The present procedure has direct relevance to the structure of decagonal quasicrystalline phases and has the potential for extension to the three-dimensional quasicrystal.

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The Description and Analysis of Composite Crystals

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Abstract

The composition of composite crystals, which contain two often incommensurate sublattices, depends on the ratio of the volumes of the sublattices and is therefore nonstoichiometric if the sublattices are incommensurate. The relation between the two sublattices is described by an interlattice matrix, which has different forms for layer and column composite structures and is restricted by space-fitting requirements. A previously derived formalism for the refinement of incommensurately modulated structures [Petricek, Coppens & Becker (1985). *Acta Cryst.* A**41**, 478-483] has been extended to composite structures and applied in a new computer program. The formalisms have been applied to the composite structures of (BEDO-TTF)$_{2.4}$I$_3$, (BEDT-TTF)Hg$_{0.776}$(SCN)$_2$ and (Bi,Sr,Ca)$_{10}$Cu$_{17}$O$_{29}$.

Introduction

As more complicated solids are being synthesized in the search for new materials, unusual structural phenomena are becoming increasingly common. Prime examples are modulations in crystals and the occurrence of composite (also called misfit) structures which contain at least two components with interpenetrating but distinct lattices.

When the ratio of the volumes of the unit cells of the two sublattices of a composite crystal is irrational, the two components will occur in nonstoichiometric ratios, the stoichiometry being dictated by the ratio of the unit-cell volumes. For ionic or partially ionic compounds, electroneutrality requirements imply that composite solids must contain ions of mixed valency. Since mixed valency is often associated with unusual properties, it is not surprising that the search for synthetic metals and superconductors has led to the discovery of many new composite solids. Some examples of inorganic and organic composite crystals are given in Table 1. Other known examples are minerals and graphite intercalation compounds (Makovicky & Hyde, 1981) and alloys (Jeitschko & Parthé, 1967).

Since the two lattices coexist in the same crystal, there is a mutual interaction which corresponds to a perturbing potential with the periodicity of the other sublattice. The perturbation causes each of the sublattices to be modulated with a repeat of the perturbing potential, which is a translation period of the second sublattice. As a result, the diffraction pattern of a composite crystal is the superposition of the diffraction patterns of the two sublattices, plus satellite reflections representing the modulations (Janner &

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Janssen, 1980; van Smaalen, 1989, 1990). Description of the pattern requires at least four indices. In the four-dimensional case one sublattice is represented by the *hkl*0 indices, while the indices of the second lattice are given by *hk*0*m*, assuming *c* to be the incommensurate axis. The restriction to four reciprocal base vectors implies the existence of a common reciprocal plane with indices (*hk*00). Reflections with all nonzero indices cannot be assigned to one of the sublattices and are the result of the interaction between the lattices. They will be referred to as satellite reflections.

Table 1. *Some examples of composite structures*

Inorganic	Reference
$Re_{17}Ge_{22}$	Jeitschko & Parthé (1967)
$Hg_{3-\delta}AsF_6$	Brown, Cutforth, Davies, Gillespie, Ireland & Vekris (1974)
$Ba_p(Fe_2S_4)_q$	Grey (1975); Hoggins & Steinfink (1977); Swinnea & Steinfink (1980)
$La_{1\cdot2}CrS_{3\cdot2}$	Otero-Diaz, Fitzgerald, Williams & Hyde (1985)
$(SnS)_{1\cdot18}NbS_2$	Meetsma, Wiegers, Haange & de Boer (1989)
$Sr_8Ca_6Cu_{24}O_{41}$	McCarron, Subramanian, Calabrese & Harlow (1988)
$Bi_{0\cdot31}Ca_{5\cdot64}Sr_{4\cdot05}Cu_{17}O_{29}$	Kato (1990); Kato, Takayama-Muromachi, Kosuda & Uchida (1988)
$Bi_{0\cdot55}Ca_{5\cdot60}Sr_{3\cdot85}Cu_{17}O_{29}$	Frost-Jensen (1990)
Organic	
$(TTF)_7I_{5-x}$	Johnson & Watson (1976)
$BO_{2\cdot4}I_3$	Present work
ET $Hg_{0\cdot776}(SCN)_2$	Present work
$ET_4Hg_{2\cdot89}Br_8$	Lyubovskaya, Zhilyaeva, Pesotskii, Lyubovskii, Atovmyan, D'yachenko & Takhirov (1987)
$Bz_9M_2I_9.CHCl_3$	Coppens, Leung, Ortega, Young & LaPorta (1983)
$TMA^+TCNQ^{2/3-}(I_3^-)^{1/3}$	Coppens, Leung, Murphy, von Tilborg, Epstein & Miller (1980)

In the following section we discuss limitations due to the nonoverlap criterion, imposed by the need to fit the two lattices in space. Subsequent sections deal with the scattering formalisms and examples of their application to two organic and one inorganic composite structures.

