

orbit can be defined by the set of points

$$\begin{aligned}
 \mathbf{r}_1 &= (5/8, 5/8, 5/8), & \mathbf{r}_2 &= (13/8, 5/8, 5/8), \\
 \mathbf{r}_3 &= (5/8, 13/8, 5/8), & \mathbf{r}_4 &= (13/8, 13/8, 5/8), \\
 \mathbf{r}_5 &= (1/8, 5/8, 5/8), & \mathbf{r}_6 &= (9/8, 5/8, 5/8), \\
 \mathbf{r}_7 &= (1/8, 13/8, 5/8), & \mathbf{r}_8 &= (9/8, 13/8, 5/8), \\
 \mathbf{r}_9 &= (5/8, 1/8, 5/8), & \mathbf{r}_{10} &= (13/8, 1/8, 5/8), \\
 \mathbf{r}_{11} &= (5/8, 9/8, 5/8), & \mathbf{r}_{12} &= (13/8, 9/8, 5/8), \\
 \mathbf{r}_{13} &= (5/8, 5/8, 1/8), & \mathbf{r}_{14} &= (13/8, 5/8, 1/8), \\
 \mathbf{r}_{15} &= (5/8, 13/8, 1/8), & \mathbf{r}_{16} &= (13/8, 13/8, 1/8).
 \end{aligned} \tag{A4}$$

These points are given not by their Cartesian coordinates but rather by contravariant coordinates relative to the oblique-angle system of reference $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$, i.e. if $\mathbf{r} = \mu_1 \mathbf{a}_1 + \mu_2 \mathbf{a}_2 + \mu_3 \mathbf{a}_3$, then we indicate three numbers (μ_1, μ_2, μ_3) . Acting on the points (A4) with the operations of the group $G_D = C2/m$ ($V'/V = 4$), we obtain the following splitting:

$$\begin{aligned}
 R_D^1 &= \{1|2/m\}, & R_D^2 &= \{2|2/m\}, & R_D^3 &= \{3,4|\bar{1}\}, \\
 R_D^4 &= \{5,6|m\}, & R_D^5 &= \{7,8|2\}, \\
 R_D^6 &= \{9,16,11,13|1\}, & R_D^7 &= \{10,15,12,14|1\}.
 \end{aligned} \tag{A5}$$

The numbers of the points of the R_D^i orbit from the set (A4) and the stabilizer that corresponds to its starting point are given for each R_D^i in the braces.

The splitting (A5) generates the scheme (1.3). Note that, for conjugate subgroups $G'_D = g_o^{-1} G_D g_o$ ($g_o \in G$), which are the symmetry groups of different domains of the G_D phase, the same splitting scheme corresponds to them, in spite of the difference in

correspondence between the points of the orbit R and the orbits R_D^i .

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Determination of Composite Crystal Structures and Superspace Groups

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Abstract

Superspace groups introduced for usual modulated structures have recently been applied to the analysis of composite crystals. This review describes the method of composite-crystal analysis based on the superspace group. This method is efficient for the analysis of any (incommensurate or commensurate) composite crystals. The method is analogous to that for the modulated structure in many respects. The description of composite crystals in superspace,

determination of their superspace groups and unified setting of the unit vectors are mentioned. Two possible approximations and a relation between the superspace and space groups for commensurate composite crystals are discussed. Space groups of chimney-ladder structures with different periods are derived from a single superspace group by the application of this relation. Possible superspace groups for known composite structures are deduced from the space groups of average substructures. Finally, the refinement method is discussed.

1. Introduction

'Composite crystal structure' is a generic name for misfit layer structures, intergrowth compounds, vernier structures and chimney-ladder structures that have two or more mutually interpenetrating substructures with incommensurate or commensurate periods along some (one or two) directions. Each substructure is modulated by the interaction with the others. Therefore, this is a general case of modulated structures. (Fig. 1).

The composite crystal structure is found in minerals, electron compounds, synthetic inorganic and organic compounds (Makovicky & Hyde, 1981; Hyde & Anderson, 1989; Petříček, Maly, Coppens, Bu, Cisarova & Frost-Jensen, 1991). For example, cannizzarite $\{[(\text{Pb},\text{Bi})\text{S}]_x[(\text{Pb},\text{Bi})_2\text{S}_3]\}$ with $x=1.7-1.71$, valleriite $\{[(\text{Mg},\text{Al}),(\text{OH})_2]_x[(\text{Fe},\text{Cu})\text{S}_2]\}$ with $x=1.53$ and cylindrite $\{[(\text{Pb},\text{Ag},\text{Sn},\text{Sb},\text{Fe})\text{S}]_x[(\text{Sn},\text{Sb},\text{Fe})\text{S}_2]\}$ are known to have composite crystal structures consisting of two substructures, each enclosed by square brackets. These are misfit layer structures in which two layers alternate in a direction normal (or nearly normal) to the layer and have periods incommensurate with each other. The other early known examples are chimney-ladder structures $\{[\text{V}]_{17}[\text{Ge}]_{31}, [\text{Mo}]_9[\text{Ge}]_{16}, [\text{Te}]_4[\text{Si}]_7, [\text{Rh}]_{17}[\text{Ge}]_{22} \text{ etc.}\}$ in which rows of groups III and IV

elements (the 'ladders') are inserted into channels (the 'chimneys') in transition metals. These so-called electron compounds are examples of commensurate composite crystals, though the superstructure period is very large ($>100 \text{ \AA}$) in some cases. A commensurate composite crystal is called a vernier structure. There are many other synthetic composite crystals, in particular, in sulfides. Some of them were known in the 1970's $\{[\text{LaS}]_x[\text{CrS}_2], [\text{Ba}]_x[\text{FeS}_2], [(\text{Mg},\text{Al})(\text{OH})_2]_x[(\text{Fe},\text{Cu})\text{S}_2]\}$; others have recently been extensively studied $[\text{TS}]_x[\text{NbS}_2]$, $T = \text{Sn, La, Ce, Ho, Y, Bi}$; $[\text{TS}]_x[\text{TaS}_2]$, $T = \text{Pb, Sm, La, Ce, Bi}$; $[\text{TS}]_x[\text{TiS}_2]$, $T = \text{Pb, Sn}$; $[\text{PbS}]_x[\text{VS}_2]$; $[\text{LaS}]_x[\text{CrS}_2]$; with $x=1.10-1.17$ (Wiegiers & Meerschaut, 1992; van Smaalen, 1992). After the discovery of superconducting oxides, several oxide composite crystals were synthesized as byproducts of superconducting oxides. These are $[\text{M}_2\text{Cu}_2\text{O}_5]_x[\text{CuO}_2]$ [$M = (\text{Bi},\text{Sr},\text{Ca})$ and Sr] and $[\text{Ba}]_x[(\text{Cu},\text{Pt})\text{O}_3]$. It was shown recently that the superconducting oxides $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ and $\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_{8+x}$ are also well described as composite crystals, $[\text{Bi}_2\text{Sr}_2\text{CuO}_4][\text{O}]_y$ and $[\text{Bi}_2(\text{Sr},\text{Ca})_3\text{Cu}_2\text{O}_6][\text{O}]_y$ ($y=2.2$), respectively, rather than modulated structures (Walker & Que, 1992). In these cases, one substructure is composed of O atoms in Bi-O layers and the other of the remaining atoms. In $[\text{Y}(\text{O},\text{F})][(\text{O},\text{F})]_y$ and $[\text{Zr}(\text{N},\text{F})][(\text{N},\text{F})]_y$, with $y=1.13-1.22$, one substructure is also composed only of anions. Organic compounds $[\text{I}]_x[\text{TTF}]$, $[\text{Br}]_x[\text{TTF}]$, $[\text{I}]_x[\text{BEDO-TTF}]$, $[\text{I}]_x[\text{Bz}_2\text{M}_2(\text{CHCl}_3)]$ ($M = \text{K, NH}_4, \text{Na}$), $[\text{Hg}]_x[\text{ET}(\text{SCN})_2]$ and $[\text{Hg}]_x[\text{ETBr}_2]$, are known to have composite crystal structures (see Table 1).*

A characteristic feature of the composite crystal structure in the diffraction pattern is that there exist two (or more) sets of three-dimensional sublattices of prominent reflections caused by interpenetrating substructures. These so-called main reflections distinguish the composite crystal from the usual crystal and the modulated structure. In addition to the main reflection, weak satellite reflections are observed, in particular by electron diffraction, showing the existence of the modulation caused by the interaction between the substructures. In some cases the satellite reflections are not observed in X-ray diffraction patterns (Fig. 2).

Several commensurate composite crystals were analyzed as superstructures in the 1960's and 1970's. On the other hand, incommensurate composite crystals have been determined by treating each substructure individually on the basis of its own space group. Therefore, the modulation is neglected in this treatment. These classical methods, however, often encounter difficulties in the structure determination.

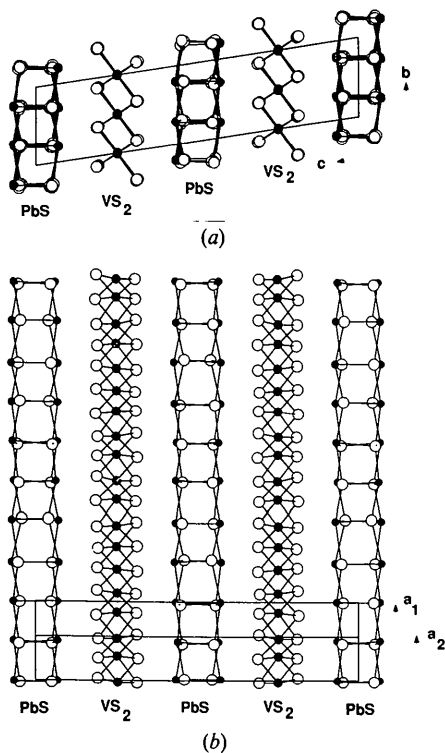


Fig. 1. Structure of $[\text{PbS}]_x[\text{VS}_2]$ with $x=1.12$ projected along (a) the a axis and (b) the b axis.

* TTF = tetrathiafulvalene; BEDO-TTF = 3,4,3',4'-bis(ethylenedioxy)-2,2',5,5'-tetrathiafulvalene; ET = BEDT-TTF = 3,4,3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene; Bz = benzoyl.

