Acta Cryst. (1983). A**39**, 671–678

Determination of the Bravais Class for a Number of Incommensurate Crystals

BY A. JANNER AND T. JANSSEN

Institute for Theoretical Physics, University of Nijmegen, Toernooiveld 1, 6525 *ED Nijmegen, The Netherlands*

AND P. M. DE WOLFF

Vakgroep Fysische Kristallografie, Technische Hogeschool, Lorentzweg 1, 2628 *CJ Delft, The Netherlands*

(*Received* 17 *November* 1982; *accepted* 23 *March* 1983)

Abstract

For a number of incommensurate crystal phases with a one-dimensional modulation and for all those with a higher-dimensional modulation which are known to the authors, the Bravais class is determined. This is done partly to illustrate the use of the complete list of Bravais classes published in a previous paper [Janner, Janssen & de Wolff (1983). *Acta Cryst.* A**39**, 658–666] partly to give an overview of the crystals having higher-dimensional modulation.

I. Introduction

In a preceding paper (Janner, Janssen & de Wolff, 1983*a*), here denoted by I, tables have been given with a complete classification of Bravais classes having less than four internal dimensions and in another (Janner, Janssen & de Wolff, 1983*b*), here denoted by II, tables of all so-called elementary Bravais classes. In those papers the principle of the derivation and the meaning of the notation adopted have been given using an algebraic and group-theoretical language. Conciseness and precision while introducing new concepts and new notations made that choice natural.

Those tables, however, are primarily intended for crystallographers as help for the structural interpretation of the diffraction pattern of incommensurate crystals. In general, for many crystallographers a geometrical and pragmatical approach may be better suited. The present article is meant to satisfy that need. Accordingly a geometrical presentation will be adopted, supplemented with examples of applications based on diffraction and structural data already published.

More detailed justification of the consistency of the superspace approach adopted can be found in I and in the other papers quoted there.

II. Point symmetry of the diffraction pattern

An incommensurate crystal phase is characterized by the fact that the reflections in the diffraction pattern cannot be labeled by three integers, but require a larger number of indices. There seems to be no unique prescription how to proceed in these cases, but on the other hand there is rarely a fundamental difficulty in finding an indexing system.

Often the incommensurate phase originates from a structure with space-group symmetry. In those cases the reflections which stem directly from reflections in the normal phase play a special role. In other cases the modulation giving rise to the incommensurability can be considered as a weak perturbation and a normal lattice of reflections stands out among weaker ones. In all these cases there is a normal set of preferred reflections which are called the main reflections.

A help to find the lattice of main reflections is the symmetry of the diffraction pattern. If the wave vectors corresponding to diffraction peaks are denoted by $\mathbf{k}$ and the intensity of the spot at $\mathbf{k}$ by $I(\mathbf{k})$, we call a point-group transformation R a symmetry transformation for the diffraction pattern if

$$I(R\mathbf{k}) = I(\mathbf{k}) \tag{1}$$

for any $\mathbf{k}$. These transformations form a group P, which is one of the Laue groups. The main reflections should be selected in such a way that they form a three-dimensional lattice Λ^* that is invariant under this point group. In the following we assume that such a choice has been made.

III. Satellite reflections

All reflections not belonging to Λ^* are satellite reflections. For their labeling the three indices of Λ^* do not suffice. Consider a satellite with wave vector $\mathbf{q}$. With respect to a conventional basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ of Λ^*, $\mathbf{q}$ can be written as

$$\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*, \tag{2}$$

where α, β, γ are not all integers or simple fractions. (If this is the case, the choice of Λ^* has been made inappropriately, because $\mathbf{q}$ would correspond to a vector of the reciprocal lattice of a superstructure.) The set of reflections which are linear combinations of $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{q}$ is then labeled by

0108-7673/83/050671-08$01.50

$$(h + m\alpha, k + m\beta, l + m\gamma) \quad (3)$$

or equivalently by

$$(h,k,l,m) \quad (4)$$

with h,k,l,m integers. If (4) does not exhaust all satellites, a second wave vector $\mathbf{q}_2$ can be found to describe (all or part of) the remaining ones by adding a term $m_2\mathbf{q}_2$ and so on until all observed satellites have been described. The general expression, therefore, is

$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1 + \ldots + m_d\mathbf{q}_d, \quad (5)$$

where h,k,l are integers and $m_1, \ldots, m_d$ are small integers. We call d the internal dimension. The set of all vectors of the form (5) is called M^*. The (basic) satellite wave vectors $\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_d$ are chosen in the Brillouin zone (BZ) of A^* in such a way that d is minimal. From the construction it follows that the diffraction vectors $\mathbf{k}$ corresponding to reflections belong to M^*.

Since we have chosen A^* in such a way that the point-symmetry group of the diffraction pattern leaves A^* invariant, this is a subgroup of the (holohedral) point group of the lattice of main reflections.

The group of symmetry transformations which determines the Bravais class of the incommensurate structure is the group K of all elements which leave M^* invariant, *i.e.* those elements R which transform each wave vector $\mathbf{k}$ of the set M^* into itself or into another one. These point transformations form a subgroup of the (holohedral) point group of A^*. If $\mathbf{k}$ belongs to the diffraction pattern and R to K, then $\mathbf{k}$ is an element of M^* and so also $R\mathbf{k}$. However, in general, $I(R\mathbf{k}) \neq I(\mathbf{k})$. Hence, the symmetry of the diffraction pattern is lower than or equal to that of M^*.

