is only 0.90, but increases to 1.00 when the two additional 3.23 \(\text{Å}\) K2-O1 distances are included.

The crystal structure is most easily visualized when viewed down the $c$-axis (Fig. 3). The BO$_3$ triangles lie approximately parallel to the $ab$ plane,
Experimental

A solution of 38.45g Sr(NO\textsubscript{3})\textsubscript{2} and 22.46g H\textsubscript{3}BO\textsubscript{3} in 153 mL H\textsubscript{2}O was blended with 226.19 g of PHF alumina hydrosol (8.2% Al\textsubscript{2}O\textsubscript{3}). The resulting sol was gelled using approximately 5 mL aqueous ammonia, and air-dried. The solid was pre-calcined by heating to 673 K at 2 K/min, to 773 K at 1 K/min, holding at 773 K for 1 h, heating to 873K at 0.5K/min, holding at 873K for 1 h, heating to 973 K at 0.5 K/min, and cooling to ambient conditions. The resulting white flakes were heated to 1023 K at 3 K/min, 1213 K at 1 K/min, held for 8 h at 1213 K, cooled to 1023 K at 1 K/min, and then cooled to ambient conditions.

A portion of the white solid was mixed with NIST 640b silicon internal standard in a Spex 8000 mixer/mill. The powder diffraction pattern was measured on a Scintag PAD V diffractometer from 5-120\(^\circ\) in 0.022 steps, counting for 18 sec/step. The pattern could be indexed [12] on a high-quality (figure of merit=108) rhombohedral cell having a = 4.904 and c = 23.936 \text{D}. A search of the Crystal Data Identification File [13] yielded a few hits, but none had the proper stoichiometry to serve as a model structure. The systematic absences were consistent with space arouos R3, R-3, R32, R3m, and Rm. MAS

\textsuperscript{11}B and \textsuperscript{27}Al NMR studies indicated that the Al atoms were tetrahedral and the B atoms trigonal planar, and that tetrahedral boron and octahedral aluminum impurities were present. These observations were consistent with the presence of a few weak unindexed peaks in the powder pattern, and a weak amorphous background. The density and the initial stoichiometry determined the cell contents as Sr\textsubscript{3}Al\textsubscript{6}B\textsubscript{6}O\textsubscript{21}.

To minimize the effects of surface roughness, microabsorption, and incomplete interception of the beam at low angles, only the 20-120\(^\circ\) portion of the pattern was included in the solution and refinement. Integrated intensities were extracted using the lowest symmetry, R3, and converted into structure factors. The 173 reflections were used as input to a Patterson synthesis [4], which indicated that the Sr atom resided at the origin. Successive cycles of least squares and difference Fourier synthesis revealed the positions of the remaining atoms. Rietveld refinements in R3 were unstable. Application of MISSYM [5] indicated the presence of 2-fold axes parallel to 100, 010, and 1 10- and thus that the true space group was R32.

All atoms were refined isotropically. Soft constraints of 1.74(l) and 1.38(l) \text{D} were applied to the Al-O and B-O bonds. These soft constraints contri-

Fig. 4. Observed, calculated, and difference diffraction patterns of SrAl\textsubscript{2}B\textsubscript{2}O\textsubscript{7}. The crosses represent the observed data points, and the solid line through them the calculated pattern. The difference pattern is plotted at the same scale as the other patterns. The bottom row of tick marks indicates the calculated reflection positions for SrAl\textsubscript{2}B\textsubscript{2}O\textsubscript{7}, and the top row marks the peaks of the Si internal standard.
buted 3% to the final reduced $P^2$. Included in the
refinements were scale factors for SrAl$_2$B$_2$O$_7$ and Si,
and the lattice parameters of SrAl$_2$B$_2$O$_7$. A March-
Dollase preferred orientation ratio (unique axis [001])
was refined. The profiles were described by pseudo-
Voigt functions. For SrAl$_2$B$_2$O$_7$, the Cauchy
$X$, $Y$, $ptec$, $stec$, and $asym$ coefficients were refined; for the
silicon internal standard, only $Y$ and $asym$ were
refined. The background was modeled by a 3-term
cosine Fourier series.

