

A NOTE ON THE SYMMETRY AND BI VALENCE OF THE SUPERCONDUCTOR $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$

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The sub-structure of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ can best be described on a non-centric orthorhombic A2aa cell, which permits the oxygen in the BiO plane to move off the center of the Bi square to approach to within 2.2 Å of a pair of Bi atoms. Each Bi then has two close oxygens within the BiO plane, and a third at 2.12 Å connecting to the CuO layer. The new structure permits the apparent Bi valence to approach 3+ with a more reasonable Bi–O co-ordination than for earlier approximate structural models. This model satisfies the high resolution neutron data of Bordet et al., while agreeing in part with the co-ordination proposed on chemical grounds by von Schnering et al.

Bordet et al. [1] used neutron diffraction to decide between alternative X-ray models [2–4] for the structure of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$. Instead of the usual Aurivillius structure with an oxygen layer between a double Bi layer [2] it was shown that there are two NaCl-type BiO layers. The problem with this model is that the O3 atoms at the center of the Bi squares imply Bi–O distances much too long (or too few) to satisfy the normal Bi^{3+} co-ordination. In fact these oxygens appear disordered in this model (fig. 1c).

von Schnering et al. [5] proposed an elegant solution to this problem, with a quite different model for the BiO layers (fig. 1a,b). They placed oxygens between the nearest Bi–Bi neighbours with distances $\text{Bi–O} = 2$ Å. Of course this would produce too many short Bi–O bonds for Bi^{3+} , but by assuming that some of the Bi was actually Bi^{5+} , and systematic absence of oxygen, they constructed an attractive model which satisfied the known co-ordinations of Bi^{3+} and Bi^{5+} , while retaining the oxygen within the Bi planes as required by the neutron data.

In this paper, we show that the details of this latter model are excluded by more detailed analysis of the

neutron data, but that the BiO co-ordination is similar to that proposed by von Schnering et al. Our new model is in agreement with the approximate structure of Bordet et al., and with a new determination of the space group by convergent beam electron diffraction [6], but no longer appears so strongly disordered. Most importantly, without any chemical constraints being imposed, the new model gives a more reasonable co-ordination for Bi, which appears to be essentially Bi^{3+} .

The space group proposed by Bordet et al. was Bbmm (or of course Amma), though the neutron data were refined in the supergroup Fmmm. von Schnering et al. proposed Amaa based on X-ray single crystal measurements, and Withers et al. [6] confirmed it as either Amaa or the non-centric subgroup A2aa by convergent beam electron diffraction. The latter technique is in principle the most definitive. It is of course difficult to determine whether an m-mirror plane exists or not (and therefore a center of symmetry) except by complete determination of the structure. The higher symmetry groups simply impose special values on certain atom co-ordinates,

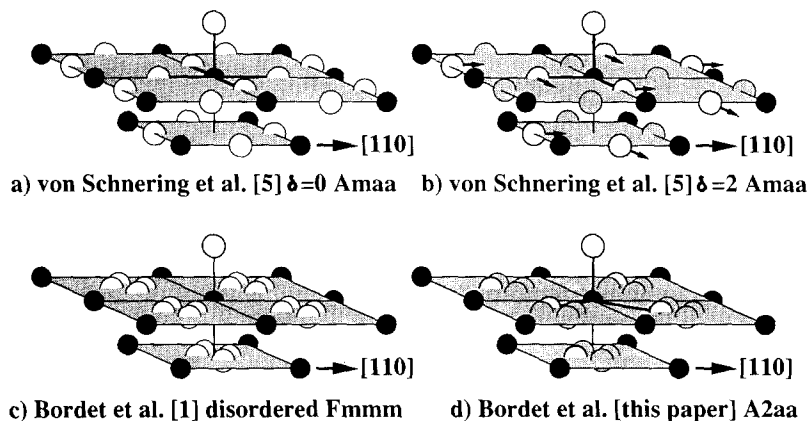


Fig. 1. The structure of the BiO planes, together with O2 connecting to the CuO layer above. (a) and (b) are the Amaa models of von Schnering et al. [5] for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{10-\delta}$ with $\delta=0$ and $\delta=2$. The arrows show the displacements necessary to obtain our new model. (c) is the Bordet et al. [1] Fmmm model with “disordered” oxygen in the BiO plane; this is the average structure of (d) the present A2aa model. The displacements of the Bi atoms are not shown, nor are the displacements necessary to produce the $5 \times b$ -axis superstructure [7].

as shown in table I, and forbid certain classes of reflections, which will in any case be very weak.

