Structure and polytypes in thallium superconductors

1988 Supercond. Sci. Technol. 1 132

(http://iopscience.iop.org/0953-2048/1/3/005)

Supercond. Sci. Technol. 1 (1988) 132–136. Printed in the UK

Structure and polytypes in thallium superconductors

J P Zhang, D J Li, H Shibahara and L D Marks
Center for Surface Radiation Damage Studies and Materials Research Center, Northwestern University, Evanston, IL 60208, USA

Received 7 July 1988

Abstract. There have been a number of small contradictions in reports of the structure of the recently discovered thallium superconducting materials, in particular the phase $Tl_2Ba_2Ca_2Cu_3O_x$, hereafter abbreviated to 2223. The structure has been reported to be pseudo-tetragonal or I4/mmm with a *c* axis of 3.625, 3.61 or 3.59 nm, and an *a* axis of 0.54, 0.547 or 0.385 nm. We report here results obtained by high-resolution electron microscopy and diffraction which show that these results are not inconsistent with each other. The *a* axis is around 0.385 nm, and the *c*/*a* axis ratio and the experimental images are genuinely variable, which we suspect is due to variations in the oxygen stoichiometry. The earlier reports of an *a* axis of 0.547 nm are due to loss of symmetry caused by intergrowths. We also report evidence for polytypism based around half unit cell blocks involving the local stoichiometries $Tl_2Ba_2Ca_1Cu_2O_x$ (2212), $Tl_2Ba_2Ca_3Cu_4O_x$ (2234), $Tl_2Ba_2Ca_4Cu_5O_x$ (2245) and $Tl_2Ba_2Ca_5Cu_6O_x$ (2256). In all these materials the *a* axis appears to remain the same but there is a small systematic contraction in the local Cu–Ca–Cu perovskite spacing along the *c* axis as the number of perovskite units increases, which we suggest could be linked to the superconducting transition temperature.

Despite the recent discovery [1] of superconducting thallium materials there have been a number of apparent contradictions in reports of the structure; particularly of the 2223 phase [2-4]. A pseudo-tetragonal structure with *a* and *c* axes of 0.54 and 3.625 was reported by Hazen *et al* [2], whereas a I4/mmm structure was reported by Fung and co-workers and Torardi and co-workers, with *a* and *c* axes of 0.547 and 3.61 [3], and 0.385 and 3.59 [4] respectively.

The specimens that we have examined were prepared as described elsewhere by Hazen *et al* [2], and here we concentrate on the samples with an initial composition of $Tl_2Ba_2Ca_2Cu_3$, which displayed an onset temperature of 120 K and zero resistivity above 100 K. For electron microscopy these specimens were crushed and mounted onto well pyrolised holey carbon films, and then examined in either a Hitachi H-700U for tilting experiments or a Hitachi H-9000 for high-resolution studies.

Figure 1 shows a set of diffraction patterns taken from a single grain of the material which serves to define the reciprocal lattice. From these data there are systematic absences when $h + k + l$ is odd, which indicates a body-centred tetragonal cell with symmetry I4/mmm and lattice parameters of $a = 0.385$ and *c* variable in the range 3.526 to 3.588 nm, from measurements of seven different grains from the same sample based upon the ratio of *c*/*a*. An exception to this is shown in figure 2 where weak (100) and (010) spots are observed, which would imply either a primitive tetragonal cell of the same size or a larger one with C4/mmm symmetry and $a = 0.547$ nm. As will be shown below, this material can contain intergrowths which destroy the local $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ symmetry translation and therefore lead to the apparently larger unit cell.

