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Structure refinement of the layered composite crystal $Sc_2B_{1.1}C_{3.2}$ in a five-dimensional formalism

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The crystal structure of a layered compound $Sc_2B_{1.1}C_{3.2}$, scandium boride carbide (M_r = 140.43), has been re-refined as a commensurate composite crystal using 1795 single-crystal X-ray diffraction intensities with $I > 2\sigma(I)$ collected by Shi, Leithe-Jasper, Bourgeois, Bando & Tanaka [(1999), *J. Solid State Chem.* **148**, 442–449]. The crystal is composed of two layered subsystem structures, *i.e.* Sc—C—Sc sandwiches and graphite-like layers of the composition $B_{1/3}C_{2/3}$. The structure refinement was performed in a five-dimensional formalism based on the trigonal superspace group $P\bar{3}m1(p00)(0p0)0m0$. The unit cell and other crystal data are $a = b = 3.387$ (1), $c = 6.703$ (2) Å, $V = 66.59$ (1) Å^3, $\boldsymbol{\sigma}_1 = (9/7\ 0\ 0)$, $\boldsymbol{\sigma}_2 = (0\ 9/7\ 0)$, $Z = 1$, $D_x = 3.501$ Mg m^{-3}. Two different three-dimensional sections through the superspace were analyzed, corresponding to two different superstructure models, one with $P\bar{3}m1$ and the other with $P3m1$. A random distribution of B and C was assumed in the graphite-like layer and 41 structural parameters were introduced. R_F/wR_F were 0.0533/0.0482 and 0.0524/0.0476, respectively, for the first and second models. Although the difference between these R_F or wR_F values was too fine to exclude one of the models definitely, the advantages of using a superspace group were obvious. It not only brought about better convergence of refinement cycles by virtue of fewer parameters, but also gave an insight into the problem of symmetry of the superstructure.

1. Introduction

The existence of a new layered compound near the nominal composition of $Sc_2B_{1.1}C_{3.1}$ was revealed during search in the Sc—B—C system (Shi, Leithe-Jasper & Tanaka, 1999). The powder X-ray diffraction and electron diffraction patterns indicated that this compound has a two-dimensional incommensurate character with basic hexagonal axes $a = 3.399$, $c = 6.714$ Å. Single crystals have been grown successfully and the electron diffraction pattern for a single crystal indicated that this single crystal has a two-dimensional commensurate 7×7 superlattice structure of the basic cell of $a = 3.387$, $c = 6.703$ Å (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999). The crystal structure determination has been performed based on a large unit cell, $A = 23.710$ (9) and $c = 6.703$ (2) Å, with the trigonal system $P\bar{3}m1$ using single-crystal X-ray diffraction intensity data collected on an Enraf–Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999). The crystal structure is composed of alternate $-[B_{1/3}C_{2/3}]-Sc-C-Sc-[B_{1/3}C_{2/3}]-$ layers (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999).

Table 1
Experimental details.

Chemical formula	$C_{157}B_{54}Sc_{98}$
Formula weight	6881.00
Crystal dimension (mm)	0.2 × 0.1 × 0.06
Unit cell for data collection	Trigonal
A (Å), c (Å)	23.710 (9), 6.703 (2)
Calculated density (Mg m^{-3})	3.501
Temperature of data collection (K)	293
Diffractometer	Enraf–Nonius CAD-4
Wavelength λ(Mo $K\alpha$) (Å)	0.71073
Scan type	ω–2θ
$2\theta_{max}$ (°)	76
Range of hkl	$0 \rightarrow 35$, $0 \rightarrow 35$, $-7 \rightarrow 11$
Total number of reflections measured	8284
$R_{int}(F^2)$	0.050
Linear absorption coefficient μ (mm^{-1})	4.785
Absorption correction	Gaussian
Former refinement	Shi, Leithe-Jasper, Bourgeois *et al.* (1999)
Number of unique reflections with $\|F\| > 4\sigma(\|F\|)$	1292
Space group	$P\bar{3}m1$
Refinement method	Full-matrix least-squares on F^2 (*SHELXL97*; Sheldrick, 1997)
Number of parameters	168
Temperature factor	Anisotropic individual (Sc), isotropic individual (B), isotropic individual ($B_{1/3}C_{1/3}$)
R_1	0.0461
wR_2	0.1031
Re-assignment and present refinement	
Chemical formula	$Sc_2B_{54/49}C_{157/49}$
Refinement method	Full-matrix least-squares on F
Computer program	*FMLSM* (Kato, 1994)
Weighting scheme	$w = 1$
Source of atomic scattering factor	International Tables for X-ray Crystallography (1974, Vol. VI)
Number of reflections [$I > 2\sigma(I)$]	1795
(1) Superspace-group approach	
Superspace group	$P\bar{3}m1(p00)(0p0)0m0$
a (Å), c (Å), Z	3.387 (1), 6.703 (2), 1
$\boldsymbol{\sigma}$ vector	σ_1 = (9/7 0 0), σ_2 = (0 9/7 0)
Temperature factor	Anisotropic (Sc), isotropic (C and $B_{1/3}C_{1/3}$)
Number of parameters	43
Structural parameter	41
Scale factor	1
Parameter for extinction correction	1
R_F, wR_F, AIC (the first model)	0.0533, 0.0482, 16373
R_F, wR_F, AIC (the secondt model)	0.0524, 0.0476, 16329
(2) Superstructure approach	
Space group	$P\bar{3}m1$
A (Å), c (Å), Z	23.710 (9), 6.703 (2), 49
Temperature factor	Anisotropic individual (Sc), isotropic common (B), isotropic common ($B_{1/3}C_{1/3}$)
Number of parameters	145
structural parameter	143
scale factor	1
parameter for extinction correction	1
R_F, wR_F, AIC	0.0506, 0.0480, 16564

B and C atoms form a graphite-like layer with a mean bond length of 1.533 Å and the 'Sc—C—Sc' units appear to be rather loosely contained between the graphite-like layers.

It has become clear that some crystals consist of plural structural units with their respective periodicity and they are called composite crystals (Janner & Janssen, 1980; Hyde & Andersson, 1989). Some of the composite crystals have been described as an interpenetration of two layered structures which alternate regularly through the crystal, in spite of the misfit between their two-dimensional lattices and they are often called misfit layer compounds (Wiegers, 1996). Such a total structure can be described based on superspace-group theory (Janner & Janssen, 1980), and many misfit layer compounds have been analyzed using four-dimensional superspace groups (Kato, 1990; van Smaalen, 1995).

The diffraction intensity data of $Sc_2B_{1.1}C_{3.2}$ seem to exhibit many absences not related to the reflection conditions with a large unit cell, A = 23.710 (9) and c = 6.703 (2) Å. Diffraction spots which are very weak or absent can be indexed as higher-order satellites in the high-dimensional description, and it may be possible to treat the structure as modulated with only lower-order modulations which thus reduce the independent parameters to be refined. Moreover, the superspace-group approach can allow a uniform treatment of the commensurate and incommensurate structures of this series and will lead to their better understanding.

In the present work, the structure of $Sc_2B_{1.1}C_{3.2}$ is treated as an interpenetration of two layered subsystem structures, *i.e.* Sc—C—Sc sandwiches and graphite-like layers of the composition $B_{1/3}C_{2/3}$. The crystal structure has been reinvestigated in a five-dimensional formalism based on the superspace-group approach for composite crystals (Janner & Janssen, 1980).

2. Single-crystal X-ray diffraction data

The same intensity data as those collected in the former work (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999) were used again. Conditions of data collection and the crystallographic data of $Sc_2B_{1.1}C_{3.2}$ are listed in Table 1.