Consider as an example a hexagonal diffraction pattern (Fig. 1) with wave vectors

$$\mathbf{k} = h\mathbf{a}^* + h\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1 + m_2\mathbf{q}_2 + m_3\mathbf{q}_3, \quad (6)$$

where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ form a hexagonal lattice: $a^* = b^*$, $\angle(\mathbf{a}^*,\mathbf{b}^*) = 60°$, $\angle(\mathbf{a}^*,\mathbf{c}^*) = 90°$, $\angle(\mathbf{b}^*,\mathbf{c}^*) = 90°$ and where

$$\mathbf{q}_1 = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*, \quad (7)$$

$$\mathbf{q}_2 = \alpha(-\mathbf{a}^* + \mathbf{b}^*) + \gamma\mathbf{c}^*,$$

$$\mathbf{q}_3 = -\alpha\mathbf{b}^* + \gamma\mathbf{c}^*.$$

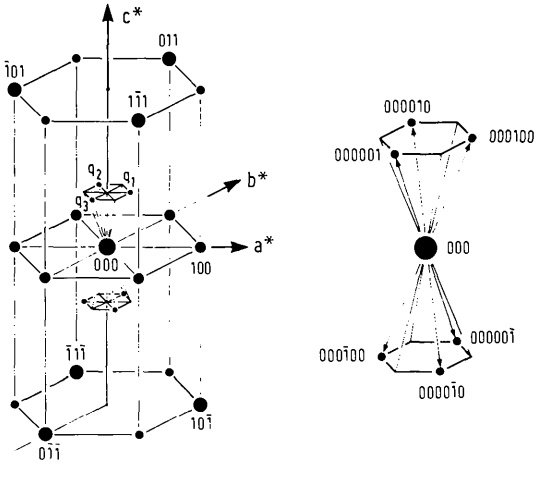
We assume that the diffraction pattern has point-symmetry group $\bar{3}$. The main reflections $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ form a primitive hexagonal lattice. The transform of $\mathbf{q}_1$ under the sixfold rotation is $\alpha\mathbf{b}^* + \gamma\mathbf{c}^*$, which is not a linear combination of the form (6). Hence the point group of M^* is lower than that of A^*: it is $\bar{3}m1$. However, the intensities of two reflections related by a mirror through the c axis are in general not the same. Hence P is a subgroup of K, which in turn is a subgroup of the (holohedral) point group K_A.

The basic satellites (7) of the example have the property that $\mathbf{q}_2$ and $\mathbf{q}_3$ are obtained from $\mathbf{q}_1$ through the action of elements of $K = \bar{3}m1$. Therefore, in order to reconstruct the set M^* it is sufficient to know K and the components of $\mathbf{q}_1$. The action of K on $\mathbf{q}_1$ gives six vectors, among which three are rationally independent, and which can be chosen as in (7). The six vectors $\{R\mathbf{q}_1\}$, for R in $\bar{3}m$, form a star.

As stated before, for the Bravais-class determination only the symmetry group K of M^* is relevant. This is just as in the case of ordinary crystals, where the vectors $\mathbf{k}$ of the diffraction pattern, *i.e.* the reciprocal lattice, determine the translation group and its Bravais class. So, in the above example, the mirror planes of M^* are elements of K, though they have to be disregarded in a space-group determination since they do not occur in the Laue group P.

So the Bravais class of an incommensurate crystal is determined by the set M^*, just as it is determined for an ordinary crystal by the Bravais lattice. (Usually the definition is stated in terms of the direct lattice, but it can equally well be expressed for the reciprocal lattice.) The actual definition in either case consists of criteria of equivalence, that is, conditions which two sets M^* – or two lattices, for ordinary crystals – should fulfill in order to be assigned to the same Bravais class.

Essentially the criteria for equivalence of two sets require that they have the same K and d and also the same Bravais class for the lattice of main reflections. Moreover, the latter must have the same orientation with respect to the elements of K. Finally, it must be



$P = P\bar{3}$; $K_A = P6/mmm$ (*a*)

$K = P\bar{3}m1(\alpha,0,\gamma)$ (*b*)

Fig. 1. (*a*) Part of the diffraction pattern for a hexagonal structure with three-dimensional modulation. The diameter of the circles represents the intensity. (*b*) The cluster of satellites around the main reflection 000.

possible to choose the vectors $\mathbf{q}_l$ such that they are expressed by the same general triplets of components. A more precise algebraic definition is given in I.

The symbol for a Bravais class consists of two parts. The first part is formed by a capital letter (*P*, *C*, *I*, *etc.*) indicating the centering type of Λ, followed by the Hermann–Mauguin symbol of K. As in every space-group symbol, the designation of K must be adapted to the lattice Λ (differentiation between $\bar{3}m1$ and $\bar{3}1m$). Moreover, the capitals *A*, *B*, *C* in the orthorhombic system need not be equivalent here, because the satellites usually create essential differences between the axes. The second part of the Bravais-class symbol is constructed by writing the set of coordinates $(\alpha_1,\beta_1,\gamma_1)$ $(\alpha_2,\beta_2,\gamma_2)$ ..., where only one triplet is written for each vector $\mathbf{Q}_l$, where $\mathbf{Q}_1$, $\mathbf{Q}_2$, ..., $\mathbf{Q}_s$ form a minimal set such that each reflection (5) is a linear combination of vectors of Λ^* and vectors obtained from $\mathbf{Q}_1$, ..., $\mathbf{Q}_s$ by the action of K.

The definition of Bravais class is just a generalization of the usual one for ordinary crystal phases. Each Bravais class of an incommensurate phase belongs to one of the 14 ordinary Bravais classes. We can call all classes belonging to one ordinary Bravais class its family. As an example the two families of the monoclinic Bravais classes are given in Fig. 2. For the primitive monoclinic class $P2/m$ the internal dimensions are $d = 1$ or $d = 2$. For $d = 1$ the basic satellite is either along the unique axis or in the mirror plane. If it is $(\frac{1}{2},0,\gamma)$ it can be seen as a centering of the one with basic satellite $(0,0,\gamma)$. If it is $(\frac{1}{2},\frac{1}{2},\gamma)$ or $(0,\frac{1}{2},\gamma)$ it can by another choice of basis be brought into the form $(\frac{1}{2},0,\gamma)$.

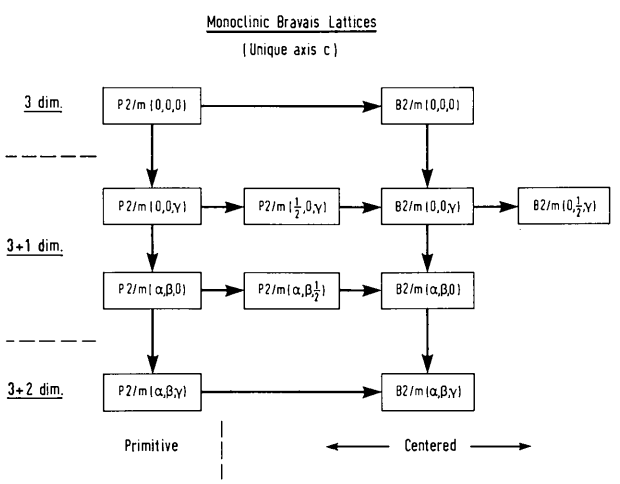


Fig. 2. The two families of monoclinic elementary Bravais classes. The six classes with symbol starting with $P2/m$ belong to the family of primitive monoclinic Bravais class, the five others to that of the centered monoclinic class. The four rows correspond to 0, 1, 2 and 3 parameters in the modulation wave vector. Each Bravais class is a centering of the first one at the left-hand side in the row.