The final refinement of 29 variables using 5005
observations yielded the residuals $wRp=0.1282,
Rp=0.0966$, $P^2=7.469$, $R(F)=0.056$, and $R(F^2) =
0.1058$. The largest peak in a difference Fourier map
was $0.98\text{e}^{-3}$, and the largest difference hole was $-1.16\text{e}^{-3}$. A normal probability plot indicated that the
standard uncertainties were underestimated by a
factor of 2.23. The largest errors in the difference
pattern (Fig. 4) are in the description of the shapes of
the low-angle peaks, and at the impurity peaks. The
refined structural parameters are reported in Table 2.

**Description of the Structure**

The B atom in this new rhombohedral structure is
trigonal planar, and the tetrahedral Al atoms occur as
Al$_2$O$_7$ pairs. The Al$_2$O$_7$ is nearly "eclipsed". The Sr
coordination is trigonal prismatic (Fig. 5). In contrast
to the network structure of K$_2$Al$_2$B$_2$O$_7$, SrAl$_2$B$_2$O$_7$
has a layered structure (Fig. 6). The BO$_3$ planes are
perpendicular to the $c$-axis, and the Al$_2$O$_7$ act as pillars
between pairs of BO$_3$ planes. Both the top and the
bottom of the pillars share corners with three BO$_3$ triangles, but the top and bottom BO$_3$ triangles are
not eclipsed. This corner-sharing arrangement results
in triangular 6-ring windows in the top and bottom
surfaces of the layers. The ABC stacking sequence of
these layers creates the trigonal prismatic cavities in
which the Sr reside. There are no channels parallel to

c; the stacking sequence and the structure of the layers
block any potential channels.

The central O1 atoms of the pillars are 4.9 D apart
in the equatorial plane, suggesting that small species
might be occluded in the cavities between the pillars.
Difference Fourier maps indicate no significant
occupation of these cavities, or significant displace-
ment of O1 off the site of 32 symmetry. The observed
powder pattern does not correspond to either the
hexagonal or cubic forms reported by MacDowell
This rhombohedral structure apparently corresponds to a third polymorph. A search for structurally-similar compounds has yielded only $\text{K}_2\text{Pb}_2\text{Ge}_2\text{O}_7$ [14], which contains layers of the same topology, with Ge playing the role of Al, and Pb serving as the analog to B. The Pb are pyramidal, but recessed into the layers, rather than at the top and bottom surfaces. The $\text{Ge}_2\text{O}_7$ units are staggered, and the K occupy the interlayer regions.

**COPPER ALUMINUM BORATE, $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$**

The unusual copper aluminum borate $\text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17}$ is useful as a dehydrogenation catalyst [8]. The average structure ($I4/m, a=10.586(1), c=5.688(2) \text{ D}$) has been known for some time [151, and has been redetermined recently using single crystal techniques [16]. Structure determination has been hampered by the difficulty of preparing homogeneous materials. Recent advances in sol-gel preparative chemistry [8] have led to the synthesis of uniformly-green material, permitting a more-detailed structural study.

The crystal structure (Fig. 7) is made up of edge-sharing chains of octahedral Al atoms parallel to the tetragonal c-axis. The $\text{AlO}_6$ chains are joined in the a- and b-directions by trigonal planar BO$_3$ groups. There is a 5-coordinate site, 50% occupied each by Cu and Al, which shares a face with the $\text{AlO}_6$ octahedron. These trigonal bipyramidal sites share equatorial corners at a square planar oxygen, O1.

Trigonal bipyramidal coordination is relatively unusual for both Cu$^{2+}$ and Al$^{3+}$. We considered it unlikely that the Cu and Al ions would occupy exactly the same position within the coordination sphere, and that a split site model might be appropriate. Attempts to refine such a model using laboratory powder data did not yield improved residuals compared to a unified-site model. To study this site in more detail, we carried out a resonant scattering experiment, exploiting the tunability of synchrotron radiation.