3. Symmetry

The strong reflections could be indexed using two sets of hexagonal axes with different a and common c: for the Sc_2C part a_1 = 3.387 and c = 6.703 Å; for the $B_{1/3}C_{2/3}$ part a_2 = 2.634 and c = 6.703 Å. Five integers, h, k, l, m and n are used in order to index all reflections. Each reflection is expressed by $\mathbf{q} = h\mathbf{a}_1^* + k\mathbf{b}_1^* + l\mathbf{c}^* + m\mathbf{a}_2^* + n\mathbf{b}_2^*$. The reciprocal vectors of the two subsystems, $\mathbf{a}_1^*$, $\mathbf{b}_1^*$, $\mathbf{c}^*$ and $\mathbf{a}_2^*$, $\mathbf{b}_2^*$, $\mathbf{c}^*$, are related to the minimal vector set in reciprocal space through the Z matrices (Janner & Janssen, 1980): Z^1 = (1 0 0 0 0 / 0 1 0 0 0 / 0 0 1 0 0) for subsystem 1 (Sc_2C part) and Z^2 = (0 0 0 1 0 / 0 0 0 0 1 / 0 0 1 0 0) for subsystem 2 ($B_{1/3}C_{2/3}$ part). As $a_1 = b_1 = A/7$ and $a_2 = b_2 = A/9$, the cell constants in a five-dimensional formalism are $a = b$ = 3.387 (1), c = 6.703 (2) Å, $\boldsymbol{\sigma}_1$ = (9/7 0 0), $\boldsymbol{\sigma}_2$ = (0 9/7 0). The possible superspace group can be derived from the

Table 2
Results of symmetry consideration.

(*a*) Generator set of symmetry operations

Space group		
Subsystem 1 (Sc_2C part)	Subsystem 2 ($B_{1/3}C_{2/3}$ part)	Superspace group $[Sc_2C][2(B_{1/3}C_{2/3})]_{81/49}$
a_1 = 3.387 c = 6.703 Å	a_2 = 2.634 c = 6.703 Å	a = 3.387 c = 6.703 Å, σ_1 = (9/7 0 0), σ_2 = (0 9/7 0)
x, y, z	x, y, z	x, y, z, u, v
$-y, x-y, z$	$-y, x-y, z$	$-y, x-y, z, -v, u-v$
$-y, -x, z$	$-y, -x, z$	$-y, -x, z, -v, -u$
$-x, -y, -z$	$-x, -y, -z$	$-x, -y, -z, -u, -v$
$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1(p00)(0p0)0m0$

(*b*) Atom position and set of modulation wavevectors related to each other.

	Subsystem	x	y	z	Modulation wavevector set
Sc	1	1/3	2/3	z	$m\mathbf{a}_2^*+n\mathbf{b}_2^*$, $n\mathbf{a}_2^*-(m+n)\mathbf{b}_2^*$, $-(m+n)\mathbf{a}_2^*+m\mathbf{b}_2^*$, $-n\mathbf{a}_2^*-m\mathbf{b}_2^*$, $-m\mathbf{a}_2^*+(m+n)\mathbf{b}_2^*$, $(m+n)\mathbf{a}_2^*-n\mathbf{b}_2^*$
C	1	0	0	1/2	$m\mathbf{a}_2^*+n\mathbf{b}_2^*$, $n\mathbf{a}_2^*-(m+n)\mathbf{b}_2^*$, $-(m+n)\mathbf{a}_2^*+m\mathbf{b}_2^*$, $-n\mathbf{a}_2^*-m\mathbf{b}_2^*$, $-m\mathbf{a}_2^*+(m+n)\mathbf{b}_2^*$, $(m+n)\mathbf{a}_2^*-n\mathbf{b}_2^*$, $n\mathbf{a}_2^*+m\mathbf{b}_2^*$, $-(m+n)\mathbf{a}_2^*+n\mathbf{b}_2^*$, $m\mathbf{a}_2^*-(m+n)\mathbf{b}_2^*$, $-m\mathbf{a}_2^*-n\mathbf{b}_2^*$, $(m+n)\mathbf{a}_2^*-m\mathbf{b}_2^*$, $-n\mathbf{a}_2^*+(m+n)\mathbf{b}_2^*$
$B_{1/3}C_{2/3}$	2	1/3	2/3	z	$h\mathbf{a}_1^*+k\mathbf{b}_1^*$, $k\mathbf{a}_1^*-(h+k)\mathbf{b}_1^*$, $-(h+k)\mathbf{a}_1^*+k\mathbf{b}_1^*$, $-k\mathbf{a}_1^*-h\mathbf{b}_1^*$, $-h\mathbf{a}_1^*+(h+k)\mathbf{b}_1^*$, $(h+k)\mathbf{a}_1^*-k\mathbf{b}_1^*$

Constraints between the cosine and sine terms of the Fourier amplitudes of modulation functions, $A_{i,m,n}$ and $B_{i,m,n}$ for $i = x, y, z$, β_{ij} of Sc, $A_{i,m,n}$ and $B_{i,m,n}$ for $i = x, y, z$ of C and $A_{i,h,k}$ and $B_{i,h,k}$ for $i = x, y, z$ of $B_{1/3}C_{2/3}$, are listed in Table I of the supplementary materials.

Table 3
Reliability factors for the first and second models based on the five-dimensional superspace-group approach.

Reflection data group	Number of reflections	R_F/wR_F – first model	R_F/wR_F – second model
All [$I > 2\sigma(I)$]	1795	0.0533/0.0482	0.0524/0.0476
00*l*/00 common	15	0.0459/0.0477	0.0459/0.0476
*hkl*00 Sc_2C part	196	0.0264/0.0279	0.0264/0.0280
00*lmn* $B_{1/3}C_{2/3}$ part	109	0.0626/0.0696	0.0639/0.0692
hklmn satellites	1475	0.0678/0.0769	0.0659/0.0755

possible space groups of the subsystems. If the space groups of the basic structures of the two parts are assumed to be both $P\bar{3}m1$, the symmetry operations of the probable superspace group are x, y, z, u, v; $-y, x-y, z, -v, u-v$; $-x+y, -x, z, -u+v, -u$; $y, x, -z, v, u$; $x-y, -y, -z, u-v, -v$; $-x, -x+y, -z, -u, -u+v$; $-x, -y, -z, -u, -v$; $y, -x+y, -z, v, -u+v$; $x-y, x, -z, u-v, u$; $-y, -x, z, -v, -u$; $y-x, y, z, v-u, v$; $x, x-y, z, u, u-v$. The superspace group can be known as $P\bar{3}m1(p00)(0p0)0m0$. The modulation functions for an atom at a special position must be invariant to the superspace symmetry operations corresponding to the site symmetry group. This gives restrictions for the Fourier amplitudes of the modulation functions with a set of modulation waves. Such a modulation wave set and the restrictions for the modulation functions could be derived through the programs *SPA* (for scalar), *SPL* (for vector) and *SPT* (for tensor) (Kato, 1994). Coordinates and sets of modulation wavevectors related to each other, of atoms in special positions, are listed in Table 2. Requirements on the atomic modulation functions were derived and summarized in Table I of the supplementary material.[1]