A similar situation occurs for a basic satellite in the mirror plane through $(0,0,\frac{1}{2})$ and for one through (0,0,0). The only Bravais class with $d = 2$ occurs for a basic satellite in a general position in the Brillouin zone (α,β,γ). Also for the centered monoclinic Bravais class there are several (4) Bravais classes of incommensurate crystal phases.

The condition that α_l, β_l, γ_l should not all be integers or simple fractions is, of course, related to the presumed incommensurate character of the crystal. The term 'simple fraction' is used while for a truly incommensurate crystal 'rational' would apply. This slackening of the condition is natural, because in general the symmetry description should not change if, for example, the components of a temperature-dependent satellite were to pass through a (non-simple) rational value. Moreover, recent work by Yamamoto (1982) shows that this point of view is useful in the determination of superstructures provided that satellites of different main reflections do not overlap so that unambiguous indexing is possible.

Let us now discuss a number of two-dimensional examples, illustrated in Fig. 3. In the picture are drawn diffraction patterns of a hypothetical two-dimensional system.

The symmetry group of the pattern (*a*) is supposed to be $2mm$. The lattice Λ^* generated by $\mathbf{a}^*$ and $\mathbf{b}^*$ has this symmetry. An arbitrary vector $\mathbf{k}$ can be written as $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + m\alpha\mathbf{a}^*$. Hence $\mathbf{q} = \alpha\mathbf{a}^*$. The set M^* is left invariant by $2mm$. So in this case $P = K = K_\Lambda$. The internal dimension is $d = 1$. We can denote the Bravais class by $pmm(\alpha,0)$.

The symmetry group of pattern (*b*) is $2mm$ again. The lattice Λ^* generated by $\mathbf{a}^* + \mathbf{b}^*$ and $-\mathbf{a}^* + \mathbf{b}^*$ is centered rectangular. A conventional basis of Λ^* is again formed by $\mathbf{a}^*$ and $\mathbf{b}^*$ whereas $\mathbf{q} = \alpha\mathbf{a}^*$. Hence the Bravais class is $cmm(\alpha,0)$, again with $d = 1$. Note that due to the centering there are systematic extinctions for $h + k$ odd.

The symmetry group of pattern (*c*) is also $2mm$. The lattice Λ^* is generated by $\mathbf{a}^*,\mathbf{b}^*$. Now an arbitrary vector $\mathbf{k}$ of M^* can be written as $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + m_1(\alpha\mathbf{a}^* + \beta\mathbf{b}^*) + m_2(-\alpha\mathbf{a}^* + \beta\mathbf{b}^*)$. Hence $\mathbf{q}_1 = \alpha\mathbf{a}^* + \beta\mathbf{b}^*$, $\mathbf{q}_2 = -\alpha\mathbf{a}^* + \beta\mathbf{b}^*$ and $d = 2$. The symmetry group K of M^* is again $2mm$. Since there is an element of K which transforms $\mathbf{q}_1$ into $\mathbf{q}_2$, the symbol for the Bravais class is $pmm(\alpha,\beta)$.

However, if in this example $\beta = \frac{1}{2}$ one can write $\mathbf{q}_2 = -\mathbf{q}_1 + \mathbf{b}^*$. Hence only $\mathbf{q}_1$ is needed as basic satellite and the internal dimension is $d = 1$ (Fig. 3*d*). Then the Bravais class is $pmm(\alpha,\frac{1}{2})$. In this case the set M^* belongs also to the set M'^* generated by $\mathbf{a}^*, \frac{1}{2}\mathbf{b}^*$ and $\mathbf{q} = \alpha\mathbf{a}^*$. This implies another definition of Λ^*. An element $h'\,\mathbf{a}^* + k'(\frac{1}{2}\mathbf{b}^*) + m'\,\alpha\mathbf{a}^*$ of M'^* is an element of M^* if $k' + m'$ is even. So the set M'^* is of Bravais class $pmm(\alpha,0)$ and M^* is a centering of it (Fig. 3*e*). The labeling with M'^* would imply systematic extinctions.

IV. Bravais-class identification from a given diffraction pattern

Knowing the diffraction pattern, for identifying the corresponding Bravais class one can proceed as follows.

(1) One looks for the (three-dimensional) point symmetry group P of the diffraction pattern.

(2) One identifies the set of main reflections as points belonging to a lattice A^* left invariant by the point group of the diffraction pattern.

(3) One determines the Bravais class to which the corresponding direct lattice A belongs.

(4) One chooses a conventional basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ for A^* according to the conventions adopted in *International Tables for X-ray Crystallography* (IT). The main reflections are then labeled by the indices h,k,l accordingly.

(5) One expresses all reflections observed by their (in general non-integral) indices with respect to the basis chosen. The general form will then be

$$(h + m_1\alpha_1 + \ldots + m_s\alpha_s,\quad k + m_1\beta_1 + \ldots + m_s\beta_s,\quad l + m_1\gamma_1 + \ldots + m_s\gamma_s),$$

with $h,k,l,m_1,\ldots,m_s$ integers and α_i, β_i, γ_i real (possibly temperature-dependent) coefficients.

(6) One chooses a minimal set $\mathbf{q}_1,\ldots,\mathbf{q}_d$ of (basic) satellite reflections in the BZ of A^*, such that any reflection can be expressed as an integral linear combination of $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q}_1,\ldots,\mathbf{q}_d$. The reflections are then labeled by the corresponding set of $3 + d$ integral indices $h,k,l,m_1,\ldots,m_d$. Note that if one (or more) of such $\mathbf{q}_i$ reaches the BZ boundary, one gets a $(3 + d)$-dimensional centered Bravais lattice, even if A is primitive. This gives rise to centering extinctions for the satellite reflections as explained for the $d = 1$ dimensional case in de Wolff, Janssen & Janner (1981; Table 1).

(7) One determines the group K which leaves the set M^* of linear combinations of $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q}_1,\ldots,\mathbf{q}_d$ invariant.