To a first approximation, X-ray scattering is an elastic process, and the atomic scattering factor is independent of the wavelength of the incident radiation. When the frequency approaches an atomic absorption edge, inelastic processes become significant, and lead to a dependence of the scattering factor on the wavelength of the incident radiation [17]. Both the real and imaginary parts of the anomalous scattering vary, and their variation can be exploited to alter the contrast between atoms. Simultaneous refinement of one structural model using several datasets collected at different wavelengths near an absorption edge can yield information about the populations of different atoms occupying...
In this study, we sought to vary the scattering contrast between Cu and Al, to permit a more detailed understanding of the 5-coordinate site.

**Experimental**

The material studied was prepared from Cu(C$_2$H$_3$O$_2$)$_2$, Al(C$_3$H$_7$O)$_3$, and B(C$_3$H$_7$O)$_3$ using sol-gel techniques and a slow programmed drying and calcination. The product was ground in a McCrone micronising mill using ethanol as the milling liquid.

Three powder diffraction patterns were measured:

1. On a Scintag PAD V diffractometer in our laboratory, using Cu K$_\alpha$ radiation (\(\theta=1.540629\) and \(1.544451\) D) from 10-140 $^\circ$ in 0.02 $^\circ$ steps, counting for 10 sec/step

2. On beamline X7A at NSLS, using a wavelength of 1.293661 D, from 9-70 $^\circ$ in 0.02 $^\circ$ steps, counting for 5-8 sec/step

3. On beamline X3A2 at NSLS, using a wavelength of 1.37957 D, from 30-75 $^\circ$ in 0.01 E steps. This wavelength is very close to the Cu K edge.

The variation in the scattering contrast produced significant differences in the relative intensities of the lines of the powder patterns.

All three powder patterns were included in a refinement of the crystal structure using GSAS [3]. The single crystal structure model [16] was used as the initial model. The Cu1/Al1 site was refined anisotropically. All other atoms were refined with isotropic displacement coefficients. The $U_{iso}$ of O2, O3, and O4 were fixed at the average value of the single crystal $U_{iso}$. The occupancies of Cu1, Al1, Al2, and Cu2 were refined subject to the constraint that the overall Cu :Al ratio was 1:3.

The powder patterns indicated the presence of a trace of CuB$_4$O$_4$ (PDF entry 25-268). This phase was included in the refinement using a fixed structural model [19]. Phase fractions for both phases were refined, subject to the constraint that the sum of the phase fractions was unity.

Included in the refinement were histogram scale factors for each pattern, and the lattice parameters of the two phases. A March-Dollase preferred orientation ratio was refined for Cu$_2$Al$_6$B$_4$O$_{17}$ (unique axis [001]). To minimize the effects of surface roughness, microabsorption, and incomplete interception of the beam, the low-angle portion of each histogram was excluded from the refinement.

The peak profiles were described by pseudo-Voigt functions. For the synchrotron data sets, a pure Cauchy profile was used, while for the in house data a Gaussian component was required. Sample transparency and displacement terms were included for the laboratory pattern. All three profiles included an isotropic size broadening term. The background of each histogram was modeled adequately by a 3-term cosine Fourier series.

An $F_{obs}$ Fourier map (using either the multiple powder data sets or the single crystal data) calculated in the $xy0$ plane, which contains Cu1/Al1 site and O1 and O2, exhibited no evidence for a split Cu1/Al1 site (Fig. 8), but shows clear evidence for multiple O1 sites displaced from the origin. Refinement of a unified Cu/Al1 site yielded the lowest residuals, but ordered and disordered O1 refinements yielded equivalent refinements. Non-crystallographic evidence can be used to distinguish between the models.