4. Structure refinement

Refinement was performed on the basis of $|F|$ through the full-matrix least-squares refinement program *FMLSM* (Kato, 1990, 1994; Kato & Onoda, 1991*a*). The intensity data were used after re-indexing based on the equations $H = 7h + 9m$ and $K = 7k + 9n$ using five integers h, k, l, m and n. On account of the commensurate feature of the lattice geometry, the summations instead of integrals in the structure–factor formula were used (Kato & Onoda, 1991*a*) with numbers of summation points 49 (subsystem 1) and 81 (subsystem 2). Besides one scaling factor and one parameter for extinction correction, atomic coordinates and thermal parameters, the Fourier amplitudes of the modulation functions were considered as structural parameters. After some trials, a model was established assuming a centrosymmetric superspace group $P\bar{3}m1(p00)(0p0)0m0$. In the model, all atoms are located at special positions, that is Sc in (1/3 2/3 z) and C in (0 0 1/2) of the first subsystem and $B_{1/3}C_{2/3}$ in (1/3 2/3 z) of the second subsystem. The sets of wavevectors, with which modulations are related to each other, are present. For Sc in subsystem 1, displacive modulations up to the third order, with modulation wavevectors $\mathbf{a}_2^*$, $\mathbf{a}_2^*+\mathbf{b}_2^*$, $2\mathbf{a}_2^*$, $2\mathbf{a}_2^*+\mathbf{b}_2^*$, $3\mathbf{a}_2^*$ and their respective fellow members belonging to the same sets, and modulations in anisotropic thermal parameters up to the first order with a wavevector $\mathbf{a}_2^*$ and its equivalents were adopted. For C in subsystem 1, displacive modulations up to the first order with a wavevector $\mathbf{a}_2^*$ and its equivalents were adopted. For B and C in subsystem 2, random distribution of B and C were assumed and displacive modulations of $B_{1/3}C_{2/3}$ up to the first order with the wavevector $\mathbf{a}_1^*$ and its equivalents were adopted. Isotropic and unmodulated thermal parameters were adopted for C in subsystem 1 and $B_{1/3}C_{2/3}$ in subsystem 2. The constraints on Fourier amplitudes listed in Table I of the supplementary materials were used. The final R_F and wR_F values were 0.0533 and 0.0482 for 1795 reflections with $I > 2\sigma(I)$ using 41 independent structural parameters and one scale factor, and one extinction correction factor. The R_F and wR_F values for four reflection data groups, common main reflections from two parts (00*l*/00), main reflections of subsystem 1 (*hkl*00 with $h \neq 0$ or $k \neq 0$), main reflections of

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: JS0110). Services for accessing these data are described at the back of the journal.

Table 4
Atomic parameters of $Sc_2B_{11}C_{32}$ for the first model (see text)".

Independent standard deviations are given in parentheses. $A_{m,n}$ and $B_{m,n}$ are the cosine and sine terms of the Fourier amplitudes with the wavevector $m\mathbf{a}_2^* + n\mathbf{b}_2^*$ for the first subsystem, and $A_{h,k}$ and $B_{h,k}$ are those with the wavevector $h\mathbf{a}_1^* + k\mathbf{b}_1^*$ for the second subsystem."

Sc	*x*	*y*	*z*	$100 \times U_{eq}$ (Å^2)
Subsystem 1				
Average	0.333333	0.666667	0.32221 (6)	0.775 (7)
$A_{1,0}$	0.0059 (1)	0.00297	0.01458 (5)	−0.096 (9)
$B_{1,0}$	−0.0299 (1)	−0.01493	0.01119 (6)	0.00 (1)
$A_{0,-1}$	−0.00297	−0.00593	0.01458	−0.096
$B_{0,-1}$	0.01493	0.02987	0.01119	0.00
$A_{-1,1}$	−0.00297	0.00297	0.01458	−0.096
$B_{-1,1}$	0.01493	−0.01493	0.01119	0.00
$A_{1,1}$	−0.0006 (1)	0.0006	0.00102 (8)	
$B_{1,1}$	0.0041 (2)	0.0041	0.0000	
$A_{1,-2}$	0.0012	0.0006	0.00102	
$B_{1,-2}$	0.0000	−0.0041	0.0000	
$A_{-2,1}$	−0.0006	−0.0012	0.00102	
$B_{-2,1}$	−0.0041	0.0000	0.0000	
$A_{2,0}$	−0.0034 (2)	−0.0017	0.00028 (9)	
$B_{2,0}$	0.0023 (2)	0.0011	0.0009 (1)	
$A_{0,-2}$	0.0017	0.0034	0.00028	
$B_{0,-2}$	−0.0011	−0.0023	0.0009	
$A_{-2,2}$	0.0017	−0.0017	0.00028	
$B_{-2,2}$	−0.0011	0.0011	0.0009	
$A_{2,1}$	0.0007 (2)	0.0028 (3)	−0.00031 (8)	
$B_{2,1}$	−0.0004 (2)	−0.0017 (3)	−0.0003 (1)	
$A_{1,-3}$	0.0021	−0.0007	−0.00031	
$B_{1,-3}$	−0.0014	0.0004	−0.0003	
$A_{-3,2}$	−0.0028	−0.0021	−0.00031	
$B_{-3,2}$	0.0017	0.0014	−0.0003	
$A_{-1,-2}$	−0.0028	−0.0007	−0.00031	
$B_{-1,-2}$	0.0017	0.0004	−0.0003	
$A_{-2,3}$	0.0021	0.0028	−0.00031	
$B_{-2,3}$	−0.0014	−0.0017	−0.0003	
$A_{3,-1}$	0.0007	−0.0021	−0.00031	
$B_{3,-1}$	−0.0004	0.0014	−0.0003	
$A_{3,0}$	0.0046 (3)	0.0023	−0.0020 (2)	
$B_{3,0}$	−0.0007 (3)	−0.0003	−0.0006 (2)	
$A_{0,-3}$	−0.0023	−0.0046	−0.0020	
$B_{0,-3}$	0.0003	0.0007	−0.0006	
$A_{-3,3}$	−0.0023	0.0023	−0.0020	
$B_{-3,3}$	0.0003	−0.0003	−0.0006	

C	*x*	*y*	*z*	$100 \times B/8\pi^2$ (Å^2)
Average	0.0	0.0	0.5	0.89 (4)
$A_{1,0}$	0.0	0.0	0.0	
$B_{1,0}$	0.0037 (8)	0.0018	−0.0233 (4)	
$A_{0,-1}$	0.0	0.0	0.0	
$B_{0,-1}$	−0.0018	−0.0037	−0.0233	
$A_{-1,1}$	0.0	0.0	0.0	
$B_{-1,1}$	−0.0018	0.0018	−0.0233	

$B_{1/3}C_{2/3}$	*x*	*y*	*z*	$100 \times B/8\pi^2$ (Å^2)
Subsystem 2				
Average	0.333333	0.666667	−0.0004 (3)	0.93 (3)
$A_{1,0}$	−0.0075 (9)	−0.0038	−0.0265 (2)	
$B_{1,0}$	−0.0019 (9)	−0.0009	−0.0214 (2)	
$A_{0,-1}$	0.0038	0.0075	−0.0265	
$B_{0,-1}$	0.0009	0.0019	−0.0214	
$A_{-1,1}$	0.0038	−0.0038	−0.0265	
$B_{-1,1}$	0.0009	−0.0009	−0.0214	

Note. Fractional coordinates of the three-dimensional superstructure, with $P\bar{3}m1$ and a unit cell of $A = 23.710$ (9) and $c = 6.703$ (2) Å, have been calculated from the parameter values listed above using a program *ATOML* and reported in Table III of the supplementary material.

subsystem 2 ($00lmn$ with $m \neq 0$ or $n \neq 0$) and satellites due to interactions between subsystems ($hklmn$ with $hm \neq 0$ or $hn \neq 0$ or $km \neq 0$ or $kn \neq 0$), are shown in Table 3.

5. Results

The atomic parameters are listed in Tables 4 and 5. In spite of a much smaller parameter/data ratio of 43/1795 than the former work's 168/1292 (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999), essentially the same model with reasonable R_F values and small standard deviations has been obtained. The structure model is illustrated using the program *PRJMS* (Yamamoto, 1992, 1993) in Figs. 1 and 2 based on the final parameters. Each C atom is coordinated by six Sc atoms in subsystem 1, and each site in subsystem 2 is randomly occupied by $B_{1/3}$ and $C_{2/3}$. The large modulation amplitudes of displacements of Sc and $B_{1/3}C_{2/3}$ indicate that Sc and $B_{1/3}C_{2/3}$ are susceptible to modulation by each other and these features are displayed clearly in Figs. 1 and 2.