(8) One takes one vector from the set $\mathbf{q}_1,\ldots,\mathbf{q}_d$ and expresses its components $(\alpha_1,\beta_1,\gamma_1)$ with respect to the conventional basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ of A^*. Then one eliminates from $\mathbf{q}_1,\ldots,\mathbf{q}_s$ all vectors that are linear combinations of vectors from A^* and the transforms of the chosen vector under K. If there remains a vector $\mathbf{q}_j$ one repeats this procedure.

(9) For $d \leq 3$ one identifies the Bravais class from Table 1 (*a*), (*b*) and (*c*) of I, which appears in the form $K(\alpha,\beta,\gamma;\ldots)$. For $d > 3$, the elementary ones (one single star) are listed in II. To combine them to non-elementary ones if necessary is very simple, as exemplified in I.

As illustrated further on 'accidental' special values of the parameters α, β, γ (not imposed by symmetry) are possible. Steps 1 to 6 should represent the normal disentanglement of a diffraction pattern. The list of Bravais classes given in I is essentially complete: disagreement can be due to the choice of a different setting.

V. Bravais-class identification for some incommensurate crystals

In the following we study the Bravais class of incommensurate crystal phases as reported in the literature. This is done partly to illustrate the notions introduced above, partly to determine the Bravais class for a number of interesting compounds. We shall follow

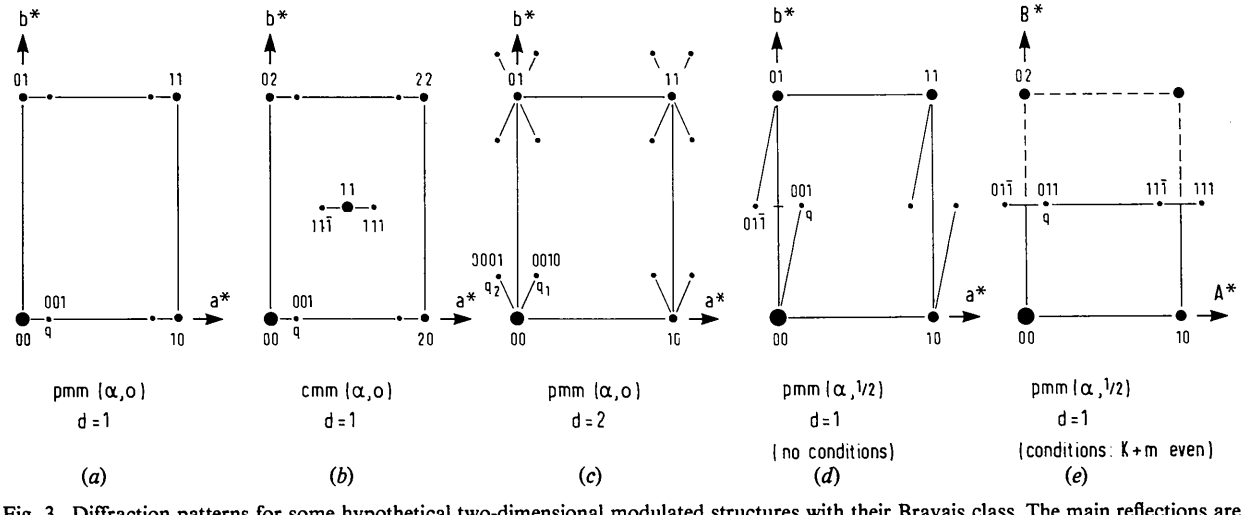


Fig. 3. Diffraction patterns for some hypothetical two-dimensional modulated structures with their Bravais class. The main reflections are labeled by hk, the satellites by hkm_1 or hkm_1m_2. [In case (*c*) *pmm* (α,0) should be *pmm* (α,β).]

the procedure as proposed in § IV. The references from which the data are reported are indicated at the end of the corresponding point. A summary of the results is given in Table 1.

(*a*) *Thiourea* $SC(NH_2)_2$

This material has a high-temperature phase with space group *Pnma* ($T > 218$ K) and a low-temperature superstructure with space group $P2_1\,ma$ ($T < 191$ K). In between there are incommensurate phases. Actually the p–T phase diagram is quite complicated, but we restrict ourselves here to atmospheric pressure. The main reflections are easily found and belong to a primitive orthorhombic lattice A^*. Hence $K_A = mmm$. In the (3) intermediate incommensurate phases all reflections may be labeled as $(h, k + m\beta, l)$. Hence $\mathbf{q} = \beta\mathbf{b}^*$ and the internal dimension is $d = 1$. The point group *mmm* leaves M^* invariant. Hence $K = mmm$. Because $d = 1$ the Bravais class of M^* may be indicated by $Pmmm(0,\beta,0)$. In the setting of the tables of I this is equivalent to $Pmmm(0,0,\gamma) = 1$–9 (Fig. 4) (Yamamoto, 1980; Moudden, Denoyer & Lambert, 1978).

Table 1. *Summary of the Bravais-class determination*

Compound	Temperature	Bravais class One-line symbol	No. (I)
Thiourea	191–218 K	$Pmmm(0,0,\gamma)$	1–9
$BaMnF_4$	<250 K	$Pmmm(\frac{1}{2},0,\gamma)$*	1–10
	<250 K	$Pmmm(\frac{1}{2},\frac{1}{2},\gamma)$†	1–11
$ThBr_4$	95 K	$I4/mmm(0,0,\gamma)$	1–21
Biphenyl	21–39 K	$P2/m(\alpha,\beta,\gamma)$	2–16
	<21 K	$P2/m(0,0,\gamma)$	1–5
TTF–TCNQ	47–54 K	$P2/m(\frac{1}{2},0,\gamma)$	1–6
	38–47 K	$P\bar{1}(\alpha,\beta,\gamma)$	1–1
	<38 K	$P2/m(\alpha,\beta,\gamma)$	2–16
$Hg_{3-x}AsF_6$	<120 K	$Fmmm(\alpha,0,0)$‡	1–17
	<120 K	$Fmmm(\alpha,0,0;\ 0,\beta,0)$§	2–47
$1H$-$TaSe_2$	90–122 K	$P6/mmm(\alpha,0,0)$	2–83
	<90 K	$Ammm(0,\mu,\nu)$	2–54
$Sr_{1-x}Cr_2Se_{4-x}$		$P6/mmm(0,0,\gamma;\ 0,0,\nu)$	2–81
γ-PAMC		$Cmmm(1,0,\gamma;\ 0,0,\nu)$	2–24
$Fe_{1-x}O$		$Fm3m(\alpha,0,0)$	3–211
Cu_9BiS_6		$Fm3m(\alpha,\alpha,\alpha)$	3–217

* X-ray scattering.
† Neutron scattering.
‡ Basis structure.
§ Modulated structure.