Table 1. Examples of possible superspace groups for known composite crystals

| Compound | Superspace group | Reference | Compound | Superspace group | Reference |
|--|--|--|--|--|--|
| (a) Composite crystals with two substructures | | | | | |
| [SnS] ₄ [NbS ₂] [†] | $M_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2m}}$ | van Smaalen (1989), Meetsma, Wiegiers, Haange & de Boer (1989) | $\frac{[MS]_4[M_2S_2]}{[M = (Pb, Bi)]}$ | $M_{\overline{2}\overline{1}\overline{1}}^{C_{2v}^{1/m}} : M_{\overline{2}\overline{1}\overline{1}}^{C_{2v}^{2/m}}$ | Matzat (1979) |
| [LaS] ₄ [NbS ₂] [†] | $I_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Meershaut <i>et al.</i> (1989), Meershaut, Rabu <i>et al.</i> (1990), Wiegiers, Meetsma, Haange, van Smaalen <i>et al.</i> (1990), van Smaalen (1991a) | [Ba] ₄ [FeS ₂] [†] | $L_{\overline{1}\overline{1}\overline{1}}^{I4mm} : L_{\overline{1}\overline{1}\overline{1}}^{I4bm}$ | Grey (1975), Hoggins & Steinfink (1977), Onoda & Kato (1991) |
| [PbS] ₄ [NbS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Wiegiers, Meetsma, Haange & de Boer (1989), Meershaut, Guemas, Auriel & Rouxel (1990), Wiegiers, Meetsma, Haange, van Smaalen <i>et al.</i> (1990) | [Rh] ₄ [Ge] [¶] | $P_{\overline{1}\overline{1}\overline{1}}^{I4_1/amd} : W_{\overline{q}\overline{1}\overline{q}\overline{1}}^{P4_1/mc}$ | Jeitschko & Parthé (1967) |
| [CeS] ₄ [NbS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Wiegiers, Meetsma, Haange & de Boer (1990) | [Mn] ₄ [Si] | $P_{\overline{1}\overline{1}\overline{1}}^{I4_1/amd} : W_{\overline{q}\overline{1}\overline{q}\overline{1}}^{P4_1/mc}$ | Knott <i>et al.</i> (1967) |
| [HoS] ₄ [NbS ₂] [†] | $M_{\overline{1}\overline{1}\overline{1}}^{C_2^1} : M_{\overline{1}\overline{1}\overline{1}}^{C_2^1}$ | van Smaalen & Petříček (1992) [‡] | [M ₂ Cu ₂ O ₃] ₄ | $Z_{\overline{1}\overline{1}\overline{1}}^{C_2^1} : Z_{\overline{1}\overline{1}\overline{1}}^{C_2^1}$ | Kato, Takayama-Muromachi, Kosuda & Uchida (1988), Kato (1990), McCarron, Subramanian, Calabrese & Harlow (1988), Petříček <i>et al.</i> (1991) |
| [YS] ₄ [NbS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_2^1} : M_{\overline{1}\overline{1}\overline{1}}^{F_2^1}$ | Rabu, Meershaut & Rouxel (1990) [§] | [Sr ₂ Cu ₂ O ₃] ₄ | $M_{\overline{1}\overline{1}\overline{1}}^{A_2^1/m} : M_{\overline{1}\overline{1}\overline{1}}^{A_2^1/m}$ | McCarron <i>et al.</i> (1988), Shishido, Ukei & Fukuda (1992) |
| [BiSe] ₄ [NbSe ₂] | $M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Zhou <i>et al.</i> (1992) | [CuO ₂] [†] | $R_{\overline{1}\overline{1}\overline{1}}^{P3_1c} : P_{\overline{1}\overline{1}\overline{1}}^{R3_1m}$ | Ukei <i>et al.</i> (1992) |
| [PbS] ₄ [TaS ₂] | $M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Wulff, Meetsma, van Smaalen, Haange, de Boer & Wiegiers (1990) | [Sr] ₄ [TiS ₃] [†] | $R_{\overline{1}\overline{1}\overline{1}}^{P3_1c} : P_{\overline{1}\overline{1}\overline{1}}^{R3_1m}$ | Onoda, Saeki, Yamamoto & Kato (1993) |
| [SmS] ₄ [TaS ₂] | $M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Wiegiers, Meetsma, Haange & de Boer (1991) | [Bi ₂ Sr ₂ CuO ₄][O] ₄ [†] | $N_{\overline{1}\overline{1}\overline{1}}^{B2/b} : P_{\overline{1}\overline{1}\overline{1}}^{I2/m}$ | Yamamoto <i>et al.</i> (1993) |
| [LaS] ₄ [TaS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | de Boer, Meetsma, Zeinstra, Haange & Wiegiers (1991) | [Y(O,F)](O,F) ₄ | $P_{\overline{1}\overline{1}\overline{1}}^{A_{2h}^{2m}} : C_{\overline{1}\overline{1}\overline{1}}^{Pmmb}$ | Mann & Bevan (1972), Bevan & Mann (1975) |
| [CeS] ₄ [TaS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_{2h}^{2a}} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Wiegiers, Meetsma, Haange & de Boer (1990) | [Zr(N,F)](N,F) ₄ | $P_{\overline{1}\overline{1}\overline{1}}^{A_{2h}^{2m}} : C_{\overline{1}\overline{1}\overline{1}}^{Pmmb}$ | Jung & Juza (1973), Bevan & Mann (1975) |
| [BiS] ₄ [TaS ₂] | $P_{\overline{1}\overline{1}\overline{1}}^{A_{2h}^{2m}} : P_{\overline{1}\overline{1}\overline{1}}^{A_{2h}^{2m}}$ | Gotoh <i>et al.</i> (1992) [§] | [MS] ₄ [TS ₂] ₄ [M = (Pb, Ag, Sn, Sb, Fe), T = (Sn, Sb, Fe)] | $P_{\overline{1}\overline{1}\overline{1}}^{P^1} : P_{\overline{1}\overline{1}\overline{1}}^{P^1}$ | Makovicky & Hyde (1981), Williams & Hyde (1988), Wang & Kuo (1991) |
| [BiSe] ₄ [TaSe ₂] | $M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m} : M_{\overline{1}\overline{1}\overline{1}}^{Fm\overline{2}m}$ | Zhou <i>et al.</i> (1992) | [M(OH) ₂] ₄ [TS ₂] ₄ [M = (Mg, Al); T = (Fe, Cu)] | $T_{\overline{p}\overline{6}m\overline{1}}^{P3_1m1} : P_{\overline{p}\overline{6}m\overline{1}}^{R3_1m}$ | Evans & Allmann (1968) |
| [PbS] ₄ [TiS ₂] [†] | $M_{\overline{2}\overline{1}\overline{1}}^{C_2^1/m} : M_{\overline{2}\overline{1}\overline{1}}^{C_2^1/m}$ | Wiegiers, Meetsma, van Smaalen, Haange & de Boer (1990), van Smaalen, Meetsma, Wiegiers & de Boer (1991) | [I] ₄ [TTF] | $P_{\overline{1}\overline{1}\overline{1}}^{I2/c} : M_{\overline{1}\overline{1}\overline{1}}^{C_2^1/m}$ | Johnson & Watson (1976), Janner & Jansen (1980) |
| [SnS] ₄ [TiS ₂] | $I_{\overline{1}\overline{1}\overline{1}}^{C_2^1} : M_{\overline{1}\overline{1}\overline{1}}^{F_2^1}$ | Wiegiers, Meetsma, de Boer, van Smaalen & Haange (1991) [§] | [Br] ₄ [TTF] | $P_{\overline{1}\overline{1}\overline{1}}^{C_2^1/m} : P_{\overline{1}\overline{1}\overline{1}}^{C_2^1/m}$ | La Placa, Corfield, Thomas & Scott (1975) |
| [PbS] ₄ [VS ₂] [†] | $M_{\overline{1}\overline{1}\overline{1}}^{F_2^1} : I_{\overline{1}\overline{1}\overline{1}}^{C_2^1}$ | Onoda <i>et al.</i> (1990) [§] | [I] ₄ [BEDO-TTF] [†] | $P_{\overline{1}\overline{1}\overline{1}}^{P^1} : P_{\overline{1}\overline{1}\overline{1}}^{P^1}$ | Petříček <i>et al.</i> (1991) |
| [LaS] ₄ [CrS ₂] [†] | $M_{\overline{1}\overline{1}\overline{1}}^{C_2^1} : M_{\overline{1}\overline{1}\overline{1}}^{C_2^1}$ | Kato, Kawada & Takahashi (1977), Kato (1990) [§] | [I] ₄ [Bz ₂ M ₂ (CHCl ₃)] [M = K, NH ₄ , Na] | $P_{\overline{1}\overline{1}\overline{1}}^{P3_1c} : P_{\overline{1}\overline{1}\overline{1}}^{P3_1m}$ | Coppens, Leung, Ortega, Young & LaPorta (1983) |
| | | | [Hg] ₄ [ETBr ₂] ₄ | $P_{\overline{1}\overline{1}\overline{1}}^{I2/c} : P_{\overline{1}\overline{1}\overline{1}}^{I2/c}$ | Lyubovskaya <i>et al.</i> (1987) |
| | | | [Hg] ₄ [ET(SCN) ₂] [†] | $P_{\overline{1}\overline{1}\overline{1}}^{P^1} : P_{\overline{1}\overline{1}\overline{1}}^{P^1}$ | Petříček <i>et al.</i> (1991) |
| (b) Composite crystals with three substructures | | | | | |
| [M ₃ CrX ₃] ₄ [M ₃ X] ₄ - [Cr ₇ X ₁₂] | $P_{\overline{p}\overline{6}2}^{P6_3/m} : P_{\overline{p}\overline{6}2}^{P6_3/m} : P_{\overline{p}\overline{6}2}^{P6_3/m}$ | Brouwer & Jellinek (1977) | | | |
| (M = Ba, Sr, Eu, Pb; X = S, Se) | | Brouwer & Jellinek (1979) | | | |
| [Hg] ₄ [Hg] ₄ [AsF ₆] | | Brown <i>et al.</i> (1975) Pouget <i>et al.</i> (1978) | | | |

[†] Determined by higher-dimensional analysis.

[‡] $c^{*2} = 2C^{*2}$ (capital letters mean axes in original papers).

[§] $a^{*1} = B^{*1}$, $a^{*2} = B^{*2}$, $b^{*} = A^{*}$.

[¶] [V]₄[Ge], [Mo]₄[Ge], [Ir]₄[Ge], [Cr]₄[Ge], [Te]₄[Si], [Rh]₄[Ga], [Ir]₄[Ga], [Ru]₄[Sn].

In commensurate cases with a long period, there are many unobserved satellite reflections, while the number of parameters grows with the period. This causes special correlation between structural parameters and leads to a singular normal matrix in the least-squares method. In incommensurate cases, a main reflection always consists of contributions from the main reflection of a substructure and the main or satellite reflection of the other substructure. As a

result, we cannot obtain the contribution from only the main reflection of a specified substructure. Therefore, it is difficult to determine accurately an average (unmodulated) substructure from the main reflection, in contrast to the usual modulated structure.

A modern technique developed recently removes difficulties such as these. It starts from the higher-dimensional description of the (incommensurate) modulated structure made by de Wolff (1974), where

the modulated structure is described as a periodic structure in higher-dimensional space (superspace) and its symmetry is specified by a higher-dimensional space group. After that, the symmetry of modulated structures was formulated as the theory of superspace groups by Janner & Janssen (1979). This is well known and has been widely used in the analysis of modulated structures. In 1980, the theory was extended to cover composite crystals (Janner & Janssen, 1980). As stated above, the composite crystal shows at least two sets of three-dimensional sublattices of main reflections. In order to index these reflections, we need $3+d$ basis vectors as in the modulated structure. It has been shown that, if the minimal number of basis vectors needed for indexing the diffraction pattern is $3+d$, the structure is described as a periodic structure in $(3+d)$ -dimensional space, similar to the modulated structure with d -dimensional modulations. The description is, however, different from that of the

modulated structure in the embedding of the three-dimensional structure into the $(3+d)$ -dimensional one. This is not unique (Janner & Janssen, 1980) and an infinite number of equivalent embeddings exists (Yamamoto, 1992). It can be shown that there exists an embedding equivalent to the standard one of the modulated structure for every modulated substructure (van Smaalen, 1991*b*; Yamamoto, 1992). This ensures that we can choose an embedding appropriate for a specific substructure, depending on the substructure. In this treatment, each modulated substructure is recognized as the usual modulated structure and every technique for the modulated structure is applicable to it. Since each modulated substructure is a usual modulated structure, its symmetry is specified by the superspace group of the modulated structure. Thus, the analysis of the composite crystal structure reduces to the analysis of each modulated substructure based on its own superspace group, though all modulated substructures have to be analyzed simultaneously.