We next consider the size of the unit cell, in particular the magnitude of the *c*/*a* ratio in these materials. In electron diffraction and imaging in an electron microscope there are possibilities of errors in absolute spacings unless an internal standard is used, but we can eliminate these errors by using the ratio *c*/*a*. From seven different grains taken from the same initial sample, we have measured *c*/*a* ratios in the range 9.16 to 9.32, where the error bar in these measurements is less than 0.3%. (Systematic errors due to astigmatism in the diffraction pattern were calibrated to be less than 0.2%.) Although these variations are fairly substantial, it should be noted that when the larger size of the unit cell is taken into account they are only twice those found between the orthorhombic and tetragonal forms of the 123 superconductor. To understand the variability of these values, figure 3 shows part of a high-resolution focal series with image simulations inset. To generate the atomic positions we used the approach of measuring the positions of the 'black dots' in the images and then using these as the first guess for the metal atom posi-

0953-2048/88/030132 + 05 $02.50

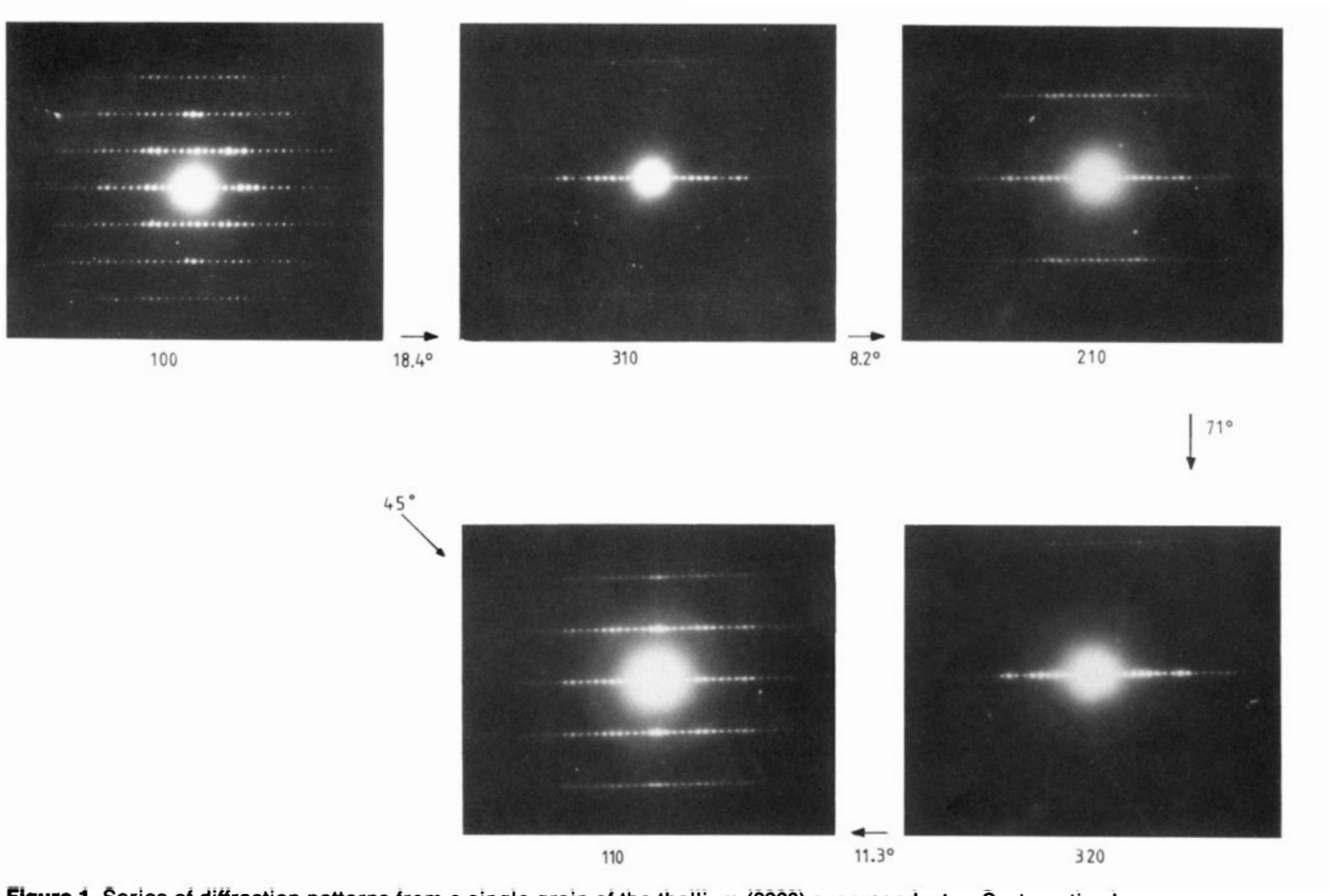

Figure 1. Series of diffraction patterns from a single grain of the thallium (2223) superconductor. Systematic absences occur when $h + k + l$ is odd indicating a body-centred tetragonal unit cell with axis $a = 0.385$ and c approximately 3.6 nm.