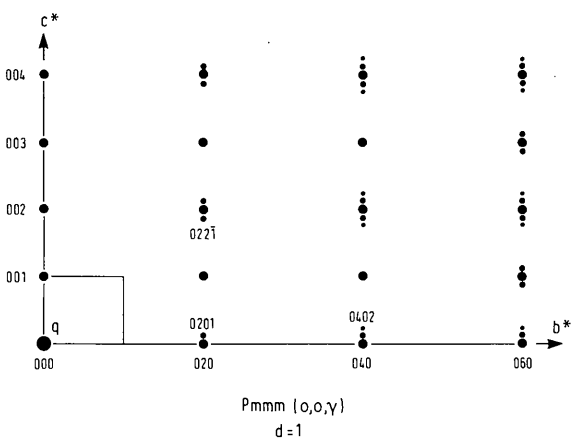


Fig. 4. The $0klm$ reflections of thiourea in the incommensurate phase.

(*b*) $BaMnF_4$

About this material there is some confusion in the literature. The diffraction pattern seems to be sample dependent. Samples with a room-temperature symmetry group $P2_12_12$ do not show a transition towards an incommensurate phase. Samples with space group $A2_1am$ at room temperature show satellites at low temperature, but these are different for X-ray scattering and for neutron scattering due to the magnetic structure. With X-rays one finds a basic satellite $(\alpha,0,\frac{1}{2})$ with $\alpha \simeq 0{\cdot}4$ in the A-centered orthorhombic lattice. (Here one has extinctions for $k + l =$ odd.) Because apart from this satellite there are also the symmetry-related ones: $(\alpha,0,-\frac{1}{2})$, $(-\alpha,0,\frac{1}{2})$ and $(-\alpha,0,-\frac{1}{2})$, the set M^* has reflections $(h + m\alpha,\ k,\ l + m/2)$, where the restriction to $k + l =$ even does not hold any longer. Hence there are new main reflections (h,k,l) determining a primitive orthorhombic lattice and the Bravais class of M^* is $Pmmm(\alpha,0,\frac{1}{2})$, which in the setting of I is denoted by 1–10. For neutron instead of X-ray scattering one finds a basic satellite $(\alpha,\frac{1}{2},\frac{1}{2})$ with $\alpha \simeq 0{\cdot}392$. Then $K = mmm$ and the Bravais class is $Pmmm(\alpha,\frac{1}{2},\frac{1}{2})$, which appears in the tables of I in the setting $Pmmm(\frac{1}{2},\frac{1}{2},\gamma) = 1$–11 (Cox, Shapiro, Cowley, Eibschutz & Guggenheim, 1979; Scott, Habbal & Hidaka, 1982; Lyons, Bhatt, Negran & Guggenheim, 1982).

(*c*) $ThBr_4$

The high-temperature phase has space group $I4_1/amd$ (Fig. 5). There is a soft-mode transition at 95 K

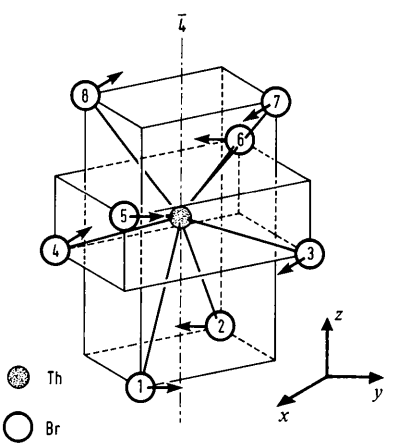


Fig. 5. The unit cell of the average structure of $ThBr_4$. The direction of the displacements in the modulated phase is indicated.

to an incommensurate phase with modulation wave vector $\mathbf{q} = \gamma\mathbf{c}^*$. The lattice of main reflections remains body-centered tetragonal, $K_\Lambda = 4/mmm$. This group also leaves M^* invariant. Hence $K = K_\Lambda$ and the Bravais class is $I4/mmm(0,0,\gamma)$, also denoted by 1–21. If one assumes that the incommensurate crystal structure represents the frozen-in soft mode, one can derive the superspace group and one finds $I4_1/amd(0,0,\gamma)(s,0,s,0)$, which in another notation (de Wolff, Janssen & Janner, 1981) can be denoted as 141–2 = $P^{I4_1/amd}_{s\,1s\,1}$ (Bernard, Currat, Delamoye, Zeyen, Hubert & de Kouchkovsky, 1983).

(*d*) *Biphenyl* $C_{12}H_{10}$

This compound has two incommensurate crystal phases (Fig. 6). In both phases there is a clear primitive monoclinic lattice of main reflections. Hence $K_\Lambda = 2/m$. The unique axis is $\mathbf{b}^*$. In the intermediate phase II there are four satellites around the position $\frac{1}{2}\mathbf{b}^*$. One may write these reflections as $(h \pm \delta_a, k \pm \frac{1}{2}(1 - \delta_b), 0)$. If these satellites all originate from the same domain, one has $d = 2$ and one may choose $\mathbf{q}_1 = (\alpha,\beta,0)$ amd $\mathbf{q}_2 = (\alpha,-\beta,0)$. Hence $K = 2/m$ and the Bravais class is $P2/m(\alpha,\beta,\gamma)$. By chance one has $\gamma \simeq 0$ in this case. The Bravais class is also indicated by 2–16 in I (in the setting with unique axis *c*). In the low-temperature phase δ_a goes to zero, which means that $\mathbf{q}_1 = (0,\beta,0)$ is the only basic satellite and therefore $d = 1$. Hence $K = 2/m$ and the Bravais class is in the setting with unique axis *c* given by: $P2/m(0,0,\gamma)$ = 1–6 (Cailleau, Baudour, Meinnel, Dworkin, Moussa & Zeyen, 1980; Cailleau, 1981).