The Fmmm structure of Bordet et al. was taken as the starting model, and the data refined in Amaa by permitting all atoms to move off the y -axis special positions y_{Bord} . Only the BiO plane oxygen O3 on site (81) in Amaa was much displaced by relaxing the symmetry from Fmmm. This is the atom that appeared most “disordered” in the Fmmm cell (where

it was labelled O2), and which is sometimes described on split sites. In Amaa, the best refinement was in fact obtained by splitting O3 between two sites to either side of the center of the Bi square, and only about 2 Å from pairs of Bi atoms. In an attempt to remove the need for split atoms, we simply removed the center of symmetry to obtain the group A2aa. O3 was then not constrained in any way, and immediately moved to occupy a position close to one pair of Bi atoms.

Table I

Atom co-ordinates (x, y, z), site “occupancies” (n) and vibrational amplitudes ($B=8\pi^2\langle u^2 \rangle \text{Å}^2$) for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ at 300 K. The space group is A2aa, but the center of symmetry in Amaa has been retained ($x=0$ or $1/4$) for all atoms except O3 oxygen within the BiO plane, which when placed in a general position, moves to within 2.2 Å of a pair of Bi atoms. Clearly, the R_{ν} factor is significantly improved by this model. Electron and X-ray diffraction [1] indicate that the superstructure may also involve x -displacements. The Bordet et al. [1] Fmmm structure would be obtained by constraining as well the y co-ordinates to y_{Bord} , clearly a good approximation for all except O3. The von Schnering et al. [5] Amaa structure is similar, except for O3($x, y_{\nu-s}$). Only the oxygen sites O1 within the CuO plane have been assumed fully occupied ($n=8$). The errors in the refined site occupancies are rather large, but may indicate Bi deficiency ($n < 8$), or may be related to Bi displacements associated with the superstructure. Cell dimensions refined to $a=5.4095(4)$, $b=5.4202(4)$, $c=30.9297(25)$. Scattering lengths are 8.526(Bi), 4.900(Ca), 7.020(Sr), 7.718(Cu), 5.805(O).

Atom	n	B	x	y	z	$x_{\nu-s}$	$y_{\nu-s}$	$z_{\nu-s}$	x, y_{Bord}
Bi 8d	7.5(2)	4.5(2)	0	0.239(3)	0.4454(2)	0	0.227	0.4478	0, 1/4
Ca 4c	3.9(2)	1.8(3)	0	3/4	1/4	0	3/4	1/4	0, 3/4
Sr 8d	8.3(2)	2.9(2)	0	0.737(2)	0.3586(2)	0	0.75	0.3592	0, 3/4
Cu 8d	8.7(2)	2.0(1)	0	0.264(2)	0.3041(2)	0	0.25	0.3034	0, 1/4
O11 8d	8	0.5(1)	1/4	-0.011(4)	0.3109(2)	1/4	0	0.302	1/4, 0
O12 8d	8	0.5	1/4	0.496(5)	0.2905(2)	1/4	1/2	0.304	1/4, 1/2
O2 8d	7.4(2)	5.4(4)	0	0.269(5)	0.3772(5)	0	0.25	0.377	0, 1/4
O3 8d	8.6(2)	9.6(9)	0.378(6)	0.359(6)	0.4397(6)	1/4	1/2	0.457	1/2, 1/4
R_{ν}				13.9					19.9

Table II

Bond lengths and resulting Zachariasen–Brown–Altermatt [9] valences V_i for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ with parameters $r_0 = 2.094$ (Bi), 1.967 (Ca), 2.118 (Sr), 1.679 (Cu). The co-ordination of Bi is now similar to that proposed on chemical grounds by von Schnering et al. [5], and the apparent valence of bismuth $V(\text{Bi})$ is more satisfactory. The Ca–O and Ba–O co-ordination is normal. The average Cu valence is larger than 2, as in all other CuO-based superconductors.

Bi–O2	2.12(2)	Ca–O11	2.66(1)×2	Sr–O11	2.42(1)
–O3	2.15(3)	–O11	2.72(1)×2	–O11	2.49(1)
–O3	2.28(3)	–O12	2.30(1)×2	–O12	2.82(1)
		–O12	2.28(1)×2	–O12	2.80(1)
–O3	3.31(4)	$V(\text{Ca})$	2.2	–O2	2.60(3)
–O3	3.43(3)	Cu–O11	2.03(2)	–O2	2.77(0)×2
–O3	3.67(2)		1.94(2)	–O2	2.94(3)
			1.90(2)	–O3	2.65(2)
			1.92(2)		
		–O2	2.26(2)		
$V(\text{Bi})$	2.5	$V(\text{Cu})$	2.2	$V(\text{Sr})$	2.1