For one-dimensionally modulated structures, a list of all relevant superspace groups is given (de Wolff, Janssen & Janner, 1981; Yamamoto, Janssen, Janner & de Wolff, 1985). This is applicable to the modulated substructure in the composite crystal (Janner & Janssen, 1980; van Smaalen, 1989). The total symmetry is specified by a superspace group that is equivalent to that of the modulated substructure as a higher-dimensional space group (van Smaalen, 1991*b*). The classification of superspace groups for the modulated structure is finer than that of higher-dimensional space groups so the superspace groups of substructures may not be equivalent to each other as the superspace group. It was proposed that, in a composite crystal with two substructures, the symmetry of the composite crystal be specified by a pair of the superspace groups of substructures (Yamamoto, 1992). Similarly, for those with three substructures, a triplet of superspace groups is available. They are equivalent as for the higher-dimensional space group, as mentioned above.

Possible superspace groups of substructures can be determined by analysis of the average substructures, according to the classical method, and by consideration of the extinction rules including satellite reflections, as in the usual modulated structure. In the present case, the main reflection of one substructure is the main or satellite reflection of the other. Therefore, even when satellite reflections are not observed, possible superspace groups are limited to a few cases. A difficulty in determining the superspace groups of substructures is that a convenient setting of the reciprocal unit vectors is often nonstandard, as the setting in the modulated structure and corresponding extinction rules are not found in the table of de

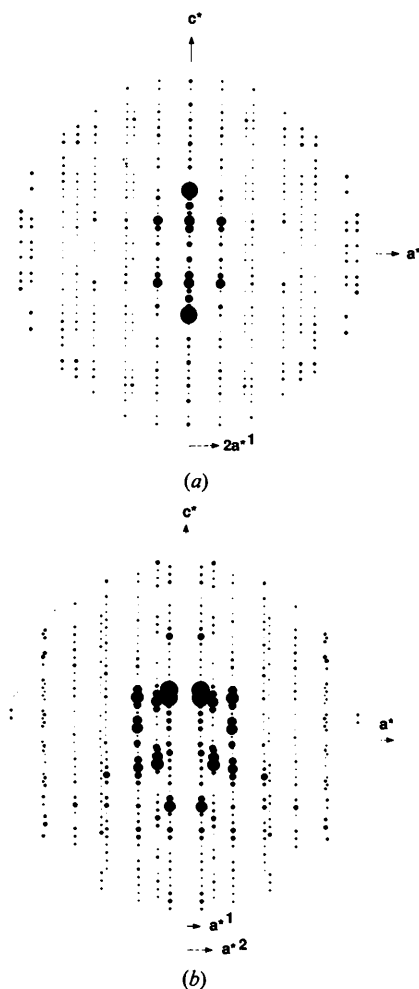


Fig. 2. Diffraction patterns of $[\text{PbS}]_x[\text{VS}_2]_z$ in (a) $(h0lm)$ and (b) $(h1lm)$ planes.

Wolff, Janssen & Janner (1981). Extinction rules for all nonstandard settings in the four-dimensional case were recently calculated (Yamamoto, 1992) to improve the situation.

The first application of the theory of Janner & Janssen (1980) to the analysis of composite crystals has been made by Kato (1990). A newly developed computer program for the refinement of composite crystal structures showed that, even in a case where no satellite reflections are observed, the introduction of modulations reduces the R factor of the main reflection remarkably. This proved that the average structure can be determined accurately only by taking into account the modulation in each substructure. Nowadays, at least three computer programs have been developed for the analysis of composite crystal structures. Two of them are based on the theory of Janner and Janssen (Kato, 1990; Petříček, Maly, Coppens, Bu, Cisarova & Frost-Jensen, 1991), while the other one is based on a simplified theory in which the settings of the unit vectors are strongly limited (Yamamoto, 1992). These three are, however, equally applicable up to six-dimensional cases. (A program by Kato is also applicable to more-than-six-dimensional cases). These are for single-crystal data, but one program for powder data was written and applied to the superconducting oxide $[\text{Ba}_2\text{Sr}_2\text{CuO}_4][\text{O}]_y$, mentioned above (Yamamoto, Takayama-Murumachi, Izumi, Ishigaki & Asano, 1993).

The method based on the superspace group and description in superspace is as efficient for commensurate composite crystals as it is for commensurate modulated structures, especially when the higher-order satellite reflections are systematically unobserved. Such an analysis has been made by Onoda & Kato (1991) for $[\text{Ba}]_6[\text{FeS}_2]_8$ and $[\text{Ba}]_{10}[\text{FeS}_2]_9$. In these cases, the longest axis of the supercell is not very long ($\sim 40\text{--}45 \text{ \AA}$) but in some electron compounds it ranges as high as 300 \AA , as mentioned before, and many satellite reflections are unobserved. In such cases, the structure can be analyzed as an incommensurate composite crystal based on a superspace group, as discussed later. Thus, the method is applicable to analyses of all kinds of composite crystals and is efficient for all cases.

It is known that there exists an exceptional case where one substructure is related to the other by a symmetry operation. The simplified theory is not applicable to it. Such cases are, however, very rare – so far only one, $[\text{Hg}]_x[\text{Hg}]_x[\text{AsF}_6]$, is known. Therefore, the simplified theory is practically general.

A general theory of symmetry is reviewed in § 2. § 3 is devoted to the unified setting and symbols of superspace groups. These give a simplified treatment that is applicable to all cases excluding that mentioned above. In the subsequent sections, the simplified treatment is described. In § 4, structure-factor

calculations are discussed. § 5 describes problems and approximations specific to the commensurate composite structure analysis in superspace. The derivation of the superspace group from the space groups of substructures and many examples of superspace groups for known structures are given in § 6. Finally, the refinement method is discussed in § 7.

2. Symmetry of the composite crystal

The composite crystal is a crystal consisting of several interpenetrating substructures with mutually incommensurate periods. Therefore, the diffraction pattern is not indexable by three reciprocal-lattice vectors and three integers (Fig. 2). We need, in general, $3+d$ vectors. So far, cases up to $d=2$ are known. There exist prominent ('main') reflections constructing several sets of three-dimensional reciprocal lattices. In some cases, the number of vectors necessary to index the main reflections may be less than $(3+d)$ because it is possible for there to exist additional modulations that are independent of the mutual incommensurability of the substructures. Janner & Janssen (1980) showed that such a modulation may be present in $[\text{Hg}]_x[\text{Hg}]_x[\text{AsF}_6]$ and discussed a general case, giving a general theory. In the following, we do not consider such additional modulations, for ease of understanding. This does not limit the applicability of the theory because most composite crystals do not show such modulations.

In addition to main reflections, weak satellite reflections are observed. In the limited cases mentioned above, these are also indexable with the same basic vectors as those needed for main reflections:

$$\mathbf{a}_1^*, \mathbf{a}_2^*, \dots, \mathbf{a}_{3+d}^* \quad (1)$$

The diffraction vector \mathbf{h} is written as $\mathbf{h} = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^*$, where h_1, h_2, \dots, h_{3+d} are integers (generalized Miller indices). This implies that the structure can be described by a periodic structure in $(3+d)$ -dimensional space (superspace); the real three-dimensional structure is a three-dimensional section of this structure, the same as the modulated structure. The structure in superspace is, however, different from the modulated structure because, in the latter, main reflections are on one three-dimensional reciprocal lattice, while the composite crystal shows two or more sets of three-dimensional lattices of main reflections. Such a crystal structure in superspace can be constructed as follows.

The basic vectors [(1)] are regarded as the projections of unit vectors in superspace onto the usual three-dimensional space (external space). In the modulated structure, the first three vectors are taken to be the unit vectors (in reciprocal space) of the average structure while, in the composite crystal, these are usually the unit vectors of one substructure

though, even if such a choice is impossible, the following description is not affected. Since the vectors of (1) are three-dimensional, \mathbf{a}_{3+j}^* ($j = 1, \dots, d$) are given by linear combinations of \mathbf{a}_1^* , \mathbf{a}_2^* and \mathbf{a}_3^* with real coefficients σ_{jk} :

$$\mathbf{a}_{3+j}^* = \sum_{k=1}^3 \sigma_{jk} \mathbf{a}_k^* \quad (j = 1, 2, \dots, d). \quad (2)$$

From the incommensurability, at least one of σ_{jk} ($k = 1, 2, 3$) is irrational.

Without loss of generality, the first three can be taken on the external space and the others oblique to this space (Janner & Janssen, 1980). Then, the unit vectors \mathbf{d}_i^* ($i = 1, 2, \dots, 3+d$) in superspace are written as

$$\mathbf{d}_i^* = (\mathbf{a}_i^*, 0) \quad (i = 1, 2, 3), \quad (3)$$

$$\mathbf{d}_{3+j}^* = (\mathbf{a}_{3+j}^*, \mathbf{b}_j^*) \quad (j = 1, \dots, d), \quad (4)$$

where \mathbf{b}_j^* ($j = 1, \dots, d$) are unit vectors in the d -dimensional subspace (internal space) orthogonal to the external space. The unit vectors reciprocal to those of (3) and (4) are

$$\mathbf{d}_i = (\mathbf{a}_i, -\sum_{j=1}^d \sigma_{ji} \mathbf{b}_j) \quad (i = 1, 2, 3), \quad (5)$$

$$\mathbf{d}_{3+j} = (0, \mathbf{b}_j) \quad (j = 1, \dots, d), \quad (6)$$

where \mathbf{a}_i and \mathbf{b}_j are the vectors in the external and internal spaces with $\mathbf{a}_i^* \cdot \mathbf{a}_j = \delta_{ij}$ ($i, j = 1, 2, 3$) and $\mathbf{b}_i^* \cdot \mathbf{b}_j = \delta_{ij}$ ($i, j = 1, 2, \dots, d$). The definitions of the unit vectors in superspace [(3)–(6)] are the same as those for d -dimensionally modulated structures. These give the coordinate systems in reciprocal and direct spaces common to all the substructures.