tions. The precise positions of the atoms were allowed to vary a little from this initial guess to optimise the agreement between the experimental and calculated images for a range of defoci and thicknesses. After we had completed these calculations we saw a preprint describing the structure as determined by x-ray studies [4], which agreed well with our positions including a high temperature factor for the thallium atoms. However, these studies [4] reported an oxygen content of 10 ($Tl_2Ba_2Ca_2Cu_3O_{10}$) and a c/a ratio of 9.32, whereas we obtained noticeably better agreement with the experimental images for an oxygen content of $10 - x$, with some redistribution of the oxygen from around the copper sites to the calcium sites, and in this particular image found a c/a ratio of 9.2. (This procedure does not necessarily give a unique structure, and for this reason we have not included the atomic positions that we used since the experimental error in them would be too large.) This implies that the variable c/a ratio may be due to changes in the exact oxygen content in the superconductors, which can be a function of the preparation conditions. It should be noted that we cannot be positive that it is only the c axis length and not both the a and c axes which are changing, and that we have also detected differences between experimental c/a ratios and those reported by x-ray analyses in the 2212 superconductor; these are currently being investigated in more detail. For reference, figure 4 shows calculated images for the positions used in our calculations and those obtained from x-rays [4]; the x-ray positions lead to too strong a contrast within the perovskite blocks, as shown by the line traces in figure 5.

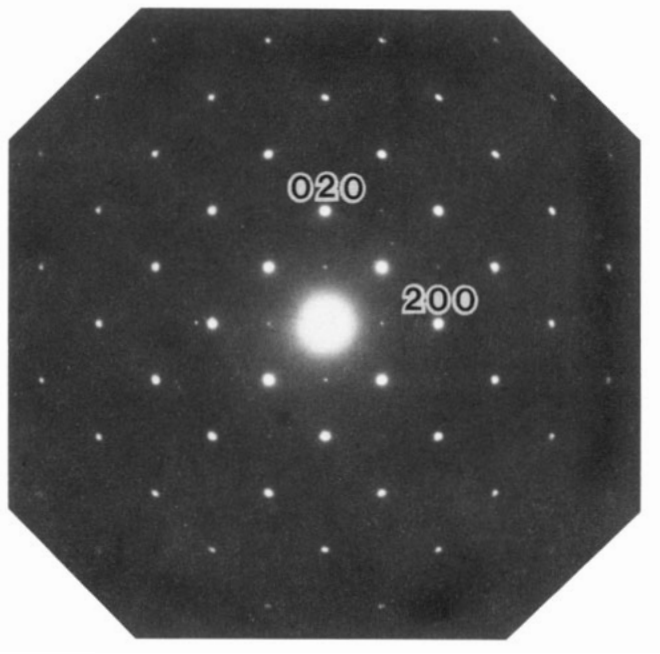

Figure 2. Diffraction patterns showing weak forbidden spots which can be attributed to intergrowths.