Interatomic distances are calculated from the parameters of Table 4 using the program *BONDL* (Kato & Onoda, 1991*a*; Kato, 1994) and are listed in Table 6 and Table II* of the supplementary materials. The mean, minimum and maximum bond lengths between C and Sc in subsystem 1 are, respectively, 2.297 (4), 2.223 (5) and 2.347 (4) Å, and those between $B_{1/3}C_{2/3}$ sites in subsystem 2 are, respectively, 1.533 (4), 1.507 (3) and 1.567 (7) Å. In Fig. 2, bounded projections along the [120] direction of seven slices of the total structure of $Sc_2B_{1.1}C_{3.2}$ are illustrated. Each Sc atom is coordinated by three C atoms within the same subsystem and by one to six $B_{1/3}C_{2/3}$ sites of subsystem 2. Distances shorter than 2.6 Å are shown by thin sticks about Sc and $B_{1/3}C_{2/3}$ sites. The minimum distance between Sc and $B_{1/3}C_{2/3}$ is 2.308 (6) Å.

6. Discussion

6.1. Comparison with conventional refinement

As a measure to compare the goodness of assumed models, the AIC, Akaike Information Criterion (Akaike, 1973), was adopted which was calculated by FMLSM (Kato, 1990) after each refinement cycle. The AIC, defined as $-2 \times$ ln (maximum likelihood) + 2 × (number of parameters), has an advantage in that it takes both the grade of fitting and the economization of parameters simultaneously into consideration. A model giving less AIC should be preferred. In the present superspace-group approach, we obtained an AIC of 16 373. As the counterpart of a comparison, we tried the three-dimensional refinement of the superstructure with $P\bar{3}m1$, $A = 23.710$ (9) and $c = 6.703$ (2) Å using FMLSM and the same set of observed data with the same weighting scheme ($w = 1$) as those used in the present study. Even in the early stage of refinement, however, it was very difficult to obtain a smooth convergence, suggesting a considerable correlation among structural parameters. To obtain a more accurate estimate of the refinement cycles we then calculated, using *ATOML* (Kato, 1990, 1994), the fractional coordinates of the atoms

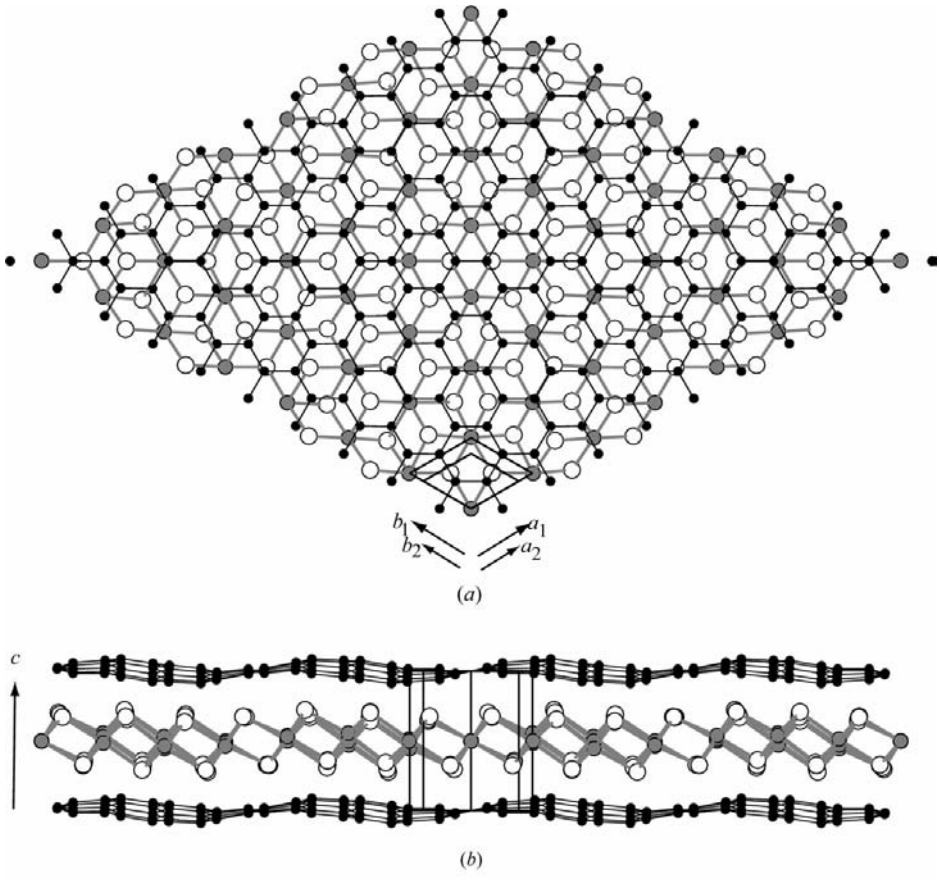

Figure 1
Projections of the structure model, the first model, of $Sc_2B_{1.1}C_{3.2}$ along (*a*) [00$\bar{1}$] and (*b*) along [110]. Large open, medium hatched and small solid circles represent Sc, C and $B_{1/3}C_{2/3}$, respectively.

Table 5
Anisotropic thermal parameters of Sc for the first model.

$A_{m,n}$ and $B_{m,n}$ are the cosine and sine terms of the Fourier amplitudes with the wavevector $m\mathbf{a}_2^* + n\mathbf{b}_2^*$. The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U^{11} + 2hka^*b^*U^{12} + 2hla^*c^*U^{13} + k^2b^{*2}U^{22} + 2klb^*c^*U^{23} + l^2c^{*2}U^{33})$. $U_{eq} = B_{eq}/(8\pi^2) = (1/3)[(\mathbf{a},\mathbf{a})a^{*2}U^{11} + (\mathbf{b},\mathbf{b})b^{*2}U^{22} + (\mathbf{c},\mathbf{c})c^{*2}U^{33} + 2(\mathbf{a},\mathbf{b})a^*b^*U^{12}]$.

Sc	$100 \times U^{11}$	$100 \times U^{12}$	$100 \times U^{13}$	$100 \times U^{22}$	$100 \times U^{23}$	$100 \times U^{33}$
Average	0.74 (1)	0.37	0.00	0.74	0.00	0.84 (2)
$A_{1,0}$	−0.22 (1)	−0.11	0.10 (1)	−0.06 (1)	0.05	−0.06 (2)
$B_{1,0}$	−0.01 (1)	−0.005	−0.04 (1)	0.01 (2)	−0.02	0.01 (1)
$A_{0,-1}$	−0.06	−0.11	−0.05	−0.22	−0.10	−0.06
$B_{0,-1}$	0.01	−0.005	0.02	−0.01	0.04	0.01
$A_{-1,1}$	−0.06	0.05	−0.05	−0.06	0.05	−0.06
$B_{-1,1}$	0.01	0.01	0.02	0.00	−0.02	0.01

within the asymmetric unit of the supercell from the parameters listed in Table 4. The results are shown in Table III of the supplementary materials with Wyckoff notations. Starting from the atomic coordinates in this table we could achieve good convergence, namely $R_F = 0.0506$, $wR_F = 0.0480$ and AIC = 16 564, using 143 structural parameters (85 positional parameters, 56 anisotropic thermal parameters for Sc and two isotropic thermal parameters, one for C and the other for $B_{1/3}C_{2/3}$), one scale factor and one parameter for extinction correction. The difference 16 373 − 16 564 = −191 in AIC between the superspace-group approach and the three-dimensional superstructure approach with $P\bar{3}m1$ corresponds almost exactly to twice the difference 43 − 145 = −102 in the numbers of variable parameters. The contribution from the slightly improved agreement of F_o and F_c, that is the sum of squared $F_o - F_c$ was reduced from $9.16E + 05$ (superspace-group approach) to $9.09E + 05$ (superstructure approach), was excessively cancelled by increasing the number of parameters. This means that the present structure can be better or more economically described with a superspace group than as a superstructure with $P\bar{3}m1$.