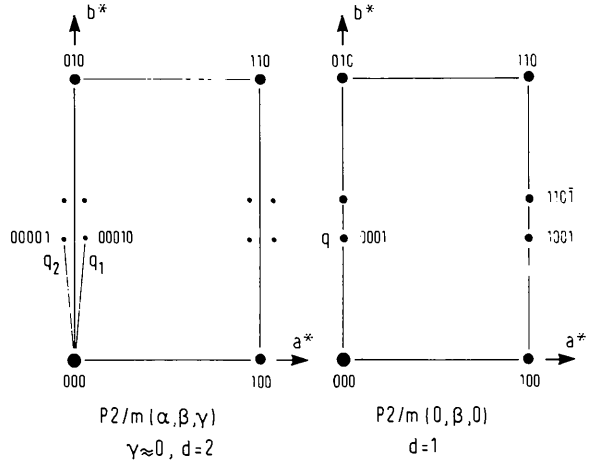


Fig. 6. The reflections near or in the plane $l = 0$ for biphenyl. Left in the region $21 < T < 39$ K, right for $T < 21$ K.

(*e*) *TTF–TCNQ*

This compound has three incommensurate phases (Fig. 7). At 54 K the ordinary crystal has a transition towards an incommensurate structure. In the region $47 < T < 54$ K, the lattice of main reflections is simple monoclinic: $K_\Lambda = 2/m$. The satellites are on the BZ boundary: $\mathbf{q}_1 = \frac{1}{2}\mathbf{a}^* + \beta\mathbf{b}^*$ (unique axis *b*). Hence $d = 1$. The set $M^* = \{(h + \frac{1}{2}m, k + \beta m, l)\}$ is left invariant by $K = 2/m$ and the Bravais class of M^* is $P2/m(\frac{1}{2},0,\gamma)$ = 1–5 in the setting with unique axis *c*. This set can be seen as a centering of the type $P2/m(0,0,\gamma)$. Below 47 K the wave vector moves away from the zone boundary: $\mathbf{q}_1 = \alpha\mathbf{a}^* + \beta\mathbf{b}^*$ for $38 < T < 47$ K. The subgroup of $K_\Lambda = 2/m$ leaving M^* invariant is now $K = \bar{1}$. This implies for the Bravais class $\bar{1}(\alpha,\beta,\gamma)$ = 1–1, where the value of $\gamma \simeq 0$ is not imposed by symmetry. Because of the triclinic point group, it may be assumed that Λ^* is not strictly speaking monoclinic, but triclinic: $K_\Lambda = \bar{1}$. Below 38 K the value of α locks in at a value $\frac{1}{4}$. The main reflections still form a monoclinic lattice: $K_\Lambda = 2/m$, but now one needs two basic satellites: $\mathbf{q}_1 = (\frac{1}{4},\beta,0)$, $\mathbf{q}_2 = (-\frac{1}{4},\beta,0)$. Then $K = 2/m$ and according to I the Bravais class is in the setting with unique axis *c*: $P2/m(\alpha,\beta,\gamma)$ = 2–16, with $\alpha = \frac{1}{4}$, $\beta \simeq 0$ (Bak & Janssen, 1978; Denoyer, Comes, Garito & Heeger, 1975; Comes, Shapiro, Shirane, Garito &

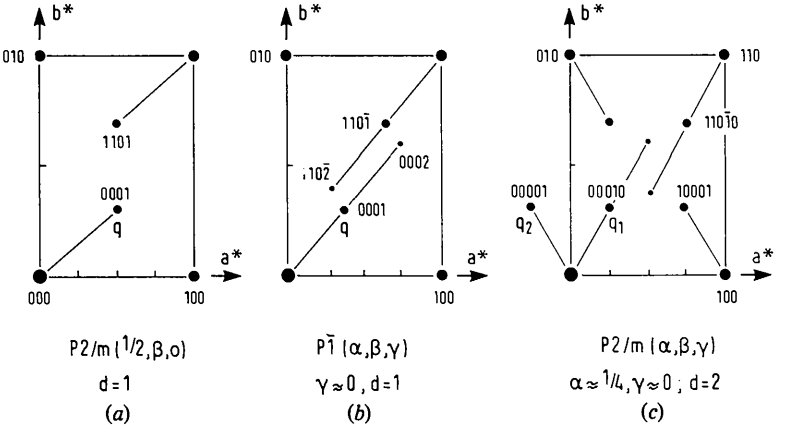


Fig. 7. The diffraction spots in the plane $l = 0$ for TTF–TCNQ. (*a*) $47 < T < 54$ K, (*b*) $38 < T < 47$ K, (*c*) $T < 38$ K.

Heeger, 1976; Khanna, Pouget, Comes, Garito & Heeger, 1977).

(*f*) $Hg_{3-x}AsF_6$

In the high-temperature phase the diffraction pattern shows a body-centered tetragonal lattice of main reflections due to the AsF_6 host lattice and diffuse streaks. The latter condense for $T < 120$ K. To start with, one keeps the original sharp reflections as main reflections: $K_\Lambda = 4/mmm$. The satellites occur at positions $(3-\delta, 1-\delta, 0)$ and $(-1-\delta, 3-\delta, 0)$. Taking $\mathbf{q}_1 = \delta(\mathbf{a}^* + \mathbf{b}^*)$ one may index $(3-\delta, 1-\delta, 0)$ by $h=3, k=1, m=-1$, and $(-1-\delta, 3-\delta, 0)$ by $h=-1$, $k=3$ and $m=-1$. Hence $d=1$. The reflections $(h+m\delta, k+m\delta, 1)$ are left invariant by mirrors m_{xy}, m_{x-y} and m_z. Hence K is an orthorhombic point group. Choose a new basis for Λ^*: $\mathbf{a}^{*\prime} = (\mathbf{a}^* + \mathbf{b}^*)/2$, $\mathbf{b}^{*\prime} = (\mathbf{a}^* - \mathbf{b}^*)/2$. Then $h = (h' + k')/2$, $k = (h' - k')/2$, $l = l'$, $m = m'$. The condition for non-extinction of elements of Λ^* is: $h + k + l =$ even. Moreover, h and k are integers. Hence for the new indices the rules for non-extinctions are $h' + k' =$ even, $h' + l' =$ even. These are the rules for a face-centered orthorhombic lattice, which has the point group $K = mmm$. In the new basis $\mathbf{q}_1 = 2\delta\mathbf{a}^{*\prime}$. Hence the Bravais class is $Fmmm(\alpha,0,0)$ or 1–17. Because the point group is now orthorhombic the lattice of main reflections is expected to have an orthorhombic deformation. This has indeed been observed: in the modulated phase the host lattice is no longer tetragonal. A finer analysis of the diffraction pattern in the modulated phase reveals additional spots due to the deformation of the mercury chains. The additional reflections may be generated by $\mathbf{q}_2 = \delta\mathbf{a}^* - \delta\mathbf{b}^* = 2\delta\mathbf{b}^{*\prime}$. This vector $\mathbf{q}_2$ is left invariant (not including the sign) by mmm, hence this is again the group K. The internal dimension is now $d=2$ and the Bravais class $Fmmm(\alpha,0,0;\ 0,\beta,0)$, where by chance one has $\alpha = \beta = 2\delta$. This relation, however, is not caused by symmetry. This would have been the case if the tetragonal symmetry of Λ^* had not been broken: it represents a kind of reminiscence of the higher symmetry of the parent phase (Pouget, Shirane, Hasting, Heeger, Miro & MacDiarmid, 1978; Janner & Janssen, 1980*b*).