The final refinement of 53 variables using 13099 observations (Fig. 9) yielded the residuals $wR_p = 0.0409$ and $R_p=0.0221$; the final reduced $P^2$ was 1.750. The largest peak in the final difference Fourier map was 0.80 e$^{-3}$ (1.85 D from Cu1/Al1, and 2.03 and 2.00 D from two different O4 in the channels parallel to the c-axis). All of the largest difference peaks are in the xy0 plane, and are near framework atoms. The largest difference hole was -0.67 e$^{-3}$ (0.90 D from the B). The structural parameters from the combined refinement are reported in Table 3.
Fig. 9. The three observed, calculated and difference powder patterns of \( \text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17} \) used in the resonant scattering study. The crosses represent the observed data points, and the solid lines through them the calculated patterns. The difference patterns are plotted at the same scales as the other patterns. The lower rows of tick marks indicate the calculated reflection positions for \( \text{Cu}_2\text{Al}_6\text{B}_4\text{O}_{17} \) and the upper rows the peaks of the \( \text{CuB}_2\text{O}_4 \) impurity.
Table 3. Structural parameters of Cu$_2$Al$_6$B$_4$O$_{17}$
Space group I4/m, a=10.57945(1), c=5.67357(6) \(\text{Å}\) at 27°C.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>(U_{iso}) (\text{Å}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1/Al1*</td>
<td>0.2424(12)</td>
<td>0.19110(12)</td>
<td>0</td>
<td>0.0267</td>
</tr>
<tr>
<td>Al2/Cu2H</td>
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<td>1/4</td>
<td>1/4</td>
<td>0.0050(5)</td>
</tr>
<tr>
<td>B</td>
<td>0.2504(6)</td>
<td>0.5054(7)</td>
<td>0</td>
<td>0.0079</td>
</tr>
<tr>
<td>O1</td>
<td>0.018</td>
<td>-0.018</td>
<td>0</td>
<td>0.0081(19)</td>
</tr>
<tr>
<td>O2</td>
<td>0.2086(3)</td>
<td>0.1501(3)</td>
<td>0</td>
<td>0.0098</td>
</tr>
<tr>
<td>O3</td>
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<td>0.3742(3)</td>
<td>0</td>
<td>0.0098</td>
</tr>
<tr>
<td>O4</td>
<td>0.4319(2)</td>
<td>0.2407(3)</td>
<td>0.2068(3)</td>
<td>0.0098</td>
</tr>
</tbody>
</table>

*Cu1/Al1 frac = 0.487(2)/0.513(2), \(U_{11}=0.0364(13), U_{22}=0.0148(10), U_{33}=0.029(11), U_{12}=0.0001(9), U_{13}=U_{23}=0\)

HAl2/Cu2 frac = 0.988(2)/0.012(2)

1 O1 frac = 1/4

Description of the Structure

The average crystal structure of Cu$_2$Al$_6$B$_4$O$_{17}$ has been confirmed, at higher precision. There was no evidence in the powder patterns for a different cell or space group. The octahedral sites reside on centers of symmetry, and are occupied completely by Al. The Al$_2$-O$_3$ and Al$_2$-O$_4$ distances of 1.934(2) and 1.943(2) \(\text{Å}\) fall within the normal range of octahedral Al-O distances, but the Al$_2$-O$_2$ distance of 1.822(2) \(\text{Å}\) is relatively short. The average deviation from the ideal octahedral angles is 4.3°. The B$_3$-O$_3$ distance of 1.388(6) \(\text{Å}\) and two B-04 distances of 1.352(4) \(\text{Å}\) fall within the expected range. The O-B-0 angles differ insignificantly from the expected 120°.

The trigonal bipyramidal Cul/Al1 site is half occupied each by Cu and Al. The axial distances to two O$_2$ are long and short (1.998(3) and 1.854(3) \(\text{Å}\)). Two of the equatorial distances (to O$_4$) are short (1.872(2) \(\text{Å}\)) and one (to O$_1$) is long (2.038(1) \(\text{Å}\)). The central Cul/Al1 site is displaced 0.24 \(\text{Å}\) from the center of the coordination polyhedron.

The atomic valences, calculated from the sums of bond valences [61, of the Cu and Al are 2.63 and 2.44, far from the expected values of 2 and 3. The calculated valence of O$_1$ is only 1.54, reflecting the relatively long bonds. These differences are indications that the refined structure represents an average.