If we project the superspace group of a composite crystal into its subsystems we obtain the space groups for the average structures of the subsystems (Kato & Onoda, 1991*b*; Kato, 1994). If the structures of the subsystems undergo no modulation, these space groups each represent their individual constraints for the subsystems and can be termed the local symmetries of the composite crystal; if the structures are modulated, however, we have its approximate local symmetries.

The amplitudes of modulations in a commensurate or incommensurate modulated structure have a general tendency to decay rapidly with an increasing order of harmonics and the higher-order satellite reflections are usually either very weak or absent. In a superspace-group approach, we take advantage of this tendency to reduce the number of structural parameters by omitting higher harmonics whose amplitudes are expected to be negligibly small. In the conventional superstructure refinement, on the other hand, we must always take a full set of atomic coordinates and other parameters, although they are in fact implicitly related through the approximate local symmetries. It is often these relations that prevent a smooth convergence of refinement cycles. In this way, the structural parameterization in terms of modulation waves is advantageous for a commensurate structure with a large superstructure cell, bringing about the reduction of parameter number validly.

Table 6
Interatomic distances (Å) calculated from the parameters listed in Table 4".

Symmetry codes based on a five-dimensional formalism are omitted from this table and appear in Table II of the supplementary material. Notations, C1, C2,..., Sc1, Sc2,..., *M*1, *M*2,..., are the same as those listed in Table III of the supplementary material."

(1) CSc_6 octahedral unit	
C1—Sc2 ×6	2.300 (5) ×6
C2—Sc8 ×2, Sc2 ×2, Sc3 ×2	2.318 (4) ×2, 2.278 (4) ×2, 2.290 (3) ×2
C3—Sc9 ×2, Sc8 ×2, Sc10 ×2	2.289 (3) ×2, 2.302 (3) ×2, 2.253 (2) ×2
C4—Sc7 ×2, Sc9 ×2, Sc12 ×2	2.286 (4) ×2, 2.299 (4) ×2, 2.288 (3) ×2
C5—Sc8 ×2, Sc10 ×2, Sc4, Sc3	2.338 (4) ×2, 2.298 (4) ×2, 2.347 (4), 2.280 (5)
C6—Sc11 ×2, Sc6 ×2, Sc1, Sc5	2.337 (4) ×2, 2.296 (3) ×2, 2.283 (3), 2.223 (5)
C7—Sc12 ×2, Sc11 ×2, Sc6, Sc7	2.282 (3) ×2, 2.305 (4) ×2, 2.271 (6), 2.329 (5)
C8—Sc11, Sc10, Sc9, Sc12, Sc4, Sc5	2.317 (4), 2.259 (3), 2.328 (4), 2.297 (4), 2.281 (4), 2.326 (4)
(2) Sc—C (<2.4 Å), *M* (<2.6 Å)	$M = B_{1/3}C_{2/3}$
Sc1—C6 ×3	2.283 (3) ×3
Sc1—*M*7 ×3, *M*6 ×3	2.456 (5) ×3, 2.523 (4) ×3
Sc2—C2 ×2, C1	2.278 (4) ×2, 2.300 (5)
Sc2—*M*1, *M*2	2.345 (6), 2.516 (5)
Sc3—C2 ×2, C5	2.290 (3) ×2, 2.280 (6)
Sc3—*M*2, *M*10 ×2	2.452 (5), 2.544 (4) ×2
Sc4—C8 ×2, C5	2.281 (4) ×2, 2.347 (4)
Sc4—*M*4	2.486 (6)
Sc5—C8 ×2, C6	2.326 (4) ×2, 2.223 (5)
Sc5—*M*17 ×2, *M*5	2.510 (4) ×2, 2.543 (5)
Sc6—C6 ×2, C7	2.296 (3) ×2, 2.271 (6)
Sc6—*M*8, *M*7	2.441 (5), 2.517 (6)
Sc7—C7, C4 ×2	2.329 (5), 2.286 (4) ×2
Sc7—*M*9, *M*16 ×2	2.308 (6), 2.563 (4) ×2
Sc8—C2, C3, C5	2.318 (4), 2.302 (3), 2.338 (4)
Sc8—*M*10, *M*11	2.444 (3), 2.503 (4)
Sc9—C3, C4, C8	2.289 (3), 2.299 (4), 2.328 (4)
Sc9—*M*14, *M*13	2.344 (3), 2.499 (4)
Sc10—C5, C8, C3	2.298 (4), 2.259 (3), 2.253 (2)
Sc10—*M*11, *M*4, *M*13, *M*12, *M*15, *M*3	2.540 (4), 2.524 (4), 2.482 (3), 2.575 (3), 2.547 (4), 2.597 (4)
Sc11—C6, C8, C7	2.337 (4), 2.317 (4), 2.305 (4)
Sc11—*M*18, *M*17, *M*8	2.384 (3), 2.512 (4), 2.507 (3)
Sc12—C8, C8, C5	2.288 (3), 2.282 (3), 2.297 (4)
Sc12—*M*16, *M*14, *M*18	2.373 (5), 2.564 (4), 2.526 (3)
(3) *M*—*M* (<1.6 Å)	$M = B_{1/3}C_{2/3}$
*M*1—*M*1, *M*1, *M*2	1.517 (3) ×2, 1.507 (3)
*M*2—*M*10, *M*10, *M*1	1.5182 (6) ×2, 1.507 (3)
*M*3—*M*11, *M*11, *M*4	1.536 (4) ×2, 1.536 (2)
*M*4—*M*15, *M*15, *M*3	1.548 (3) ×2, 1.536 (2)
*M*5—*M*17, *M*17, *M*6	1.547 (4) ×2, 1.557 (6)
*M*6—*M*7, *M*7, *M*5	1.534 (1) ×2, 1.557 (6)
*M*7—*M*6, *M*6, *M*8	1.534 (1) ×2, 1.546 (4)
*M*8—*M*18, *M*18, *M*7	1.535 (4) ×2, 1.546 (4)
*M*9—*M*16, *M*16, *M*9	1.508 (3) ×2, 1.511 (3)
*M*10—*M*10, *M*2, *M*11	1.554 (6), 1.5182 (6), 1.546 (4)
*M*11—*M*10, *M*12, *M*3	1.546 (4), 1.547 (4), 1.536 (4)
*M*12—*M*12, *M*11, *M*13	1.567 (7), 1.547 (4), 1.531 (2)
*M*13—*M*12, *M*14, *M*15	1.531 (2), 1.525 (4), 1.529 (2)
*M*14—*M*14, *M*16, *M*13	1.533 (4), 1.518 (2), 1.525 (4)
*M*15—*M*13, *M*4, *M*17	1.529 (2), 1.548 (3), 1.550 (6)
*M*16—*M*9, *M*14, *M*18	1.508 (2), 1.518 (2), 1.510 (2)
*M*17—*M*5, *M*15, *M*18	1.547 (4), 1.550 (6), 1.527 (3)
*M*18—*M*17, *M*8, *M*16	1.527 (3), 1.535 (4), 1.510 (2)