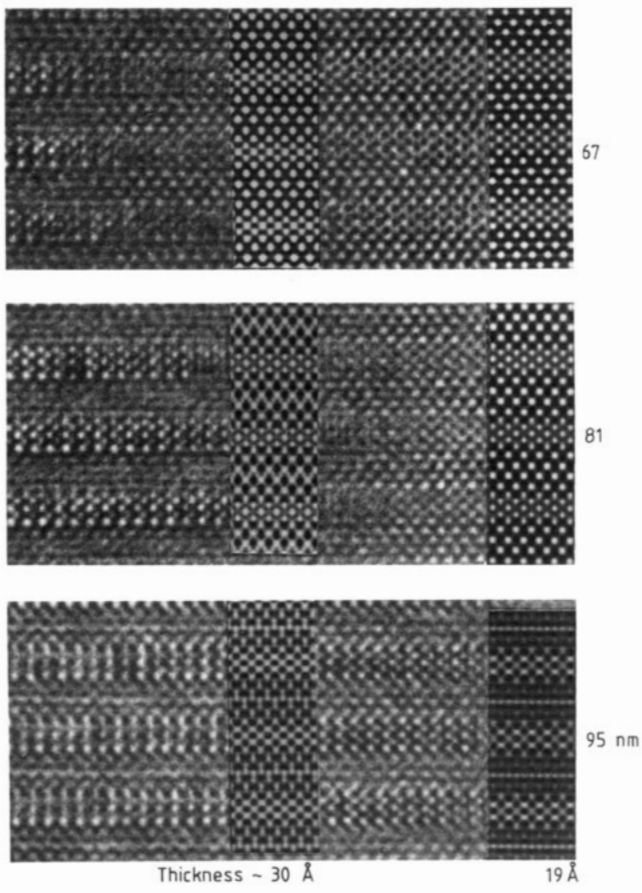

Figure 3. High-resolution electron microscope images with image simulations inset for defoci of (*a*) −67, (*b*) 81 and (*c*) 95 nm, The thicknesses for the calculations which are inset in the images are 1.9 nm on the right and 3.1 nm on the left. For this particular grain the structure determined by x-ray techniques gives a worse agreement with the experimental images—see figure 4.

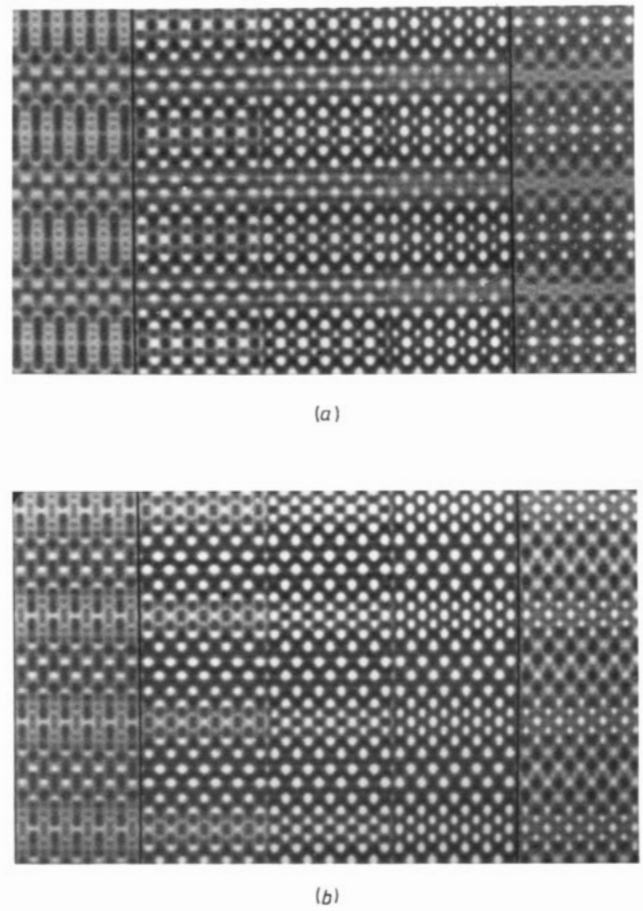

Figure 4. Comparison of calculated images for the structure (*a*) given in reference [4] and (*b*) that used in figure 3 for a thickness of 30 Å and defoci from −530 to −810 Å. The x-ray structure leads to too much contrast within the perovskite blocks relative to the BaTlTlBa layers.