Analysis of 81 Cu$^{2+}$O$_5$ coordination spheres located in the Inorganic Crystal Structure Database [20] indicates that the typical CuO$_5$ coordination sphere contains four bonds in the range 1.90-2.05 \(\text{Å}\), and one longer bond, averaging 2.2-2.3 \(\text{Å}\). The average Cu coordination sphere is therefore very unusual, in that all five bonds are shorter than 2.04 \(\text{Å}\). The Cul-O$_2$ bond of 1.85 \(\text{Å}\) is among the shortest Cu-O bonds ever reported.

XAFS experiments [21] provide evidence for Cu clustering. Each Cu has at least one Cu in its second coordination sphere. This observation, and the appearance of the \(F_{\text{obs}}\) map, suggest a new model for the local structure.

Consider the four 5-coordinate sites surrounding individual O$_1$. Stoichiometry mandates that there are two Cu and two Al in the average “4-ring” around O$_1$, and that there is only one oxygen atom at the center of the “4-ring”. If, according to the XAFS results, the Cu ions occur in “cis” pairs, a displacement of the central oxygen away from the two Cu in the xy plane would result in two long Cu-O$_1$ bonds and two short Al$_1$-O$_1$ bonds (Fig. 10). A displacement of approximately 0.27 \(\text{Å}\) along [10], to 0.018, -0.018, 0, permits the bonding requirements of all atoms to be better-satisfied, is consistent with the XAFS data, yields comparable residuals to the ordered model for O$_1$, and describes the same average structure. The combination of crystallographic and spectroscopic information has resulted in a new model for the local structure, a model consistent with all observations and with the catalytic properties of...
this material. This model could be tested by carrying our diffraction anomalous fine structure (DAFS) experiments on reflections containing large contributions from the Cul/Al1 site.

**Evolution of the Structure as a Function of Temperature**

Important to determining the catalytic properties of a material are its crystallinity and average crystallite size. These attributes can often be controlled by controlling the thermal history of the material. Accordingly, the properties of copper aluminum borate were studied as a function of calcination temperature. When a study from 600-900°C indicated that the most dramatic changes in properties occurred between 700 and 850°C, this temperature range was studied in more detail (Fig. 11). Separate portions of an initial gel were calcined at 710, 740, 780, 810, and 850°C. The powder patterns were measured on a Scintag PAD V diffractometer; in addition, patterns of the 740 and 810°C materials were measured on beamline X7A at NSLS, using a wavelength of 1.29366 Å. Aliquots calcined for 8 and 24 hours were essentially identical.

Trends can be seen in both the global and structural parameters. The crystallinity can be derived from the refined scale factors. Crystallization is complete for calcinations at 780°C and higher (Fig. 12). The average crystallite size increases with calcination temperature, and is slightly anisotropic. The appropriate crystallite size, morphology, and crystallinity can be obtained by control of the calcination temperature.

We can gain a hint (but only a hint) at the structural changes which occur during calcination. The structure of copper aluminum borate calcined at 780, 810, and 850°C is essentially identical to that reported above. The material calcined at 710°C is not...
crystalline enough to obtain useful structure structural information from the powder pattern. The multiple data sets collected on the 740, 810, and 850°C materials permit refinement of some structural detail.

The most significant changes in the structure occur at the Cul/Al1 site (Fig. 13). At all three temperatures, the total electron density at this site corresponds to half occupancy by Al and Cu, but at the lower temperatures, the average cation location is much closer to one of the oxygens O2 than to the other. In the 740 and 810°C materials, the anisotropic “thermal” ellipsoid is elongated approximately in the direction of the O2–Cu–O2 vector. At 740°C, the environment looks essentially like the superposition of a tetrahedral AlO4 site and a trigonal bipyramidal CuO5 site. It has not proven to be possible to refine split site models of this site.

It is tempting to conclude that the average structure reported here represents a “metastable high-temperature disordered” form of a more-complex reality present at lower temperatures. While it is possible to answer many structural questions using X-ray powder diffraction data, it is not always possible to gain all the information one desires. More knowledge about the structural changes in copper aluminum borate with temperature will probably require in situ neutron diffraction studies.

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