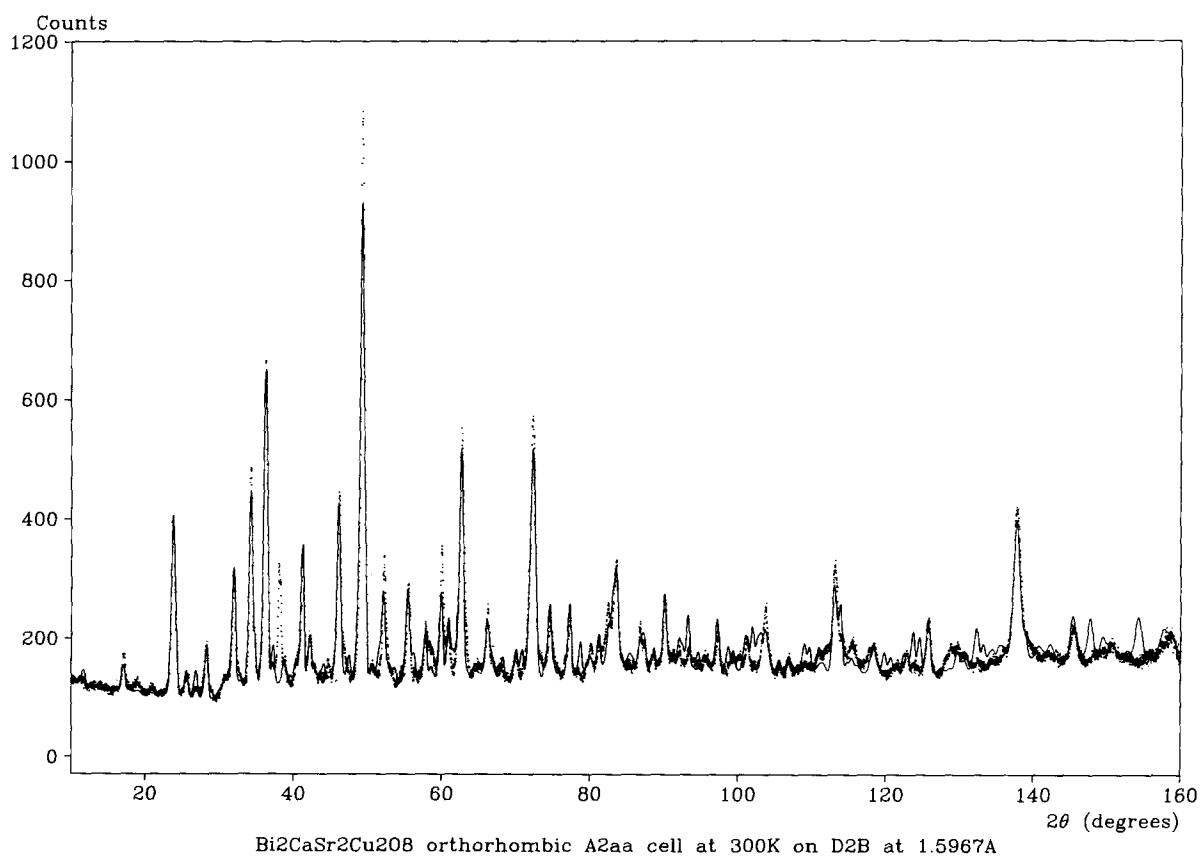


Fig. 2. Observed and calculated neutron powder diffraction patterns for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ at room temperature measured with neutrons of wavelength 1.5967 Å on D2B at ILL Grenoble. There are still important differences between the observed and calculated profile, since no attempt has been made to model the strong superstructure observed with electrons [7].

The resulting structure is significantly different for the BiO layer to that proposed by von Schnering et al., but the Bi–O co-ordination is similar (fig. 1). Each Bi has three close oxygens at between 2.12 Å and 2.28 Å (table II), opposite the “lone pair” of electrons on Bi^{3+} and three oxygens at much larger distances. This co-ordination is much more satisfactory than that obtained with the Fmmm cell, but all Bi remains Bi^{3+} and there is no experimental evidence for Bi^{5+} . The formula is close to $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$, though table II indicates that as much as 6(3)% of the Bi may be missing. There is no evidence for missing Sr [8]. Of course, this refinement in the sub-cell takes no account of possible Bi displacements associated with the ~ 4.75 Å superstructure [7].

von Schnering et al. placed all atoms except Bi on special values of y . Presumably this was because only Bi(y) could be refined from their X-ray data. In particular, O3 (their O4) is fixed to special position (8h) determined by chemical arguments. When we start from these special positions (slightly offset to break the symmetry) and refine in space group A2aa, O3 moves away from this special position toward the center of the Bi square (fig. 1b) and we obtain the structure reported here. In fig. 2 there are still important differences between the observed and calculated profiles, since no attempt has been made to model the strong superstructure observed with electrons [7].

The final result shows that the structure of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ refined in the A2aa subcell retains the satisfactory Bi–O co-ordination proposed by von Schnering et al., but that there is now no need to in-

voke Bi^{5+} . Furthermore, it is consistent with the tetragonal structure of the Tl analogue $\text{Tl}_2\text{Ca}_1\text{Ba}_2\text{Cu}_2\text{O}_8$, which has also been obtained by neutron diffraction [10,11], and for which the Tl^{5+} valence state does not exist.

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