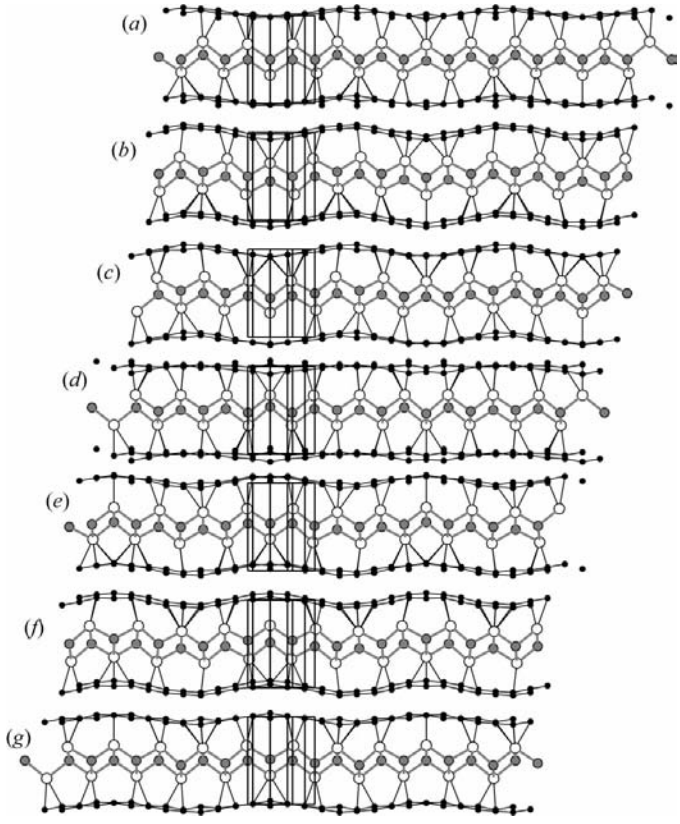

Figure 2
Bounded projections along the [120] direction of slices of the first structure model of $Sc_2B_{1.1}C_{3.2}$. The limits are (*a*) $-0.2 < y < 1.3$ for Sc, C and $B_{1/3}C_{2/3}$; (*b*) $0.8 < y < 2.2$ for Sc, C and $B_{1/3}C_{2/3}$; (*c*) $1.8 < y < 3.2$ for Sc, C and $B_{1/3}C_{2/3}$; (*d*) $2.8 < y < 4.2$ for Sc and C, and $2.5 < y < 4.2$ for $B_{1/3}C_{2/3}$; (*e*) $3.8 < y < 5.2$ for Sc and C, and $3.5 < y < 5.2$ for $B_{1/3}C_{2/3}$; (*f*) $4.8 < y < 6.2$ for Sc and C, and $4.5 < y < 6.2$ for $B_{1/3}C_{2/3}$; (*g*) $5.8 < y < 7.2$ for Sc and C, and $5.6 < y < 7.4$ for $B_{1/3}C_{2/3}$, where *y* is based on the basic cell of the first subsystem.

6.2. Another possible model"

If we express atomic positions in an $(3 + n)$-dimensional model of a composite crystal as (**x**,**t**), with three-dimensional subsystem coordinates **x** and variable *n*-dimensional supplementary coordinates **t**, the real three-dimensional structure of the composite crystal appears as a three-dimensional section at $t = 0$ of the $(3 + n)$-dimensional model, where the section extends through an infinite number of $(3 + n)$-dimensional unit cells. Suppose that all the segments of the section within various unit cells are translated into one and the same unit cell at the coordinate origin, so the segments will fill the unit cell without leaving any free space if the composite crystal is incommensurate. In the case of a commensurate composite crystal, however, only a finite number of discrete parallel sections at $t = 0$, $t1$, $t2$,... within the unit cell at the coordinate origin will be obtained and thus we need only to sum up the contributions of the atoms appearing in these sections in order to calculate the structure factors. A general algorithm for finding $t1$, $t2$,... has been given by Kato & Onoda (1991*a*) and Kato (1994).

Table 7
Fractional coordinates of the three-dimensional superstructure, with $P\bar{3}m1$ and a unit cell of A = 23.710 (9) and c = 6.703 (2) Å, corresponding to the second model of $Sc_2B_{1.1}C_{3.2}$ (see text).

Standard deviations, estimated from errors of interatomic distances using the program *BONDL* (Kato & Onoda, 1991*a*; Kato, 1994), are listed in parentheses (M = $B_{1/3}C_{2/3}$).

	x	y	z	Site
Sc1	0.3333	−0.3333	0.2725 (8)	1(*b*)
Sc2	0.0447 (1)	−0.0447	0.3556 (7)	3(*d*)
Sc3	−0.0922 (1)	0.0922	0.3056 (6)	3(*d*)
Sc4	0.1910 (1)	−0.1910	0.3267 (5)	3(*d*)
Sc5	−0.2395 (1)	0.2395	0.3044 (6)	3(*d*)
Sc6	−0.3825 (1)	0.3825	0.3352 (7)	3(*d*)
Sc7	0.4778 (1)	−0.4778	0.3627 (4)	3(*d*)
Sc8	0.0470 (1)	0.2351 (1)	0.3215 (5)	6(*e*)
Sc9	0.0463 (1)	0.3870 (1)	0.3346 (3)	6(*e*)
Sc10	−0.0914 (1)	0.2450 (1)	0.2865 (2)	6(*e*)
Sc11	0.3385 (1)	−0.1829 (1)	0.3068 (4)	6(*e*)
Sc12	−0.3858 (1)	0.0921 (1)	0.3416 (4)	6(*e*)
Sc13	−0.3333	0.3333	0.6751 (10)	1(*b*)
Sc14	−0.0518 (1)	0.0518	0.7118 (6)	3(*d*)
Sc15	0.0955 (1)	−0.0955	0.6849 (6)	3(*d*)
Sc16	−0.1889 (1)	0.1889	0.6377 (4)	3(*d*)
Sc17	0.2416 (1)	−0.2416	0.6613 (6)	3(*d*)
Sc18	0.3789 (1)	−0.3789	0.6453 (6)	3(*d*)
Sc19	−0.4746 (1)	0.4746	0.7213 (4)	3(*d*)
Sc20	−0.0538 (1)	−0.2440 (1)	0.6547 (5)	6(*e*)
Sc21	−0.0511 (1)	−0.3787 (1)	0.6837 (3)	6(*e*)
Sc22	0.0935 (1)	−0.2395 (1)	0.6705 (3)	6(*e*)
Sc23	−0.3271 (2)	0.1910 (2)	0.6810 (4)	6(*e*)
Sc24	0.3776 (1)	−0.1019 (1)	0.7017 (5)	6(*e*)
C1	0	0	0.5606 (10)	1(*a*)
C2	0.14263 (5)	−0.14263	0.50061 (1)	3(*d*)
C3	−0.14294 (2)	0.14294	0.4450 (9)	3(*d*)
C4	0.2860 (1)	−0.2860	0.4570 (7)	3(*d*)
C5	−0.2853 (1)	0.2853	0.4954 (1)	3(*d*)
C6	0.42861 (1)	−0.42861	0.5138 (2)	3(*d*)
C7	−0.4290 (1)	0.42901	0.5276 (4)	3(*d*)
C8	−0.00056 (5)	0.1422 (1)	0.5112 (2)	6(*e*)
C9	−0.0009 (2)	0.28545 (4)	0.4838 (3)	6(*e*)
C10	−0.0002 (1)	0.4288 (1)	0.5454 (7)	6(*e*)
C11	0.1427 (1)	0.4292 (2)	0.5053 (1)	6(*e*)
C12	−0.14261 (1)	−0.4282 (1)	0.4745 (4)	6(*e*)
*M*1	0	0	0.0801 (8)	1(*a*)
*M*2	0.3333	−0.3333	−0.0947 (8)	1(*b*)
*M*3	−0.3333	0.33333	0.0157 (7)	1(*c*)
*M*4	0.1117 (1)	−0.1117	0.0192 (5)	3(*d*)
*M*5	−0.1108 (1)	0.1108	−0.0500 (5)	3(*d*)
*M*6	0.2215 (1)	−0.2215	−0.0010 (5)	3(*d*)
*M*7	−0.2229 (1)	0.2229	−0.0574 (5)	3(*d*)
*M*8	0.4446 (1)	−0.4446	0.0393 (5)	3(*d*)
*M*9	−0.4441 (1)	0.4441	0.0521 (5)	3(*d*)
*M*10	0.0007 (1)	0.1117 (2)	0.0362 (4)	6(*e*)
*M*11	0.0016 (1)	0.22311 (5)	−0.0230 (3)	6(*e*)
*M*12	0.0012 (1)	0.3338 (1)	0.0004 (3)	6(*e*)
*M*13	0.00019 (5)	0.4444 (1)	0.0677 (7)	6(*e*)
*M*14	0.1119 (1)	0.33340 (5)	0.0133 (6)	6(*e*)
*M*15	0.1113 (2)	0.4436 (1)	0.0282 (3)	6(*e*)
*M*16	0.2215 (1)	−0.3329 (1)	−0.0423 (5)	6(*e*)
*M*17	0.33320 (5)	0.1104 (3)	−0.0799 (7)	6(*e*)
*M*18	0.4451 (2)	0.1112 (2)	−0.0041 (4)	6(*e*)
*M*19	−0.3336 (1)	0.2233 (1)	0.0072 (4)	6(*e*)
*M*20	−0.0373 (1)	0.0374	0.0740 (7)	3(*d*)
*M*21	0.0749 (1)	−0.0749	0.0364 (4)	3(*d*)
*M*22	−0.14813 (3)	0.14813	−0.0756 (7)	3(*d*)
*M*23	0.18493 (3)	−0.18493	−0.0153 (7)	3(*d*)
*M*24	−0.2598 (1)	0.2598	−0.0267 (3)	3(*d*)
*M*25	0.2961 (1)	−0.2961	−0.0658 (6)	3(*d*)
*M*26	−0.3698 (1)	0.3698	−0.0093 (6)	3(*d*)
*M*27	0.4072 (1)	−0.4072	−0.0108 (4)	3(*d*)
*M*28	−0.48124 (4)	0.48124	0.0898 (8)	3(*d*)
*M*29	0.0751 (1)	0.26020 (5)	−0.0143 (5)	6(*e*)
*M*30	0.0750 (1)	0.3698 (1)	0.0058 (4)	6(*e*)
*M*31	0.0747 (1)	0.4810 (1)	0.0634 (6)	6(*e*)
*M*32	0.1856 (2)	0.1491 (1)	−0.0113 (4)	6(*e*)
*M*33	0.1853 (1)	−0.2951 (1)	−0.0127 (3)	6(*e*)
*M*34	0.2956 (1)	0.2594 (2)	−0.0409 (4)	6(*e*)
*M*35	0.4077 (1)	0.1485 (1)	−0.0502 (6)	6(*e*)
*M*36	0.40663 (5)	0.3697 (1)	0.0341 (5)	6(*e*)
*M*37	−0.3697 (1)	0.1496 (1)	0.0229 (3)	6(*e*)