The unit vectors of the ν th sublattice in reciprocal space are given by integral linear combinations of (1) (Janner & Janssen, 1980):

$$\mathbf{a}_i^{*\nu} = \sum_{k=1}^{3+d} (Z^\nu)_{ik} \mathbf{a}_k^* \quad (i = 1, 2, 3). \quad (7)$$

This defines the $3 \times (3+d)$ integral matrix Z^ν , which relates the basic vectors in the ν th substructure ($\nu = 1, 2, \dots, N$) to the common basic vectors. The modulation wave vectors for the ν th substructure can be chosen as follows. Among diffraction vectors $\mathbf{h} = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^*$, select a vector $\mathbf{a}_4^{*\nu}$ that does not belong to an integral linear combination of $\mathbf{a}_1^{*\nu}, \dots, \mathbf{a}_3^{*\nu}$. (This means that the selected vector is not a lattice vector of the ν th substructure.) Next, choose a vector $\mathbf{a}_5^{*\nu}$ that does not belong to an integral linear combination of $\mathbf{a}_1^{*\nu}, \dots, \mathbf{a}_4^{*\nu}$. This is repeated until the d th wave vector $\mathbf{a}_{3+d}^{*\nu}$ is obtained. In general, the wave vectors obtained are expressed by integral linear combinations of (1) (van Smaalen, 1991b,c):

$$\mathbf{a}_{3+j}^{*\nu} = \sum_{k=1}^{3+d} (V^\nu)_{jk} \mathbf{a}_k^{*\nu} \quad (j = 1, 2, \dots, d). \quad (8)$$

The modulation wave vectors of the ν th substructure are written in terms of $\mathbf{a}_1^{*\nu}$, $\mathbf{a}_2^{*\nu}$ and $\mathbf{a}_3^{*\nu}$:

$$\mathbf{a}_{3+j}^{*\nu} = \sum_{k=1}^3 (\sigma^\nu)_{jk} \mathbf{a}_k^{*\nu} \quad (j = 1, 2, \dots, d). \quad (9)$$

The matrix σ^ν is expressed in terms of σ and Z^ν , and V^ν (van Smaalen, 1991b):

$$(\sigma^\nu)_{jk} = [(V_3^\nu + V_d^\nu \sigma)(Z_3^\nu + Z_d^\nu \sigma)^{-1}]_{jk}, \quad (10)$$

where V_3^ν and V_d^ν are the first $d \times 3$ and next $d \times d$ parts of V^ν while Z_3^ν and Z_d^ν are the first 3×3 and next $3 \times d$ parts of Z^ν . The setting of $\mathbf{a}_i^{*\nu}$ ($i = 1, 2, \dots, 3+d$) is not unique. Janner & Janssen (1980) employed a primitive cell for $\mathbf{a}_i^{*\nu}$ ($i = 1, 2, 3$), while recent structure analyses by Kato (1990) and van Smaalen (1991b) used the conventional cell. Yamamoto (1992) proposed a strongly limited setting with a special choice for (1), Z^ν and V^ν , so the W^ν , defined below, becomes a permutation matrix. This setting is possible for all the known cases except $[\text{Hg}]_x[\text{Hg}]_x[\text{AsF}_6]$, where two mercury substructures are related by a symmetry operation of the third substructure. This is discussed in the next section. Equations (7) and (8) are merged into a single expression:

$$\mathbf{a}_i^{*\nu} = \sum_{k=1}^{3+d} (W^\nu)_{ik} \mathbf{a}_k^* \quad (i = 1, 2, \dots, 3+d), \quad (11)$$

where $(W^\nu)_{ik} = (Z^\nu)_{ik}$ ($i = 1, 2, 3$) and $(W^\nu)_{3+j,k} = (V^\nu)_{jk}$ ($j = 1, 2, \dots, d$).

Corresponding unit vectors in superspace are obtained by replacing \mathbf{a}_k^* with \mathbf{d}_k^* .

$$\mathbf{d}_i^{*\nu} = \sum_{k=1}^{3+d} (W^\nu)_{ik} \mathbf{d}_k^* \quad (i = 1, 2, \dots, 3+d). \quad (12)$$

From the definition of \mathbf{d}_k^* [(3) and (4)], it is clear that $\mathbf{d}_k^{*\nu}$ is projected onto $\mathbf{a}_k^{*\nu}$ by the projection parallel to the internal space. Vectors reciprocal to those of (12) are

$$\mathbf{d}_i^\nu = \sum_{k=1}^{3+d} (W^\nu)_{ki}^{-1} \mathbf{d}_k \quad (i = 1, 2, \dots, 3+d). \quad (13)$$

The matrices W^ν and $(W^\nu)^{-1}$ also transform coordinates, x_i , referred to \mathbf{d}_i , and indices, h_i , referred to \mathbf{d}_i^* , into corresponding ones of the ν th substructure.

$$x_i^\nu = \sum_{k=1}^{3+d} (W^\nu)_{ik} x_k \quad (i = 1, 2, \dots, 3+d), \quad (14)$$

$$h_i^\nu = \sum_{k=1}^{3+d} (W^\nu)_{ki}^{-1} h_k \quad (i = 1, 2, \dots, 3+d). \quad (15)$$

Each atom in the ν th substructure is continuous in the subspace spanned by $\mathbf{d}_{3+j}^{*\nu}$ ($j = 1, 2, \dots, d$). Then, the atomic coordinates x_1^ν , x_2^ν and x_3^ν are continuous functions of x_{3+j}^ν ($j = 1, \dots, d$). Since $\mathbf{d}_{3+j}^{*\nu}$ ($j = 1, 2, \dots, d$) are orthogonal to $\mathbf{d}_i^{*\nu}$ ($i = 1, 2, 3$) and the latter are fixed by Z^ν , the matrix Z^ν determines the

subspace where the atoms of the ν th substructure are continuous (van Smaalen, 1991b).

In the composite crystal, each substructure is modulated because of the interaction between substructures. The amplitudes of the displacement waves in each substructure are always parallel to the external space. An example of a one-dimensional case described in two-dimensional space is shown in Fig. 3.

The resulting composite crystal structure is periodic in superspace along $3 + d$ directions with the fundamental periods \mathbf{d}_i ($i = 1, 2, \dots, 3 + d$). The symmetry of the $(3 + d)$ -dimensional crystal is therefore specified by a $(3 + d)$ -dimensional space group (superspace group). The setting of the wave vectors for each substructure is not unique, as in the modulated structure. One possible set of wave vectors can be obtained by the procedure mentioned above, but these wave vectors are equivalent to others that are different from the original ones by reciprocal-lattice vectors of the ν th substructure (integral linear combinations of \mathbf{a}_1^ν , \mathbf{a}_2^ν and \mathbf{a}_3^ν). Superspace groups in different settings as mentioned above should be equivalent, though the equivalence relations (sufficient conditions) suitable for composite crystals are not known.

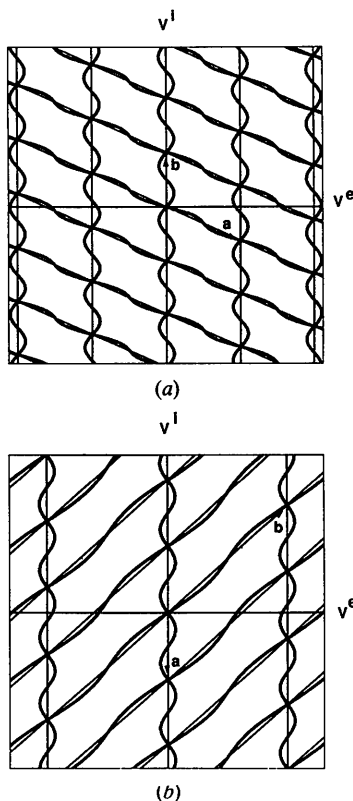


Fig. 3. Two equivalent representations of the same composite crystal. The sections on the external space V^e give the same structure.

3. Unified setting and symbols of superspace groups

In the unified setting of the unit vectors describing the composite crystal in superspace (Yamamoto, 1992), we take all the basic vectors \mathbf{a}_i^ν ($i = 1, 2, \dots, 3 + d$) among the set of lattice vectors of main reflections [(1)], that is, one of \mathbf{a}_i^ν ($i = 1, 2, \dots, 3 + d$). Then, the matrix W^ν becomes a permutation matrix P^ν . In the following, \mathbf{a}_1^ν , \mathbf{a}_2^ν , \mathbf{a}_3^ν are written as $\mathbf{a}^{\nu*}$, $\mathbf{b}^{\nu*}$, $\mathbf{c}^{\nu*}$ and \mathbf{a}_{3+j}^ν ($j = 1, 2, \dots, d$) as \mathbf{k}_j^ν ($j = 1, \dots, d$) for convenience. All composite crystals known so far are of either the type I or the type II discussed by Yamamoto (1992), where two or one in (1) are common to all the substructures. For example, in the simplest case of type I, we can take \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^{*1} and \mathbf{c}^{*2} to index the diffraction pattern and recognize them as the projections of the unit vectors in the four-dimensional lattice onto the external space, where \mathbf{a}^* and \mathbf{b}^* are the unit vectors common to the two (average) substructures and \mathbf{c}^{*1} and \mathbf{c}^{*2} are the third unit vectors for the first and second substructures. As stated above, each substructure is modulated by the period of the others. The modulation wave vector for the first modulated substructure is therefore \mathbf{c}^{*2} , while that for the second is \mathbf{c}^{*1} ; $\mathbf{k}^1 = \mathbf{c}^{*2}$ and $\mathbf{k}^2 = \mathbf{c}^{*1}$. Then, $W^1 = P^1 = \begin{pmatrix} 1, 2, 3, 4 \\ 1, 2, 3, 4 \end{pmatrix} = (1)$, $W^2 = P^2 = \begin{pmatrix} 1, 2, 3, 4 \\ 1, 2, 4, 3 \end{pmatrix} = (3, 4)$.

A similar consideration can be made for a case of type II. We consider a simple case with \mathbf{a}^{*1} , \mathbf{a}^{*2} , \mathbf{b}^{*1} , \mathbf{b}^{*2} , $\mathbf{c}^{*1} = \mathbf{c}^{*2}$, which appears in valleriite $\{[(\text{Mg,Al})_2(\text{OH})_2]_x[(\text{Fe,Cu})\text{S}_2]_y\}$, Evans & Allmann (1968). In this case, the wave vectors of the modulation waves for the first substructure are \mathbf{a}^{*2} and \mathbf{b}^{*2} , while those for the second are \mathbf{a}^{*1} and \mathbf{b}^{*1} . That is, the unit vectors of the ν th substructure and wave vectors of the modulation waves, $\mathbf{a}^{\nu*}$, $\mathbf{b}^{\nu*}$, $\mathbf{c}^{\nu*}$, \mathbf{k}_1^ν , \mathbf{k}_2^ν , are obtained from \mathbf{a}^{*1} , \mathbf{b}^{*1} , \mathbf{c}^{*1} , \mathbf{a}^{*2} , \mathbf{b}^{*2} by the permutation P^ν , where $P^1 = \begin{pmatrix} 1, 2, 3, 4, 5 \\ 1, 2, 3, 4, 5 \end{pmatrix} = (1)$ and $P^2 = \begin{pmatrix} 1, 2, 3, 4, 5 \\ 4, 5, 3, 1, 2 \end{pmatrix} = (1, 4)(2, 5)$. In particular, we take the identity permutation for the first substructure. This simplifies the treatment of composite crystals in superspace. We consider the five-dimensional reciprocal lattice, the unit vectors of which are projected onto the independent basic vectors selected above (\mathbf{a}^{*1} , \mathbf{b}^{*1} , \mathbf{c}^{*1} , \mathbf{a}^{*2} , \mathbf{b}^{*2}). Then $(\mathbf{a}^{\nu*}, \mathbf{b}^{\nu*}, \mathbf{c}^{\nu*}, \mathbf{k}_1^\nu, \mathbf{k}_2^\nu) = [\mathbf{d}_1^{\nu*}, \mathbf{d}_2^{\nu*}, \mathbf{d}_3^{\nu*}, \mathbf{d}_4^{\nu*}, \mathbf{d}_5^{\nu*}]^e = [P^\nu(\mathbf{d}_1^*, \mathbf{d}_2^*, \mathbf{d}_3^*, \mathbf{d}_4^*, \mathbf{d}_5^*)]^e$, by definition, where the superscript e indicates the external component of a five-dimensional vector.

The superspace group symbol for the ν th substructure (appearing in the superspace group of the composite crystal) is obtained from that of the first substructure by the permutation P^ν , because the permutation matrix transforms the matrix representation of a symmetry element in the first substructure into the corresponding one in the ν th substructure (see the next section). This means that the superspace

groups of modulated substructures are equivalent to each other as a higher-dimensional space group (van Smaalen, 1991b).