To emphasise the fact that there is a genuine structural variability, rather than one due to experimental errors, figure 6 shows simulated and experimental images from a second area where the experimental images are in fact much closer to those obtained using the x-ray data [4], except that there is too much contrast at the barium sites in the calculated images—see also the line trace in figure 5(*c*). (The experimental images were obtained in this case by direct acquisition into an Apollo computer via a Gatan TV camera and a digital framestore, with eight unit cells averaged to reduce shot noise.) Although at first sight this supports the x-ray structure, there was clear evidence in the diffraction pattern for a periodic modulation of the struc-

Table 1. Structure variants in the Tl–Ba–Ca–Cu–O system. The variants can be indexed in terms of the compositions $(Tl_2Ba_2O_4):CuO(CaCuO_2)_n$, with some possible variation in the oxygen content. Shown in the table are the compositions, the observed *c* axis lattice parameters and the Cu–Ca–Cu spacing in the perovskite blocks with the variation relative to the $n = 1$ structure shown. All measurements were from intergrowths within the host 2223 structure, with the host spacing used as an internal calibrant, and were obtained by measuring the size of the perovskite block and then dividing by the number of repeats with an accuracy of about 2%.

	Composition					Metal	*c*/2	Perovskite spacing	
n	Tl	Ba	Ca	Cu	O	layers	(nm)	(nm)	(%)
1	2	2	1	2	8	7	1.45	0.326	100
2	2	2	2	3	10	9	1.78	0.313	96
3	2	2	3	4	12	11	2.08	0.304	93
4	2	2	4	5	14	13	2.38	0.296	91
5	2	2	5	6	16	15	2.67	0.291	89

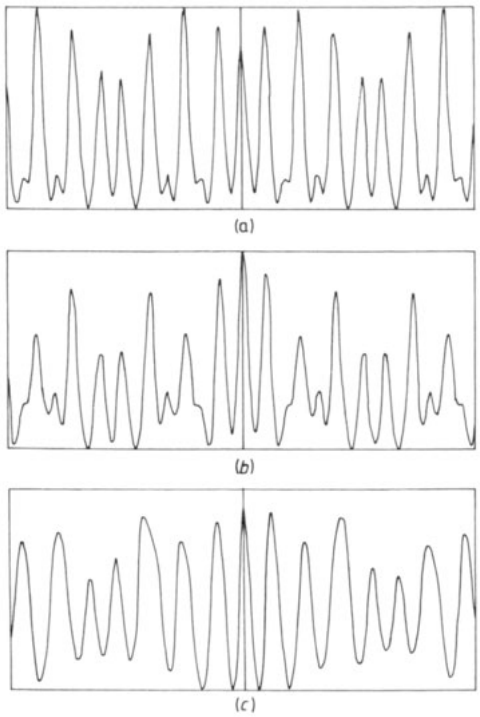

Figure 5. Line traces from the calculated images (*a*) from the modified structure, (*b*) from the x-ray structure and (*c*) experimental data from a second region with a slowly varying component removed. Comparing (*a*) and (*b*), the intensity variations in (*b*), where the maxima are at the sites of the cations, are larger than in the experimental images. Redistributing the oxygen leads to (*a*) which is in better agreement with the results in figure 3. It should be noted that (*c*), in contrast, agrees better with (*b*).