If we shift the $(3 + n)$-dimensional model parallel within the superspace and then take a section at $t = 0$, we obtain another three-dimensional structure in the commensurate case, which is generally different from the original one. It is clear that we can derive this new structure, instead of shifting the model, by taking an appropriate section at $t = t0$ or the corresponding parallel sections at $t = t0, t1 + t0, t2 + t0,...$ within a unit cell at the coordinate origin. Different values of $t0$ lead to different three-dimensional structures, but most of them will not possess the required symmetry and need not be taken into account. In our case of $Sc_2B_{1.1}C_{3.2}$, there are only two structures which are trigonal and hence worth further consideration, as the structure must be trigonal because its diffraction pattern has a Laue symmetry of $\bar{3}m$.

Tables 4, 5 and 6 describe a model refined with respect to the section through the coordinate origin (0,0,0,0,0), namely the section at $t = 0$. This model will be termed the first model hereafter in this report. The three-dimensional superstructure corresponding to this section has the symmetry $P\bar{3}m1$ and a large unit cell of A = 23.710 (9) and c = 6.703 (2) Å, as shown in Table III of the supplementary materials. This is the highest symmetry space group for the superstructure which is created by a combination of two subsystems with the respective basic space group $P\bar{3}m1$.

Based on the same superspace group and the same atomic positions as those listed in Table 2, the second model was derived by shifting the section from (0,0,0,0,0) to (0,0,0, −1/3,−2/3). The generator set of the superspace group is, namely, x, y, z, u, v; $-y, x - y, z, -v, u - v$; $-y, -x, z, -v, -u$; $-x, -y, -z, -u, -v$, Sc in 2*d* and C in 1*b* of the first subsystem and $B_{1/3}C_{2/3}$ in 2*d* of the second subsystem. To refine this model through FMLSM, which takes always the section with $t = 0$ for commensurate structures, a translation of (0,0,0,1/3, 2/3) was added to all the 12 superspace-group symmetry operations as a common addendum; that is, the model was shifted instead of the section. The R_F, wR_F and AIC values were 0.0524, 0.0476 and 16 329, respectively, using 1795 reflections and 41 independent structural parameters. The structural parameter values and their standard deviations, which are listed in Table IV and Table V of the supplementary materials, are extremely close to those listed in Table 4 and Table 5. Interatomic distances are calculated from the parameters of Table IV using the program *BONDL* (Kato & Onoda, 1991*a*; Kato, 1994) and listed in Table VI of the supplementary materials. The minimum distance between Sc and $B_{1/3}C_{2/3}$ was calculated to be 2.283 (8) Å. The space group

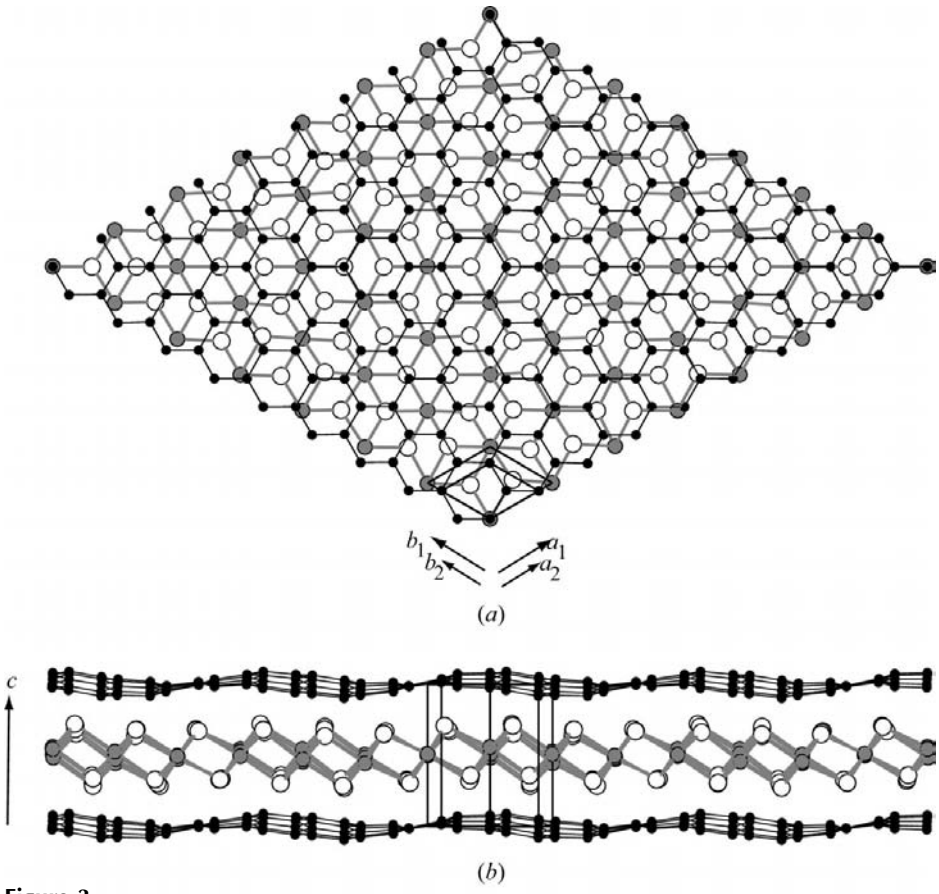

Figure 3
Projections of the second model (see text) of $Sc_2B_{1.1}C_{3.2}$ along (*a*) [00$\bar{1}$] and (*b*) along [110]. Large open, medium hatched and small solid circles represent Sc, C and $B_{1/3}C_{2/3}$, respectively.