In the unified setting mentioned above, the selection of unit vectors is strongly limited, because the unit vectors of each modulated substructure in the reciprocal space are chosen from a set of reciprocal-lattice vectors of average substructures. Furthermore, the same vector is used when an axis is common to several substructures. Therefore, the setting of the unit vectors is unique except for the ambiguity in the choice of the unit vectors in each average substructure. On the other hand, such unit vectors may lead to a superspace group in a nonstandard setting, as is shown in §6.

The symmetry of composite crystals can be expressed by a superspace group for the modulated structure (Janner & Janssen, 1980). However, this causes difficulty in some cases. For the setting in Fig. 3(a), the first substructure gives the main reflections, which are on the external space (Fig. 4a). In this setting, we have some superspace group, while the other setting in Fig. 3(b), where the first three vectors in (1) are taken from the unit vectors of the second

average substructure, may give a superspace group that is not equivalent to the former because the reflections coming from the second substructure are regarded as the main reflections. For example, in a case shown below, the first setting gives the superspace group R_{111}^{P31c} , while the second gives P_{15}^{R3m} (see § 6). These two superspace groups are nonequivalent under the equivalence relation for the modulated structure (de Wolff, Janssen & Janner, 1981). Furthermore, if we allow a setting different from these two, we may obtain another superspace group.

The symmetry of a composite crystal with two substructures is properly specified by two superspace groups, which give the symmetries of two modulated substructures. In the present case, it is written as $R_{111}^{P31c} : P_{15}^{R3m}$. Similarly, in a composite crystal with three substructures, a triplet of the superspace-group symbols for three modulated substructures is used. In this notation, each substructure is treated equivalently, because the interchange of the first and second substructures simply means the interchange of the two superspace-group symbols. Therefore, these two superspace groups are called equivalent. This gives the necessary condition for the equivalence relation of the superspace groups for composite crystals: the superspace groups obtained from each other by the interchange of substructures are equivalent. A possible definition of equivalence in the superspace groups of composite crystals may be as follows. If the pair (or triplet *etc.*) of superspace groups is equivalent to the other pair (triplet *etc.*) as the superspace group under the restriction of a unified setting, then they are equivalent to the superspace group of the composite crystal. A complete theory of the equivalence is, however, not known.

As mentioned above, the choice of unit vectors is restricted in the unified setting. As a result, the setting may be nonstandard, not only for the superspace group of the modulated substructure but also for the space group of the average substructure. We have to use, for example, a face-centered lattice for a monoclinic structure in some cases and a wave vector, such as $\mathbf{k} = \mathbf{a}^* + \mathbf{b}^* + \gamma\mathbf{c}^*$, for which the symbol of the superspace group is not given. (See § 6.) Several symbols have been introduced for four-dimensional superspace groups in addition to those introduced by de Wolff, Janssen & Janner (1981). Additional rational components of the wave vector \mathbf{k} and all the reflection conditions for these wave vectors have been given (Yamamoto, 1992). The reflection conditions are, however, easily derived, as follows.

These wave vectors appear only when the average substructure has a centered lattice. Note that rational components appear when the wave vector of the modulation wave \mathbf{k}' is at the Brillouin-zone boundary of the average substructure. A 1 in the rational

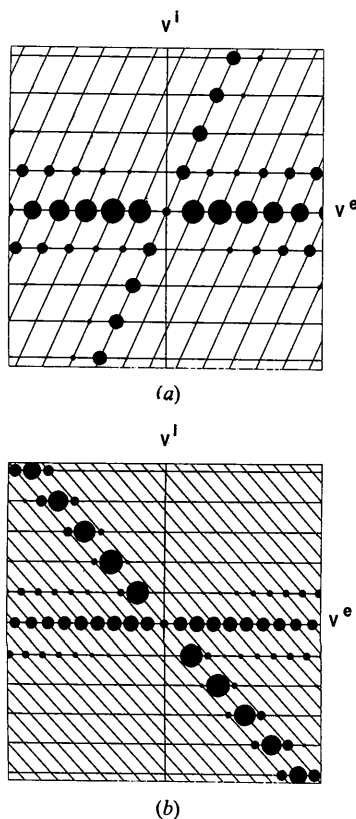


Fig. 4. Diffraction patterns of the two two-dimensional crystals in Figs. 3(a) and (b). The observed diffraction patterns corresponding to the structure on the external space V^e in Figs. 3(a) and (b) are obtained by the projection parallel to the internal space V^i . These give the same pattern.

component means that the average substructure has a centered lattice because, in the primitive lattice, the Brillouin-zone boundary is at 1/2 along all the principal axes. When the rational component is 1/2, the corresponding axis in the direct space is doubled (de Wolff, Janssen & Janner, 1981). The reflection conditions calculated are those referred to the new unit cell. All the reflection conditions for general reflections are obtained from those of the Bravais lattice of the average substructure or from the cell doubling mentioned above. In the following, the unit vectors of the original cell and indices referred to them are represented by capital letters, while those to the new cell are represented by small letters. For example, consider the case where the rational component is $(\frac{1}{2}, 1, 0)$ and the average structure has the *A*-centered lattice. Then, $\mathbf{A}^* = 2\mathbf{a}^*$, $\mathbf{B}^* = \mathbf{b}^*$, $\mathbf{C}^* = \mathbf{c}^*$ and $\mathbf{K} = \mathbf{a}^* + \mathbf{b}^* + \mathbf{k}$. ($\mathbf{k} = \gamma\mathbf{c}^*$). From $\mathbf{h} = H\mathbf{A}^* + K\mathbf{B}^* + L\mathbf{C}^* + M\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{k}$ and $K + L = 2n$, reflection conditions $h + m = 2n$, $k + l + m = 2n$ and $h + k + l = 2n$ are obtained. The reflection conditions imply that there are centering translations $\{E|\frac{1}{2}, 0, 0, \frac{1}{2}\}$, $\{E|0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ and $\{E|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0\}$ in the superspace group.

It should be noted that, in the unified setting, the basic vectors [(1)] defining a coordinate system common to all the substructures are those referred to the new cell mentioned above, while the symbols of the superspace groups of substructures are related to the original ones. In the usual analysis, from the reflection condition referred to (1) and the rational and irrational components of the wave vector, the lattice type (represented by the prefix and the Bravais lattice of the average substructure) can be determined. In the superspace group, the same reflection conditions for general reflections are shared by several lattice types.

4. Structure factor

If we use the coordinates referred to \mathbf{d}^ν , the modulated substructure is described in the same manner as the usual modulated structure. For a $(3 + d)$ -dimensional case, the atom coordinates x_i^ν with respect to \mathbf{d}_i^ν ($i = 1, 2, \dots, 3 + d$) are given by

$$x_i^\nu = \bar{x}_i^\nu + \mathbf{d}_i^{*\nu} \cdot \mathbf{u}^\nu(\bar{x}_4^\nu, \dots, \bar{x}_{3+d}^\nu), \quad (16)$$

where \bar{x}_i^ν ($i = 1, 2, \dots, 3 + d$) are the atom coordinates for the ν th substructure, obtained from the coordinates \bar{x}_i in the fundamental structure with respect to \mathbf{d}_i by the matrix W^ν [see (14)] and \mathbf{u}^ν is the displacement from the fundamental structure parallel to the external space and a periodic function of \bar{x}_{3+i}^ν ($i = 1, \dots, d$). (See Fig. 3.) The modulation functions of the ν th modulated substructure have the same forms as the corresponding ones in the usual modulated structure.

The structure factor is given by

$$F_h = \sum_{\nu=1}^N (v^1/v^\nu) F_h^\nu. \quad (17)$$

$$F_h^\nu = \sum_{\{R^\nu|\tau^\nu\}} \sum_{\mu} a^{\mu\nu} \int_0^1 d\bar{x}_4^{\mu\nu} \dots \int_0^1 d\bar{x}_{3+d}^{\mu\nu} f^{\mu\nu}(\mathbf{h}^\nu) P^{\mu\nu} \\ \times \exp \left[- \sum_{i,k=1}^{3+d} h_i^\nu (R^\nu B^{\mu\nu} \tilde{R}^\nu)_{ik} h_k^\nu \right. \\ \left. + 2\pi i \sum_{i=1}^{3+d} h_i^\nu (R^\nu \mathbf{x}^{\mu\nu})_i + h_i^\nu \tau_i^\nu \right], \quad (18)$$

where $\{R^\nu|\tau^\nu\}$ runs over symmetry operators and μ over independent atoms of the ν th substructure. The multiplicity, atomic scattering factor, occupation probability and temperature factor of the μ th independent atom are denoted $a^{\mu\nu}$, $f^{\mu\nu}$, $P^{\mu\nu}$ and $B^{\mu\nu}$, respectively. The rotation matrix and the non-primitive translation vector are related to those in the common coordinate system, R_{ij} and τ_i , as (van Smaalen, 1989)

$$(R^\nu)_{ij} = \sum_{k,l=1}^{3+d} (W^\nu)_{ik} R_{kl} (W^\nu)_{lj}^{-1} \quad (19)$$

and

$$\tau_i^\nu = \sum_{j=1}^{3+d} (W^\nu)_{ij} \tau_j. \quad (20)$$

In particular, in the unified setting, these quantities are simply related by a permutation matrix P^ν instead of a general integral matrix W^ν . The structure factor of the ν th substructure (18) has the same form as the corresponding formula for the usual modulated structure (Yamamoto, 1982a) because each modulated substructure is the usual modulated structure. The structure factor of the total structure [(17)] is the summation of the structure factors of modulated substructures with the weight proportional to the inverse of the unit-cell volume of the average substructure v_ν . Two computer programs by Petříček *et al.* (1991) and Yamamoto (1992) are essentially based on (17) and (18) while another, by Kato (1990), uses a different expression, in which x_i^ν ($i = 1, 2, 3$) and t_j ($j = 1, 2, \dots, d$) [coordinates referred to \mathbf{b}_j in (6)] are used instead of x_i^ν ($i = 1, 2, \dots, 3 + d$).

In the modulated structure analysis, Fourier amplitudes of possible modulation waves are limited when atoms are located at special positions in the average structure. Then possible modulation waves are constrained by the site symmetry as in the modulated structure. In order to find possible modulation waves, we can apply the same method as in the modulated structure (Yamamoto & Nakazawa, 1982; Yamamoto, 1982b,c; van Smaalen, 1989; Kato, 1990). In this case, the superspace group of the modulated substructure plays the same role in that substructure as the superspace group in the modulated structure.

5. Commensurate composite crystals

As mentioned earlier, there are many commensurate composite crystals. It is well known that the chimney-ladder structures in electron compounds are commensurate composite crystals. For example, in $[\text{Rh}]_{17}[\text{Ge}]_{22}$, the a and b axes are common to both substructures and the c axes of Rh (c^1) and Ge (c^2) have a rational ratio, $17c^1 = 22c^2$, while, in $[\text{Mn}]_{15}[\text{Si}]_{26}$, $15c^1 = 26c^2$ (Fig. 5). These are usually analyzed as the superstructure based on the space group.

This can be described in superspace. Then, each atom is not continuous along any direction because of the commensurability of the wave vectors. The symmetry of commensurate composite crystals is therefore given by the space group. This method, however, has merits in several cases. When the modulation wave of the ν th substructure $\mathbf{k}^\nu = (l_1\mathbf{a}^{*\nu} + l_2\mathbf{b}^{*\nu} + l_3\mathbf{c}^{*\nu})/L^\nu$ has a large denominator L^ν , higher-order satellite reflections are not observed in many cases. In such cases, the classical analysis has difficulty because, in order to obtain weak intensities for unobserved satellite reflections, highly correlated atom positions have to be considered, while the number of parameters increases with L^ν . On the other hand, the description in superspace easily gives such a structure by neglecting higher-order harmonics in the modulation waves. This reduces the number of parameters and makes the analysis feasible.