(*g*) $1H\,TaSe_2$

In the $1H$ polytype this dichalcogenide has an incommensurate phase for $90 < T < 122$ K. In this phase the diffraction pattern has seemingly a hexagonal symmetry, although at present it is not clear if 2 or 3 $\mathbf{q}$ wave vectors are involved. In any case the main reflections form a hexagonal lattice: $K_\Lambda = 6/mmm$. The satellites are $\alpha\mathbf{a}^*$, $\alpha\mathbf{b}^*$ and $-\alpha(\mathbf{a}^* + \mathbf{b}^*)$ which belong to M^* for $\mathbf{q}_1 = \alpha\mathbf{a}^*$, $\mathbf{q}_2 = \alpha\mathbf{b}^*$. Then M^* is invariant under the whole group $K_\Lambda = K = 6/mmm$. The Bravais class of M^* is $P6/mmm(\alpha,0,0) = 2$–83. In the low-temperature phase ($T < 90$ K) the compound forms a superstructure which is pseudo-hexagonal: the basis of the orthorhombic lattice is $\mathbf{a}^{*\prime} = \mathbf{a}^*/6$, $\mathbf{b}^{*\prime} = \mathbf{a}^*/6 - \mathbf{b}^*/3$, with systematic extinctions for $h' + k' =$ odd. Hence the Bravais class is C-centered orthorhombic. Taking this as the starting point for the description of the satellite reflections, the main reflections form a C-centered lattice: $K_\Lambda = mmm$ with basis $\mathbf{a}^{*\prime\prime} = \frac{1}{2}\mathbf{a}^*$, $\mathbf{b}^{*\prime\prime} = \frac{1}{2}\mathbf{a}^* - \mathbf{b}^*$, where now $\mathbf{a}^*$ and $\mathbf{b}^*$ no longer span a hexagonal lattice. The satellites are now at $2\alpha\mathbf{a}^{*\prime\prime}$, $\alpha(\mathbf{a}^{*\prime\prime} - \mathbf{b}^{*\prime\prime})$ and $-\alpha(3\mathbf{a}^{*\prime\prime} - \mathbf{b}^{*\prime\prime})$. Thus one can choose $\mathbf{q}_1 = \alpha(\mathbf{a}^{*\prime\prime} - \mathbf{b}^{*\prime\prime})$ and $\mathbf{q}_2 = \alpha(\mathbf{a}^{*\prime\prime} + \mathbf{b}^{*\prime\prime})$. Hence M^* is invariant under $K = K_\Lambda$ and the Bravais class is in the setting of I: $Ammm(0,\mu,\nu)$ with $\mu = \nu = \alpha$. It is also denoted by 2–54 (Fung, McKernan, Steeds & Wilson, 1981; Moncton, Axe & DiSalvo, 1977; Janner & Janssen, 1980*a*).

(*h*) $Sr_{1-x}Cr_2Se_{4-x}$

The structure can be described as a hexagonal host lattice of Cr_2Se_{4-x} with $c_0 = 3{\cdot}63$ Å and Sr in the hexagonal channels with a different interatomic distance: $c_1 \simeq 6{\cdot}0$ Å for atoms located at the sixfold axes, $c_2 = 4{\cdot}6$ Å for those at the threefold axes. The diffraction pattern is hexagonal. The main reflections, due to the host lattice, have $K_\Lambda = 6/mmm$. Because of the different periodicities in the channels there are satellites $(h, k, l + m_1\gamma + m_2\nu)$. Hence $d=2$ and $\mathbf{q}_1 = \gamma\mathbf{c}^*$, $\mathbf{q}_2 = \nu\mathbf{c}^*$. The set M^* is left invariant by $K = K_\Lambda$. Hence the Bravais class of M^* is $P6/mmm(0,0,\gamma;\ 0,0,\nu) = 2$–81 (Brouwer, 1978).

(*i*) *γ-PAMC*

The average structure is reported to be $Abma$. Hence for the main reflections one has $K_\Lambda = mmm$. There are two sets of satellites (Fig. 8). Up to now it has not been fully clear if these are really independent. The first set is $(h \pm m_1\delta_1, k, l)$ with $k + l + m_1 =$ even. The second set, where only first-order satellites have been observed, consists of $(h \pm m_2\delta_2, k, l)$ with $k + l =$ odd for $m_2 = 1$. The set of diffraction vectors can be generated by $\mathbf{q}_1 = \alpha\mathbf{a}^* + \mathbf{c}^*$, $\mathbf{q}_2 = \alpha'\mathbf{a}^* + \mathbf{c}^*$. Hence $d=2$. Since M^* is left

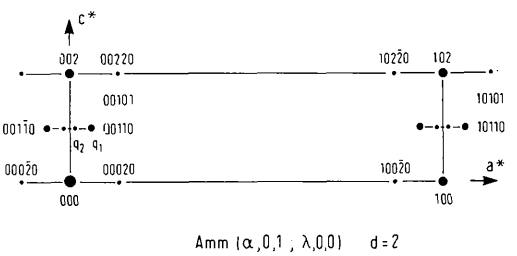


Fig. 8. Diffraction spots in the plane $k=0$ for γ-PAMC. Indexing $h0l m_1 m_2$ for the satellites is according to a two-dimensional modulation. Spots labeled $h0l$ are main reflections.