of the three-dimensional superstructure was confirmed to be *P*3*m*1. Fractional coordinates of the independent sites in the superstructure model with *P*3*m*1 were calculated from the parameters of Table IV using the program *ATOML* and shown in Table 7. In the superlattice with A = 23.710 (9) and c = 6.703 (2) Å, 98 Sc atoms are located in two 1(*b*) sites, 12 3(*d*) sites and ten 6(*e*) sites; 49 C atoms are located in one 1(*a*) site, six 3(*d*) sites and five 6(*e*) sites; 162 $B_{1/3}C_{2/3}$ are located in one 1(*a*) site, one 1(*b*) site, one 1(*c*) site, 15 3(*d*) sites and 19 6(*e*) sites. Although small differences of R_F, wR_F and AIC between the first and second models based on the superspace-group approach seemed to indicate that the second model brought slightly improved agreement of F_c and F_o compared with the first model, it is difficult to exclude one of the two models as the less probable one judging from the trivialness of the convergence difference and the remarkable resemblance of interatomic distances between the two models.

The second model can be expressed through another superspace group with a generator set x, y, z, u, v; $-y, x-y, z, -v, u-v$; $-x, -y, -z, 2/3-u, 1/3-v$; $y, x, -z, 2/3+v, 1/3+u$, which is created by a combination of two $P\bar{3}m1$ groups with an origin shift of $P\bar{3}m1$ for the second subsystem. This expression gave almost the same convergence of structure refinement as that for the above-mentioned analysis with symmetry operations of the common translation (0, 0, 0, 1/3, 2/3). Fourier amplitudes of atomic parameters also agree exactly with those for the above-mentioned analysis after a phase shift of $-2\pi/3$. The second model is illustrated in Fig. 3 and the atomic arrangement shows a strong likeness to that of the first model (Fig. 1), except for an origin shift.

If we try to refine the second model using the conventional three-dimensional approach, it is necessary to adopt 274 structural parameters following the parameter choice manner in the superstructure approach of the first model, namely 173 positional parameters, 100 anisotropic thermal parameters for Sc, one common and the other common isotropic thermal parameter for C and for $B_{1/3}C_{2/3}$. Parameter reduction in the superspace-group approach, in which 41 structural parameters was adopted, has been much more drastic for the second model than that for the first model, because, in addition to the vanishing higher harmonic modulation waves, those atomic positions which are not explicitly related on account of lacking inversion centers in the superstructure can still be related indirectly through a superspace-group inversion. For Sc and C we can find in Table 7 the pairs of such atomic positions, namely Sc1 and Sc13, Sc2 and Sc14,..., Sc12 and Sc24, C2 and C3,..., C11 and C12. For *M* (= $B_{1/3}C_{2/3}$), however, a shift of coordinate origin will be necessary to discover the implicit relations between, for example, *M*1 and *M*21, *M*4 and *M*20 *etc*.

The five-dimensional models described by the two superspace groups, one in Table 2 and the other given above, are essentially the same, the only difference being in their absolute positions in the superspace. This difference, however, leads to the different space groups of the three-dimensional structure derived from the five-dimensional models for the commensurate case. While the atomic arrangements within the subsystems approximately accord with $P\bar{3}m1$, the relative arrangement of the subsystems can be either $P\bar{3}m1$ or *P*3*m*1. The key to select the correct space group is the superposed main reflections of two subsystems, such as 90*l*00 (= 00*l*70) and 09*l*00 (= 00*l*07); their intensities are directly affected by the relative arrangement of the subsystems. Unfortunately, however, these reflections were not included in the set of observed intensities, because they were positioned at 2θ angles which were too high or even outside the range of Mo $K\alpha$ measurement, and consequently we could not determine the relative arrangement of the subsystems unambiguously. The

difference between the two possible arrangements was too fine to be detected by conventional normal-resolution structure determination using Mo $K\alpha$ radiation.

6.3. Features of modulations in five-dimensional models

We give a brief account of the features of modulations common to the first and the second models, as we cannot focus on one model. The large modulation amplitudes of the displacements of Sc and M (= $B_{1/3}C_{2/3}$) indicate that Sc and M are susceptible to modulation by each other, and these features are illustrated in Figs. 1 and 2 or Fig. 3. If atoms suffer no modulation, the minimum distances between Sc and M in the first and the second models are both 2.157 Å and the value is too short because the atomic radii can be estimated as 1.65 Å for Sc, 0.71 Å for C and 0.87 Å for B in the graphite-like compounds (Wörle & Nesper, 1994; Shi *et al.*, 1999). In the modulated structure the minimum Sc—M distances are 2.308 (6) and 2.283 (8) Å, respectively, in the first and the second models, and the repulsive interaction between Sc and M is regarded as the primary origin of the modulation. The M—M distances range from 1.507 (3) to 1.567 (7) Å with a mean value of 1.533 (3) Å in the first model and from 1.505 (3) to 1.565 (7) Å with a mean value of 1.533 (3) Å in the second model. Dispersion of the M—M distance could be due to a reflection of ordering tendency of C and B in the graphite-type layer. When we adopted the substitution modulation in the graphite-type layer in the refinement of two models by way of a trial, the Fourier amplitudes of substitution were small but larger than two standard deviations. They seemed to suggest an ordering of C and B, in spite of a slight improvement of R_F and AIC by the substitution modulation, because of small differences in the scattering factors of B and C. The subject compound would be worth studying in further detail based on a measurement with higher precision.

6.4. Specimens with incommensurate structure

In previous work (Shi, Leithe-Jasper & Tanaka, 1999), powder specimens of $Sc_2B_{1.1}C_{3.2}$ showed a two-dimensional incommensurate character in electron diffraction experiments. As a single crystal showed a commensurate character (Shi, Leithe-Jasper, Bourgeois *et al.*, 1999), the modulations might be locked in a commensurate superstructure through crystal growth procedures. In superspace, all crystal structures of incommensurate and commensurate specimens would have the same superspace-group symmetry. The present study shows that the structure with $\boldsymbol{\sigma}_1$ = (9/7 0 0) and $\boldsymbol{\sigma}_2$ = (0 9/7 0) could be refined using a small number of parameters by application of a five-dimensional superspace group $P\bar{3}m1(p00)(0p0)0m0$, and is an example of the description in a superspace-group symmetry applied to a commensurate composite crystal.

7. Conclusions

Although the lack of resolution prevented the exclusion of the wrong model from two possible ones, the structure of $Sc_2B_{1.1}C_{3.2}$ has been characterized more appropriately by the five-dimensional superspace group than by the conventional three-dimensional space group, $P\bar{3}m1$ or $P3m1$. The advantage of using a superspace group consists, first of all, in the possibility to express approximate local symmetries, which are one of the essential features of the structure, but are completely omitted in a description using a three-dimensional space group based on an enlarged unit cell. It is by virtue of this advantage that a good R_F could be achieved while introducing less structural parameters.

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