Many unobserved higher-order satellite reflections make the determination of the absolute phase of modulation waves difficult. In order to fix the commensurate structure, the determination of the absolute phase is necessary, in contrast to the case for the

incommensurate modulated or composite crystal structure. This is because, even if the modulation wave is the same, the atoms are at discrete points on the modulation waves. Therefore, the absolute phase shift of all the modulation waves gives a different structure (Figs. 6a and b). The determination of the absolute phase is, however, difficult, for the following reason. As is shown in Fig. 7, each observed reflection is the sum of an infinite number of reflections parallel to the internal space V^i . (For any integer n , $h^\nu - nl_1$, $k^\nu - nl_2$, $l^\nu - nl_3$, $m^\nu + nL^\nu$ are superposed on $h^\nu k^\nu l^\nu m^\nu$ by the projection.) When the phase is shifted by φ^ν , the structure factors of the m th-order satellite reflections are multiplied by an additional phase factor $\exp(2\pi im^\nu \varphi^\nu)$, leaving its absolute value unchanged. As a result, the phase difference changes the observed intensity. However, if one of the superposed reflections is very strong and the others are negligibly weak, the absolute phase change is not reflected in the observed intensity. Therefore, the determination of the superstructure is difficult in such a case. (The analyses based on different space groups sometimes give similar R factors). However, the modulation wave can be determined by regarding the commensurate structure as an incommensurate one. This is called an incommensurate approximation for the commensurate structure. Then, the structure factor for the incommensurate composite crystal [(18)] and a superspace group are employed. This analysis is easier than that based on the description in superspace and on the space group mentioned above, because the analysis includes less parameters in most cases.

It is noted that the indexing of reflections is ambiguous in this case because of the superposition of reflections mentioned above. In the analysis, the

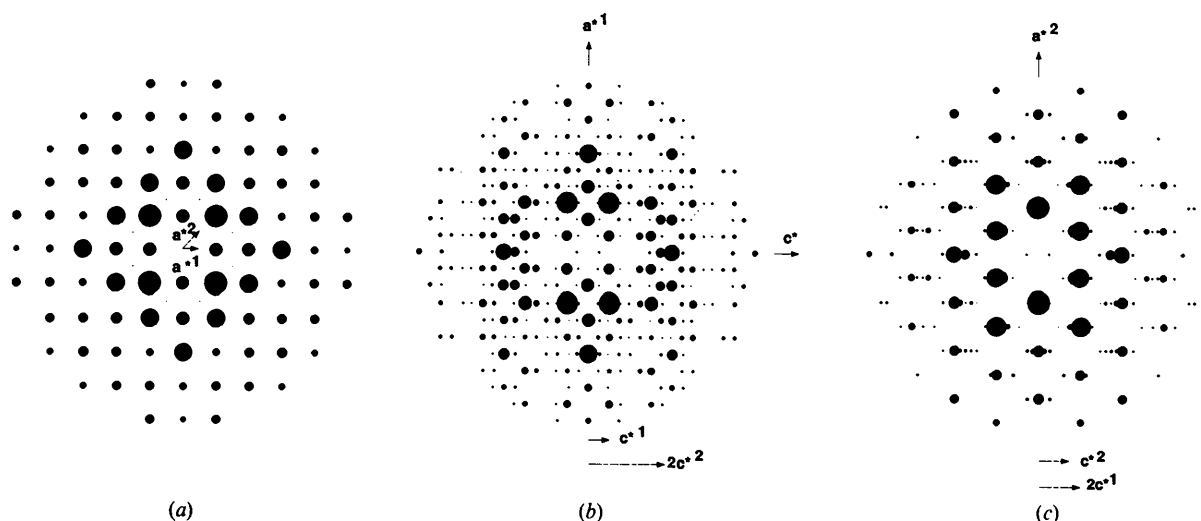


Fig. 5. Diffraction patterns of the commensurate chimney-ladder structure $[\text{Mn}]_{15}[\text{Si}]_{26}$. The three reciprocal planes are (a) $(hk00)$, (b) $(h0lm)$ and (c) $(hhlm)$. The unit vector \mathbf{c}^* of the superstructure is $\mathbf{c}^{*1}/15$ or $\mathbf{c}^{*2}/26$. Note that the higher-order satellite reflections of the composite crystal are not observed.

lowest satellite index is employed for each reflection: $-n < m^\nu \leq n$ with $n = L^\nu/2$ (L^ν even) or $-n \leq m^\nu \leq n$ with $n = (L^\nu - 1)/2$ (L^ν odd). (The zero-order satellite reflection means the main reflection.) Then, harmonics higher than the n th order can be dropped in the modulation wave. Except for this point, the analysis in the incommensurate approximation is the same as that for the usual incommensurate composite crystals.

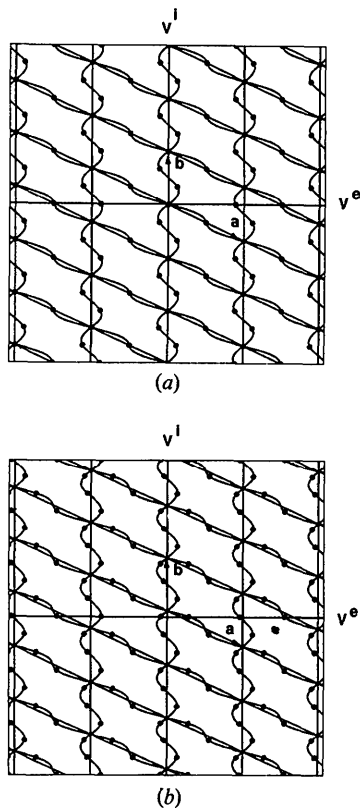


Fig. 6. Commensurate composite crystals. The positions corresponding to the points on the external space are denoted by dots. Two different sections (a) and (b) give different structures.

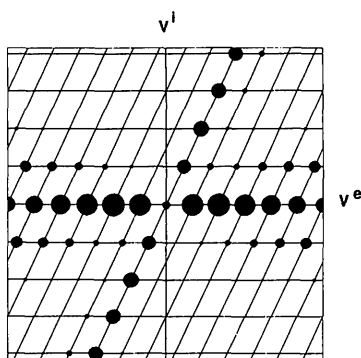


Fig. 7. Diffraction pattern of the composite crystals shown in Fig. 6. Note that an infinite number of reflections is projected onto the same position in the external space V^e .

In order to obtain the structure factors of commensurate composite crystals, the contributions from all superposed reflections have to be summed up. This leads to the slightly different structure-factor formula where the integration in (18) is replaced by summation over the points within a period along the internal space (Yamamoto, 1982a). Provided that the first wave vector is commensurate [$\mathbf{k}_1^\nu = (l_1 \mathbf{a}^{*\nu} + l_2 \mathbf{b}^{*\nu} + l_3 \mathbf{c}^{*\nu})/L^\nu$] and the others are incommensurate, it is written as

$$F_h^\nu = \sum_{\{R^\nu | \tau^\nu\}} \sum_{\mu} a^{\mu\nu} (1/L^\nu) \sum_{j=1}^{L^\nu} \int d\bar{x}_5^{\mu\nu} \dots \int_0^1 d\bar{x}_{5+d}^{\mu\nu} f^{\mu\nu}(\mathbf{h}^\nu) P^{\mu\nu} \times \exp \left[- \sum_{ik=1}^{3+d} h_i^\nu (R^\nu B^{\mu\nu} \tilde{R}^\nu)_{ik} h_k^\nu + 2\pi i \sum_{i=1}^{3+d} h_i^\nu (R^\nu \mathbf{x}^{\mu\nu})_i + h_i^\nu \tau_i^\nu \right], \quad (21)$$

where $\bar{x}_4^{\mu\nu} = \sum_{i=1}^3 \sigma_{i1}^\nu \bar{x}_i^{\mu\nu} + j/L^\nu$ and $\{R^\nu | \tau^\nu\}$ runs through all the symmetry operators with

$$\sum_{i=1}^3 \sigma_{i1}^\nu \tau_i = \tau_4 \pmod{1/L^\nu}, \quad (22)$$

which correspond to symmetry operators in the space groups (Yamamoto & Nakazawa, 1982).

There is another approximation, which lies between the two methods mentioned above. In this approximation, (21) is used and $\{R^\nu | \tau^\nu\}$ runs symmetry and pseudosymmetry operators. The latter are defined as follows. Some symmetry operators in the superspace group transform a point (an atom position) on the modulation wave into a point where there is no atom (an unoccupied position). Therefore, they are not symmetry operators in the present case. We consider a pseudosymmetry operator, which transforms an atom into an atom position nearest to the unoccupied position on the same modulation wave. Then, $\bar{x}_{4j}^{\mu\nu}$ in (16) and (21) is replaced by $\bar{x}_{4j}^{\mu\nu} + \Delta\bar{x}_{4j}^{\mu\nu}$, where $\Delta\bar{x}_{4j}^{\mu\nu} = (R^\nu)_{44}^{-1} \times (\sum_{i=1}^3 \sigma_{i1}^\nu \tau_i^\nu - \tau_4^\nu) \pmod{1/L^\nu}$. From (22), $\Delta\bar{x}_{4j}^{\mu\nu}$ is zero in symmetry operators of the space group but non-zero in pseudosymmetry operators.

Such an approximation was used in the analysis of $[\text{Ba}]_9[\text{Fe}_2\text{S}_4]_8$ and $[\text{Ba}]_{10}[\text{Fe}_2\text{S}_4]_9$ on the basis of the superspace group L_{155}^{I4mm} , L_{155}^{I4bm} . The superspace group has a centering translation $\{E | \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$. For $[\text{Ba}]_9[\text{Fe}_2\text{S}_4]_8$, $\mathbf{k}^1 = 8\mathbf{c}^{*1}/9$ and $\mathbf{k}^2 = 9\mathbf{c}^{*2}/8$, while in $[\text{Ba}]_{10}[\text{Fe}_2\text{S}_4]_9$, $\mathbf{k}^1 = 9\mathbf{c}^{*1}/10$ and $\mathbf{k}^2 = 10\mathbf{c}^{*2}/9$. For these wave vectors, the centering translation is a pseudosymmetry operator. This shows that the space group has no centering translation. A similar consideration leads to the space group $P4nc$ for the former and $P4cc$ for the latter. The corresponding centrosymmetric space groups are $P4/mnc$ and $P4/mcc$. If we consider the centrosymmetric superspace groups, $L_{155}^{I4/mmm}$, $L_{155}^{I4/mbm}$, these space groups are

derived as the highest symmetry groups from the same condition. In this case, the superspace group includes $(\frac{1}{2})$, $(\frac{m}{n})$, $(\frac{2}{n})$, $(\frac{2}{n})$. Their τ_4 depends on the selection of the origin in the internal space. From (22), they become symmetry operators or pseudo-symmetry operators depending on the selection of the origin. The shift in the origin along the internal space is equivalent to the shift of the absolute phase of all modulation waves. Consequently, the space group is dependent on the absolute phase of the modulation waves. A different consideration was proposed by Hoggins & Steinfink (1977), in which the possible space groups are derived as the intersections of the space groups of the barium and Fe_2S_4 substructures, $I4/mmm$ and $I4/mcm$. The above results agree with those of Hoggins & Steinfink.