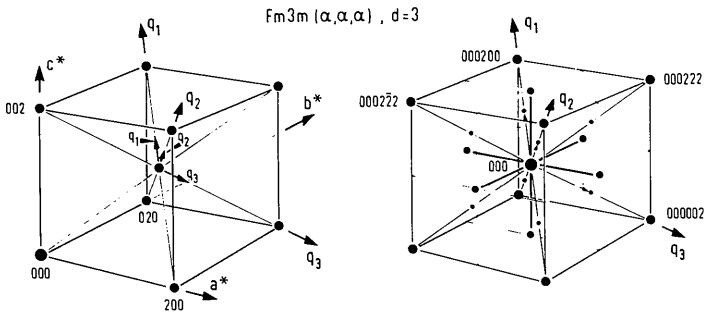


Fig. 9. Diffraction spots of Cu_9BiS_6. (*a*) Spots in the unit cell of the reciprocal lattice with three basic satellites and their axes. (*b*) The cluster of satellites around the main reflection 000.

invariant by K_Λ one has $K = K_\Lambda$. The Bravais class is, in the setting of I, $Cmmm(1,0,\gamma;\ 0,0,\nu) = 2$–24 (Depmeier, 1981)

(*j*) *Wustite* $Fe_{1-x}O$

The lattice of main reflections is that of a f.c.c. lattice. Hence $K_\Lambda = m3m$. Around the main reflections the satellites are ordered in an octahedral fashion: one may choose $\mathbf{q}_1 = \alpha\mathbf{a}^*$, $\mathbf{q}_2 = \alpha\mathbf{b}^*$, $\mathbf{q}_3 = \alpha\mathbf{c}^*$. Hence $d = 3$. Since again M^* is left invarient by K_Λ one has $K = m3m$ and the Bravais class of M^* follows immediately: $Fm3m(\alpha,0,0) = 3$–211. This was the first known example of an incommensurate crystal phase with $d = 3$ (Yamamoto, 1982).

(*k*) Cu_9BiS_6

The diffraction pattern shows main reflections belonging to a f.c.c. lattice: $K_\Lambda = m3m$. The main reflections are surrounded by satellites in octahedral configuration (Fig. 9): $(h \pm 2\alpha, k, l)$, $(h, k \pm 2\alpha, l)$, $(h, k, l \pm 2\alpha)$, $(h \pm \alpha, k \pm \alpha, l \pm \alpha)$, which can be described with $\mathbf{q}_1 = (-\alpha,\alpha,\alpha)$, $\mathbf{q}_2 = (\alpha,-\alpha,\alpha)$, $\mathbf{q}_3 = (\alpha,\alpha,-\alpha)$. Locally these span a f.c.c. reciprocal lattice. Here again $d = 3$. Although the intensities of the satellites are asymmetric, the positions of M^* are left invariant by $K = K_\Lambda$. Hence the Bravais class of M^* is $Fm3m(\alpha,\alpha,\alpha) = 3$–217 (Tomeoka & Ohmasa, 1982).

References

BAK, P. & JANSSEN, T. (1978). *Phys. Rev. B*, **17**, 436–439.

BERNARD, L., CURRAT, R., DELAMOYE, P., ZEYEN, C. M. E., HUBERT, S. & KOUCHKOVSKY, R. DE (1983). *J. Phys. C*, **16**, 433–456.

BROUWER, R. (1978). Thesis, Univ. of Groningen, The Netherlands.

CAILLEAU, H. (1981). Thesis, Univ. of Rennes I.

CAILLEAU, H., BAUDOUR, J. L., MEINNEL, J., DWORKIN, A., MOUSSA, F. & ZEYEN, C. M. E. (1980). *Faraday Discuss. Chem. Soc.* **69**, 7–18.

COMES, R., SHAPIRO, S. M., SHIRANE, G., GARITO, A. F. & HEEGER, A. J. (1976). *Phys. Rev. B*, **14**, 2376–2383.

COX, D. E., SHAPIRO, S. M., COWLEY, R. A., EIBSCHUTZ, M. & GUGGENHEIM, H. J. (1979). *Phys. Rev. B*, **19**, 5754–5772.

DENOYER, F., COMES, R., GARITO, A. F. & HEEGER, A. J. (1975). *Phys. Rev. Lett.* **35**, 445.

DEPMEIER, W. (1981). *Acta Cryst.* B**37**, 330–339.

FUNG, K. K., MCKERNAN, S., STEEDS, J. W. & WILSON, J. A. (1981). *J. Phys. C*, **14**, 5417–5432.

International Tables for X-ray Crystallography (1969). Vol. I. Birmingham: Kynoch Press.

JANNER, A. & JANSSEN, T. (1980*a*). *Acta Cryst.* A**36**, 399–408.

JANNER, A. & JANSSEN, T. (1980*b*). *Acta Cryst.* A**36**, 408–415.

JANNER, A., JANSSEN, T. & DE WOLFF, P. M. (1983*a*). *Acta Cryst.* A**39**, 658–666.

JANNER, A., JANSSEN, T. & DE WOLFF, P. M. (1983*b*). *Acta Cryst.* A**39**, 667–670.

KHANNA, S. K., POUGET, J. P., COMES, R., GARITO, A. R. & HEEGER, A. J. (1977). *Phys. Rev. B*, **16**, 1468–1479.

LYONS, K. B., BHATT, R. N., NEGRAN, T. J. & GUGGENHEIM, H. J. (1982). *Phys. Rev. B*, **25**, 1791–1804.

MONCTON, D. E., AXE, J. D. & DISALVO, F. J. (1977). *Phys. Rev. B*, **16**, 801–819.

MOUDDEN, A. H., DENOYER, F. & LAMBERT, M. (1978). *J. Phys. (Paris)*, **39**, 1323–1330.

POUGET, J. P., SHIRANE, G., HASTING, J. M., HEEGER, A. J., MIRO, N. D. & MACDIARMID, A. G. (1978). *Phys. Rev. B*, **18**, 3645–3656.

SCOTT, J. F., HABBAL, F. & HIDAKA, M. (1982). *Phys. Rev. B*, **25**, 1805–1812.

TOMEOKA, K. & OHMASA, M. (1982). *Am. Mineral.* **67**, 360–372.

WOLFF, P. M. DE, JANSSEN, T. & JANNER, A. (1981). *Acta Cryst.* A**37**, 625–636.

YAMAMOTO, A. (1980). *Phys. Rev. B*, **22**, 373–379.

YAMAMOTO, A. (1982). *Acta Cryst.* A**38**, 1451–1456.