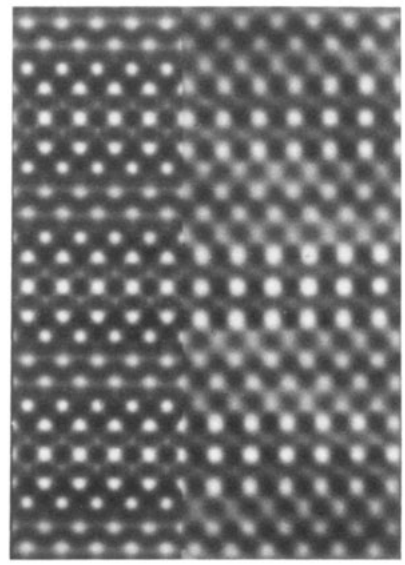

Figure 6. Comparison of experimental and calculated images using the x-ray structure for a defocus of −625 Å and a thickness of 30 Å for a second region. Except for the fact that there is too much contrast in the calculations at the barium sites, the agreement is excellent. However, this region showed a superstructure in the diffraction pattern and had a different unit cell.

ture similar to that observed by Zandbergen *et al* [5]. From the image, the structure appears to agree but the unit cell is quite different. (It should be mentioned that Zandbergen *et al* [5] presented diffraction data indicating genuine structural variations.)

The final result is that these materials appear to form intergrowths/polytypes in a very similar way to materials such as silicon carbide [6, 7] or copper titanium [8]. As an example, figure 7 shows areas where there are intergrowths of (2212) and (2245) in the host (2223). (The intergrowth unit is half a unit cell along the *c* axis.) From these images we can see that the intergrowths all appear to share the same *a* unit cell parameter, and measurement of the width of the BaTlTlBa block indicates that the structure of this unit of atoms appears to remain the same. The only variable in the structure is the number of Cu–Ca–Cu perovskite blocks between any pair of BaTlTlBa units. One interesting feature is that there is a small contraction in the Cu–Ca–Cu spacing of the perovskite unit cell which can be

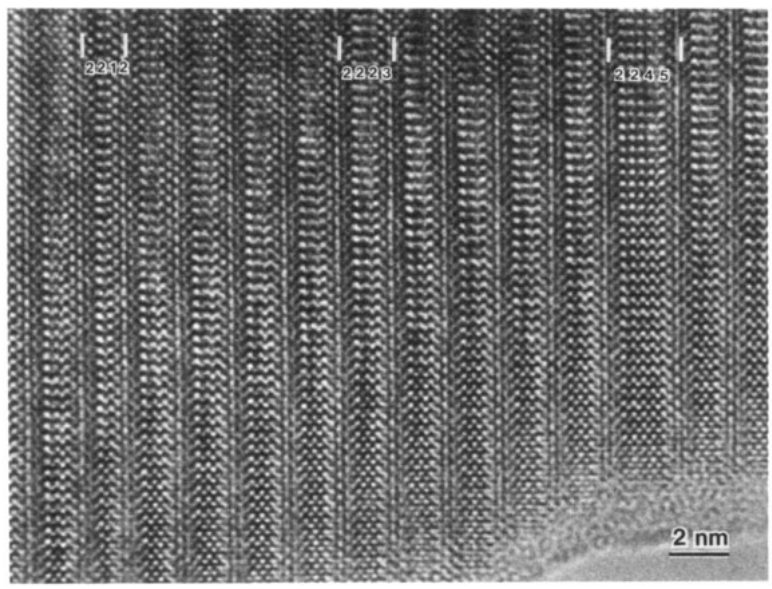

Figure 7. High-resolution electron micrograph showing intergrowth of (2212) and (2245) in the host (2223).