Another example is $[\text{Rh}]_{17}[\text{Ge}]_{22}$. This is one of the chimney-ladder structures with a long period along the c axis widely found in electron compounds (Jeitschko & Parthé, 1967). The a^* and b^* axes are common to two substructures while $22c^{*1} = 17c^{*2}$. Therefore, the wave vector for each substructure is commensurate. However, the commensurability is neglected when superspace groups are considered. The space group of the first substructure, rhodium, is $I4_1/amd$. The space group of the second one is not clear but we may take $P4/nmc$. The unit vectors \mathbf{a}^{*2} and \mathbf{b}^{*2} for the second (average) substructure are related to those of the first one by $\mathbf{a}^{*2} = \mathbf{a}^{*1} + \mathbf{b}^{*1}$, $\mathbf{b}^{*2} = -\mathbf{a}^{*1} + \mathbf{b}^{*1}$, but \mathbf{c}^{*2} is incommensurable with \mathbf{c}^{*1} . (See Fig. 5.) This implies $\mathbf{k}^1 = (0, 0, \gamma_1)^1$ and $\mathbf{k}^2 = (\frac{1}{2}, \frac{1}{2}, \gamma_2)^2$. Their independent vectors are \mathbf{a}^{*1} , \mathbf{b}^{*1} , \mathbf{c}^{*1} and \mathbf{c}^{*2} . The space groups imply $h + k + l = 2n$ for $hk0$, $l = 4n$ for $00l$, $h = 2n$ for $hk00$, $2h + l = 4n$ for $hh0$, $h + k = 2n$ for $hk0m$, $m = 2n$ for $0klm$ and $h + m = 2n$ for $hh0m$. These suggest $h + k + l = 2n$ for $hk0$, $l = 4n$ for $00lm$, $h = 2n$ for $hk00$, $m = 2n$ for $0klm$ and $2h + l + 2m = 4n$ for $hh0m$. A possible superspace group is $P_{15}^{I4_1/amd} : W_{15}^{P4/nmc}$. This includes $P_{15}^{I4_1/amd} : W_{15}^{P4/nmc}$ and $P_{15}^{I4_1/amd} : W_{15}^{P4/nmc}$ as subgroups.

Many electron compounds take one of the space groups $I4_1/amd$, $P4c2$ and $P4n2$, depending on the period along the c axis (Jeitschko & Parthé, 1967; Knott, Mueller & Heaton, 1967). They are explained by the relation of the superspace group and the space group in the commensurate cases discussed above. When $\gamma_1 = m/n$ (m and n being integers), they are determined by the parities of m and n . There are three cases with: m even, n odd; m odd, n even; and m odd, n odd, corresponding to the three space groups (Table 2).

As is clear from the above discussion, the analysis based on the pseudosymmetry or in the incommensurate approximation has fewer parameters than that based on the superstructure. Even when the structure can be analyzed on the basis of the true space-group

Table 2. Space groups of commensurate chimney-ladder structures deduced from the superspace group

$$P_{15}^{I4_1/amd} : W_{15}^{P4/nmc}$$

The space groups are classified into three cases according to the parities of m and n (m even, n odd; m odd, n even; m odd, n odd) in the wave vector $\mathbf{k}^1 = (0, 0, m/n)$.

| Compound | Space group | Wave vector |
|------------------------------------|-------------|-------------|
| $[\text{Mo}]_9[\text{Ge}]_{16}$ | $I4_1/amd$ | (0,0,16/9) |
| $[\text{Mn}]_{15}[\text{Si}]_{26}$ | $I4_1/amd$ | (0,0,26/15) |
| $[\text{Rh}]_{17}[\text{Ge}]_{22}$ | $I4_1/amd$ | (0,0,22/17) |
| $[\text{Tc}]_4[\text{Si}]_7$ | $P4c2$ | (0,0,7/4) |
| $[\text{Rh}]_{10}[\text{Ga}]_{17}$ | $P4c2$ | (0,0,17/10) |
| $[\text{Ru}]_3[\text{Sn}]_5$ | $P4c2$ | (0,0,3/2) |
| $[\text{Ir}]_4[\text{Ge}]_5$ | $P4c2$ | (0,0,5/4) |
| $[\text{V}]_{17}[\text{Ge}]_{31}$ | $P4n2$ | (0,0,31/17) |
| $[\text{Mo}]_{13}[\text{Ge}]_{23}$ | $P4n2$ | (0,0,23/13) |
| $[\text{Cr}]_1[\text{Ge}]_{19}$ | $P4n2$ | (0,0,19/11) |
| $[\text{Mn}]_{11}[\text{Si}]_{19}$ | $P4n2$ | (0,0,19/11) |
| $[\text{Ir}]_3[\text{Ga}]_5$ | $P4n2$ | (0,0,5/3) |

symmetry, these approximations are efficient at least as the first approximation. It is clear that the space-group symmetry depends on the wave vector while, in these approximations, the structure can be analyzed with the same symmetry. It should, however, be noted that they are a good approximation only when the higher-order harmonics are weak enough, as in the case of $[\text{Mn}]_{15}[\text{Si}]_{26}$, shown in Fig. 5.

6. Superspace groups of composite crystals

The determination process of the superspace group is similar to that of the modulated structure. The rotational symmetry of the diffraction pattern determines the point group and the nonprimitive translations are obtained from the systematic extinction rules. The first step is the analysis of the average substructure based on main reflections of that substructure. As stated above, this is affected by the modulation of the other substructure. However, our experience shows that a rough average substructure can be determined from main reflections. The position of the substructure relative to the other substructure is determined by the main reflections common to both substructures. From such an analysis, the space groups of the average substructures are given.

In the next step, we consider the superspace group of each substructure. This can be found in the same manner as in the modulated structure. Many composite crystals show no satellite reflections, but the main reflection of the other substructure has to obey the symmetry requirement of the superspace group of the substructure considered. Regarding the main reflections of the other substructure as the satellite (or main for common main) reflections, we can obtain possible superspace groups from the extinc-

tion rules. Thus, the symmetry elements of the superspace group for each substructure are obtained. Then, from the inverse relations of (19) and (20), the matrix representation of the symmetry operator with respect to the common coordinate system is obtained. If different sets of symmetry operators are obtained from different substructures, we have to take common elements constructing a superspace group. Three examples having orthorhombic, trigonal and monoclinic superspace groups are shown below.

(a) $[\text{LaS}]_x[\text{NbS}_2]$. There are many misfit layer sulfides with two substructures (Wiegers, Meetsma, Haange, van Smaalen, de Boer, Meerschaut, Rabu & Rouxel, 1990). This is one of them. It was analyzed first by the classical method (Meerschaut, Rabu & Rouxel, 1989; Meerschaut, Rabu, Rouxel, Monceau & Smontara, 1990) and reinvestigated on the basis of the superspace group (van Smaalen, 1991a). Two substructures have common \mathbf{b}^* ($=\mathbf{b}^{*1}=\mathbf{b}^{*2}$) and \mathbf{c}^* ($=\mathbf{c}^{*1}/2=\mathbf{c}^{*2}$) while \mathbf{a}^{*1} and \mathbf{a}^{*2} are incommensurate with each other. The first substructure (LaS) has the space group $Cm2a$, while the second has $Fm2m$. Satellite reflections are observed. Diffraction patterns are indexable with \mathbf{a}^{*1} , \mathbf{b}^{*1} , \mathbf{c}^{*1} and $\mathbf{k}^1=\mathbf{a}^{*2}+\mathbf{b}^{*1}+\mathbf{c}^{*1}/2=(\alpha_1, 1, \frac{1}{2})^1$ or with \mathbf{a}^{*2} , \mathbf{b}^{*2} , \mathbf{c}^{*2} and $\mathbf{k}^2=\mathbf{a}^{*1}+\mathbf{b}^{*2}=(\alpha_2, 1, 0)^2$. This implies the superspace group $I_{\frac{1}{2}}^{Cm2a}: M_{\frac{1}{2}}^{Fm2m}$, where '?' is unknown at present. [For the prefix I , see Yamamoto (1992).] When the diffraction vector is written as $\mathbf{h}=\mathbf{h}\mathbf{a}^{*1}+\mathbf{k}\mathbf{b}^{*1}+\mathbf{l}\mathbf{c}^{*2}+\mathbf{m}\mathbf{a}^{*2}$, reflection conditions of the space group become $h+k+l=2n$, $h+k+m=2n$, $l+m=2n$ for $hkl0$ and $0klm$ and $h=2n$ for $hk00$. The former three can be regarded as the reflection conditions for general reflections $hklm$ and the last as that for $hk0m$. The latter implies the existence of (?) in the first substructure, leading to the superspace group $I_{\frac{1}{2}}^{Cm2a}$. The symmetry elements of the superspace group of the second (average) substructure are related to those of the first substructure by the permutation (1,4) so that the superspace group is given by $I_{\frac{1}{2}}^{Cm2a}: M_{\frac{1}{2}}^{Fm2m}$.

Another method of finding possible superspace groups is to use the common unit vectors. Then, the first substructure gives reflection conditions $h+k=2n$ and $l=2n$ for $hkl0$, $h=2n$ for $hk00$, and the second leads to $m+k=2n$, $k+l=2n$ and $m+l=2n$ for $0klm$. These are combined into $h+k+m=2n$, $l+m=2n$ and $h+k+l=2n$ for $hklm$ and $h=2n$ for $hk0m$. The reflection conditions and the irrational parts of the wave vectors $(\alpha_1, 0, 0)^1$ and $(\alpha_2, 0, 0)^2$ also give the same superspace group (Yamamoto, 1992).

(b) $[\text{Ba}]_x[(\text{Pt}, \text{Cu})\text{O}_3]$. This is an example of composite crystals obtained as byproducts of superconducting oxides. Both substructures are indexable with the same \mathbf{a}^* in the hexagonal lattice and \mathbf{c}^{*1} and

\mathbf{c}^{*2} are incommensurate to each other. However, the second substructure has a rhombohedral lattice spanned by a unit vector $(\mathbf{a}^*+\mathbf{b}^*+\mathbf{c}^{*2})/3$ and two vectors obtained from it by the threefold rotations around the c^* axis. The first substructure has the space group $P31c$ and the second $R3m$. The wave vector of the first substructure is therefore $\mathbf{k}^1=(\frac{1}{3}, \frac{1}{3}, \gamma_1)^1$ and that of the second is $\mathbf{k}^2=(0, 0, \gamma_2)^2$. The reflection conditions are $h-k-l=3n$ for $hklm$ and $l=2n$ for $hhl m$, leading to $R_{11}^{P31c}: P_{15}^{R3m}$ (Ukei, Yamamoto, Watanabe, Shishido & Fukuda, 1992).

(c) $[\text{Bi}_2\text{Sr}_2\text{CuO}_4][\text{O}]_y$. This is not a typical composite crystal. It was first considered to be a modulated structure. The modulated structure model, however, necessitates an artificial description, as employed by Yamamoto, Onoda, Takayama-Muromachi, Izumi, Ishigaki & Asano (1990) or Petříček, Gao, Lee & Coppens (1990). Recently, it was shown that this is well described as a composite structure rather than a modulated structure, though the displacement of atoms in the second substructure is extremely large (Walker & Que, 1992; Yamamoto *et al.*, 1993). In this case, the second substructure consists of the O atoms in the Bi-O layer. The remaining atoms construct the first substructure. The modulation wave vector of the first substructure is $\mathbf{k}^1=(0, \beta, 1-\gamma)$ with $\beta=0.2$, $\gamma=0.0-0.6$. Therefore, this has a monoclinic superspace group, though the unit cell of the first substructure seems to be orthorhombic. It was analyzed on the basis of the superspace group with a nonstandard setting for the comparison with $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{8+x}$. The sublattice of the first substructure is B centered while that of the second is I centered. Its superspace group is $N_{\frac{1}{2}}^{B2/b}: P_{\frac{1}{2}}^{I2/m}$, which is equivalent to $P_{\frac{1}{2}}^{B2/b}: P_{\frac{1}{2}}^{I2/m}$ in the standard setting.

Similar considerations were made for known composite crystals. Possible superspace groups are listed in Table 1. In the table, valleriite, $[\text{M}(\text{OH})_2]_x[\text{TS}_2]$, $M=(\text{Mg}, \text{Al})$, $T=(\text{Fe}, \text{Cu})$, has a five-dimensional superspace group $T_{p6m1}^{P3m1}: P_{p6m}^{R3m}$, where the prefix T means $(0, 0, \frac{1}{3})$ (Janner, Janssen & de Wolff, 1983). It has a common \mathbf{c}^* but \mathbf{a}^{*1} and \mathbf{a}^{*2} are incommensurable (Evans & Allmann, 1968). The wave vectors of the first substructure are $\mathbf{k}_1^1=(\alpha_1, 0, \frac{1}{3})^1$, $\mathbf{k}_2^1=(-\alpha_1, \alpha_1, \frac{1}{3})^1$. In $[\text{BiS}]_x[\text{TaS}_2]$ and $[\text{BiSe}]_x[\text{TaSe}_2]$, the first substructure has two modulation waves along the \mathbf{a}^* axis, of which one is incommensurate and the other commensurate (Gotoh, Onoda, Akimoto, Goto & Oosawa, 1992; Zhou, Meetsma, de Boer & Wiegers, 1992). The former agrees with \mathbf{a}^{*2} but the latter is independent of it. The commensurate wave vectors are $\mathbf{k}_2=2\mathbf{a}^{*1}/5$ in $[\text{BiS}]_x[\text{TaS}_2]$ and $\mathbf{k}_2=\mathbf{a}^{*1}/6$ in $[\text{BiSe}]_x[\text{TaSe}_2]$. Their four-dimensional superspace groups are $P_{\frac{1}{2}}^{Am2m}: P_{\frac{1}{2}}^{Am2m}$ and $M_{\frac{1}{2}}^{Fm2m}: M_{\frac{1}{2}}^{Fm2m}$. In $[\text{BiS}]_x[\text{TaS}_2]$ (Wulff, Meetsma, Haange, de Boer & Wiegers, 1990); a completely incommensurate structure with complicated modulations is also found.

Examples of composite crystals with three substructures are found in a series of chromium sulfides and selenides with $[M_3CrX_3]_x[M_3X]_y[Cr_7X_{12}]$ ($M = \text{Ba, Sr, Eu, Pb}$ and $X = \text{S, Se}$) (Brouwer & Jellinek, 1977). One of them ($M = \text{Ba, } X = \text{Se}$) is commensurate, the others are incommensurate. Their symmetry may be given by a unified five-dimensional superspace group $P_{p62}^{P6/m} : P_{p62}^{P6/m} : P_{p62}^{P6/m}$ or its subgroups.

An exceptional composite crystal, $[\text{Hg}]_x[\text{Hg}]_x[\text{AsF}_6]_x$, consists of three substructures, the first two of which are related by a symmetry operator. Its superspace group is five-dimensional, but one modulation wave may be independent of the incommensurability among substructures (Janner & Janssen, 1980). Two mercury substructures have monoclinic space groups $A2/m$ and $B2/m$, while AsF_6 has the tetragonal one $I4_1/amd$ (Pouget, Shirane, Hastings, Heeger, Miro & MacDiarmid, 1978). A d -glide plane in the space group of the third substructure transforms the first substructure into the second and when the additional modulation is neglected the total symmetry is equivalent to P_{11s}^{Fddd} (Janner & Janssen, 1980). The superspace group for such a case may be given by the superspace-group symbol of the third substructure (Janner & Janssen, 1980; van Smaalen, 1991*b*) but this symbol does not imply the specific features of composite crystals, in contrast to the symbol mentioned above.

In Table 1, 12 compounds (marked with †) were analyzed by single-crystal X-ray diffraction on the basis of superspace groups. Two cases $\{[\text{Bi}_2\text{Sr}_2\text{CuO}_4][\text{O}]_x$ and $[\text{Sr}]_x[\text{TiS}_3]\}$ (also marked with †) were determined by neutron and/or powder X-ray diffraction experiments. For the other cases, the superspace groups are derived from the space groups of their substructures. As mentioned previously, the analysis of average substructures can be accurately determined only by taking into account modulation waves. Therefore, these superspace groups suggest only one possibility for each case and the true symmetry may be its subgroup (or supergroup).

7. Refinement method

Since the analysis of composite crystal structures is reduced to that of modulated substructures based on their superspace groups, our experience for the structure refinement of modulated structures is applicable to it. So far, many modulated structures have been determined by the refinement technique. This was, in particular, successful for one-dimensionally modulated structures. For two- or higher-dimensional modulations, careful consideration is necessary in the selection of initial amplitudes (Hagiya, Ohmasa & Iishi, 1992). This will also be true in composite crystals. In any case, the dis-

placement from the fundamental structure is expanded in terms of a Fourier series and a Fourier amplitude of each harmonic is taken as a refinable parameter. In some cases, the modulation of the temperature factor or occupation probability will be needed. In the single-crystal method, we refine the average structure first by using main reflections and the superspace group, where only the zeroth-order harmonic (constant term) is used in the Fourier series. The refinement can be made by the conventional program in two steps. The first step determines each substructure individually by using main reflections excluding those common to the other substructures. Next, the relative positions of the substructures are obtained from the common reflections. However, the program based on the superspace description of the composite crystals enables us to refine all the average substructures at the same time.

As mentioned before, even if no satellite reflections are observed, the introduction of the modulation improves the R factor. One of the problems in this case is that we cannot know how many harmonics should be used in the modulation wave. Some substructures may be hard, others soft. More Fourier terms will be necessary for the latter than for the former. In any case, Fourier amplitudes to be included are selected by trial and error. On the other hand, if satellite reflections are observed, the corresponding Fourier terms are first taken into account and additional ones are added later by trial and error. (Note that the n th-order harmonic of a substructure mainly contributes to the n th-order satellite reflections of that substructure.) For commensurate cases, there exists an upper limit to the number of harmonics in the modulation wave, as mentioned in § 5.

It has been shown that, in complicated modulated structures, it is efficient to impose the soft constraint on the interatomic distance to obtain smooth convergence of the least-squares method (Yamamoto, Nakazawa, Kitamura & Morimoto, 1984). It is also effective for composite crystals, in particular in Rietveld analyses, to complement lack of information from powder diffraction data. The penalty function for the interatomic distances within a substructure can be defined in the same manner as in the modulated structure. For that between atoms belonging to different substructures, only the lower limit can be introduced because they range to infinity (Onoda, Kato, Gotoh & Oosawa, 1990; van Smaalen, 1991*a*). To calculate such interatomic distances, the coordinates for each substructure need to be transformed to a common coordinate system. From the inverse relation of (14), we obtain the coordinates referred to the common unit vectors (which are usually the unit vectors of the first substructure). From (5) and (6), the external space com-

ponents are x_1 , x_2 and x_3 , while the internal space components t_j ($j = 1, 2, \dots, d$) are $-\sum_{i=1}^3 \sigma_{ji} x_i + x_{3+j}$. This defines a $(3+d) \times (3+d)$ matrix M , which projects a $(3+d)$ -dimensional vector into the external and internal spaces. The projection matrix is given by (Kato, 1990)

$$\begin{aligned} (M)_{ik} &= \delta_{ik} \quad (i \leq 3; k = 1, 2, \dots, 3+d), \\ (M)_{3+j,k} &= -\sigma_{jk} \quad (j = 1, 2, \dots, d; k \leq 3), \\ (M)_{3+j,k} &= \delta_{3+j,k} \quad (j = 1, 2, \dots, d; k \geq 4). \end{aligned} \quad (23)$$

The interatomic distance has to be calculated from the atom positions with the same t_j ($j = 1, 2, \dots, d$) (see Fig. 3). The distance is obtained from the coordinates x_i ($i = 1, 2, 3$) of the ν th substructure at $\bar{x}_{3+j}^\nu = \sum_{k=1}^3 \sigma_{jk}^\nu \bar{x}_k^\nu + \sum_{k=1}^d (V_d^\nu - \sigma^\nu Z_d^\nu)_{jk} t_k$ as a function of t_j (van Smaalen, 1991a, 1992).

In molecular crystals, the rigid-molecule approximation may be applicable. Then, each atom position of a molecule is calculated from the position of the center of mass and the orientation of the molecule. An infinitesimal rotation is represented by a vector $d\Omega$, which is parallel to the rotation axis and has a length $d\varphi$ (φ being the rotation angle). The displacement of an atom at \mathbf{r} from the center of mass is given by $-\mathbf{r} \times d\Omega$. This is incorrect for a finite rotation but is still a good approximation for a small-angle rotation. The vector $d\Omega$ has transformation properties of the axial vector. On the other hand, the displacement of the center of mass is the (usual) polar vector (Petříček, Coppens & Becker, 1985; Petříček & Coppens, 1988). When the molecule belongs to the ν th substructure, these two vectors are periodic functions of \bar{x}_{3+j}^ν ($j = 1, 2, \dots, d$), the $(3+j)$ th coordinates of the center of mass. This approximation reduces the number of parameters drastically. Therefore, it will be efficient at least as the zeroth approximation for molecular composite crystals.

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Approximate Model for the Crystal Structure of Precipitates in NaF Doped with AlF_3

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Abstract

The crystal structure of precipitates in a mixed crystal of NaF and 1 mol% AlF_3 has been studied at room temperature using both stationary-crystal and rotating-crystal X-ray photographic methods. It has been found that almost all the reflections can be assigned to a face-centered-cubic (f.c.c.) lattice with unit-cell parameter 7.77 Å. The main feature of the diffraction pattern is that the 311 reflection is very strong while the 222 reflection is practically zero, in contrast to the case of high-form cryolite, *i.e.* cubic Na_3AlF_6 . These features are explained by assuming an f.c.c. arrangement of AlF_6 octahedra that are rotated around the (111) axes by about 47° from the highest-symmetry orientation. It has also been shown that the F ions in each octahedron make large overlaps with the Al ion at the center of the octahedron. A random distribution of rotation axes is

also proposed to conform to the cubic symmetry of the lattice structure of the precipitate.

1. Introduction

In several previous papers concerning mixed crystals of alkali halides doped with divalent cations, we have reported segregation of some kinds of metastable centers (Miyake & Suzuki, 1954*a,b*; Suzuki, 1955, 1958, 1961). As an extension of these investigations, it seems interesting to try to use trivalent cations for impurity doping. When a trivalent cation replaces a monovalent cation constituting a matrix lattice, it is accompanied by two cation vacancies and several types of dipole interactions may be expected.

A study of NaF doped with AlF_3 was tried because: (i) according to the phase diagram shown in Fig. 1 (Fedotieff & Iljinskii, 1913),† this system is

† We have referred to this phase diagram, which is published in *Phase Diagrams for Ceramists*, 4th printing, 1979, The American Ceramic Society, Ohio, USA.

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