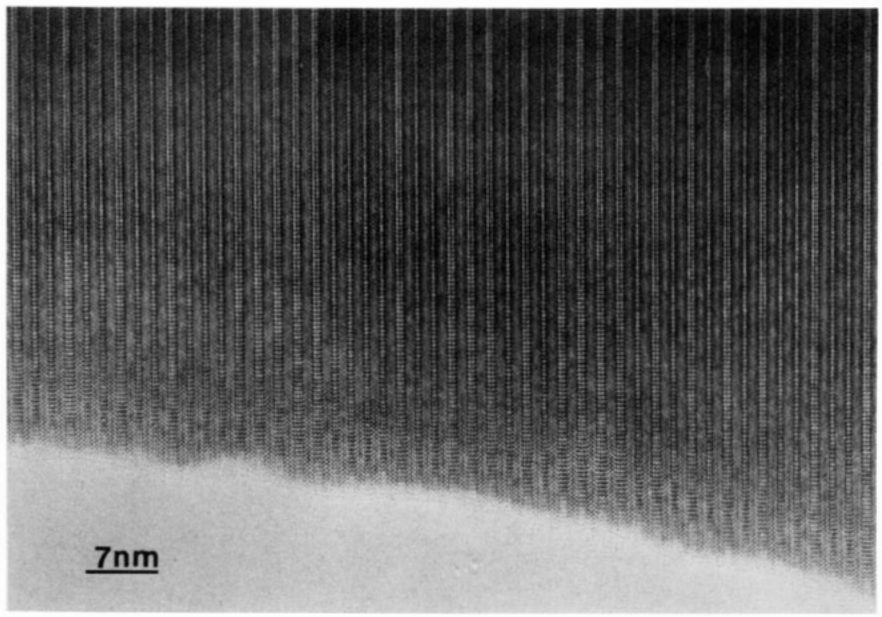

Figure 8. Area of the thallium superconductor showing polytypes based upon (2212) and (2223) half-unit-cell units; in the image the (2212) units show one white line of contrast and the (2223) two white lines for the defocus used. Polytypes such as {(2212) (2223)} and {$(2212)_2$ (2223)} are evident.

measured from these and similar images, and our results are summarised in table 1. There would appear to be a possible link between the local perovskite spacing and the superconducting transition temperature, which is an interesting avenue to explore; we suspect that this may be a more fundamental source than simply the increase in the number of perovskite blocks leading to a rise in the superconducting transition temperature, since the latter argument runs into a logical problem with bulk perovskites. In terms of the possible polytypes that can occur in these structures, we have to date detected the repeat units {(2212) (2223)}; {$(2212)_2$ (2223)}; {$(2212)_3$ (2223)}; {$(2212)_4$ (2223)} and {(2234) (2256)} where the unit in the curly brackets is repeated at least a few times, in addition to simple intergrowths; an example is shown in figure 8. We suspect that essentially any intergrowth/polytype struture can occur to accommodate the local cation stoichiometry.

Acknowledgments

This work was supported by the National Science Foundation through Northwestern University Materials Research Center on Grant number 85-20280 and the Airforce Office of Scientific Research on Grant number 86-0344 DEF. The authors are indebted to Professor R M Hazen for the specimens.

References

[1] Sheng Z Z and Hermann A M 1988 *Nature* **332** 138–9
[2] **Hazen R M, Finger L W, Angel R J, Prewitt C T, Ross N L and Hadidiacos C G 1988 *Phys. Rev. Lett* 60 1657–60**
[3] Fung K K, Zhang Y L, Xie S S and Zhou Y Q 1988 *preprint*
[4] Torardi C C, Subramanian M A, Calabrese J C, **Gopalakrishnan J, Morrissey K J, Askew, T R, Flippen R B, Chowdry U and Sleight A W 1988** *Science* in press
[5] Zandbergen H W, van Tenderloo G, van Landuyt J and Amelinckx S *Appl. Phys.* C to be published
[6] **Smith D J Jepps N W and Page T F 1978 *J. Microsc.* 114 1**
[7] **Jepps N W and Page T F 1980 *J. Microsc.* 119 177**
[8] Ye H Q and Amelinckx S 1985 *Phys. Status Solidi* a **88** 483