Classification of composite structures

The possibilities for the coexistence of two lattices in one crystal are restricted by space-fitting requirements. In *column composite structures*, which in the case of alloys have been described as 'chimney ladder structures' (Jeitschko & Parthé, 1967), the two lattices consist of parallel columns. In *layer composite structures* sheets of the two components are interleaved. The two cases are illustrated in Figs. 1(*a*) and (*b*), respectively.

In general, we may describe the relation between the two direct-space lattices of a composite crystal structure by the equation

$$\mathbf{A}^{(2)} = \boldsymbol{\sigma}\mathbf{A}^{(1)}, \qquad (1)$$

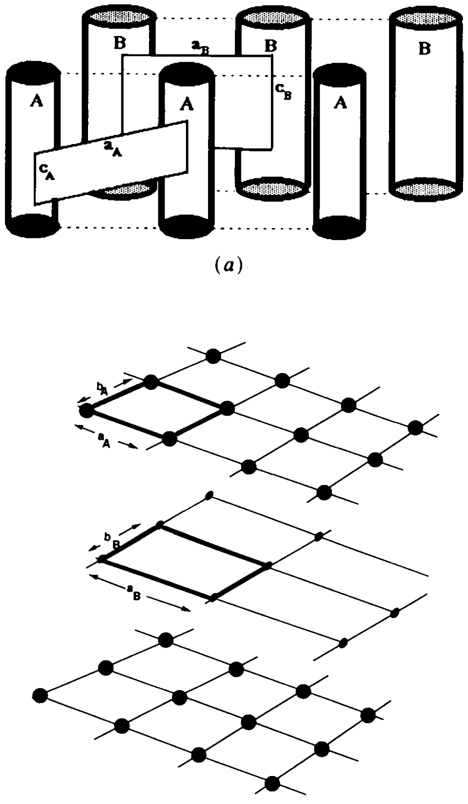
where $\boldsymbol{\sigma}$ is an interlattice matrix relating the direct-space translations of the sublattices. The corresponding reciprocal-space ralationship is

$$\mathbf{A}^{(2)*} = (\boldsymbol{\sigma}^{-1})^T\mathbf{A}^{(1)*} = \boldsymbol{\sigma}^*\mathbf{A}^{(1)*}. \qquad (2)$$

The transformation matrix $\boldsymbol{\sigma}$ is restricted by the space-fitting requirement. In column composite structures the columns of sublattices *A* and *B* have different periodicity along the column axis. The condition that the columns be parallel restricts the interlattice matrix $\boldsymbol{\sigma}$ to the following form:

$$\boldsymbol{\sigma} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ 0 & 0 & \sigma_{33} \end{bmatrix}, \qquad (3)$$

where **c** is taken as the common column direction. A further restriction follows from the space-fitting requirements. The necessity for the columns to fit together into an infinite array implies that we can define, without loss of generality, the $\mathbf{a}_B$ and $\mathbf{b}_B$ axes to be in the planes respectively defined by $\mathbf{a}_A$ and $\mathbf{c}_A$ and by $\mathbf{b}_A$ and $\mathbf{c}_A$. This leads to the following form



(*a*)

(*b*)

Fig. 1. (*a*) Illustration of a column composite structure. The two unit cells in the *ac* plane are indicated. The dotted lines are added for perspective. (*b*) Illustration of a layer composite structure, showing three parallel layers.

for the direct-space interlattice matrix:

$$\boldsymbol{\sigma}=\begin{bmatrix}\sigma_{11} & 0 & \sigma_{13}\\ 0 & \sigma_{22} & \sigma_{23}\\ 0 & 0 & \sigma_{33}\end{bmatrix}. \qquad (4)$$

Furthermore, to avoid overlap of the two types of columns the diagonal elements σ_{11} and σ_{22} must be integers or integer fractions. Values different from one are mathematically possible, but are the exception. A two-dimensional example of the relation described by the first and third row of matrix (4) is outlined in Fig. 1(*a*).

The reciprocal-space interlattice matrix corresponding to (4) is obtained with (2) as

$$\boldsymbol{\sigma}^*=\begin{bmatrix}1/\sigma_{11} & 0 & 0\\ 0 & 1/\sigma_{22} & 0\\ -\sigma_{13}/(\sigma_{11}\sigma_{33}) & -\sigma_{23}/\sigma_{22}\sigma_{23} & 1/\sigma_{33}\end{bmatrix}. \qquad (5)$$

Expression (5) implies that a^* and b^* axes of the two lattices are parallel, and identical for $\sigma_{11}=\sigma_{22}=1$. Thus, the diffraction pattern can be described with only four indices. The organic examples discussed below, $(ET)Hg_{0\cdot776}(SCN)_2$ and $BO_{2\cdot4}I_3$ are column composite structures of this type.

In layer composite structures, also known as misfit layer structures (Macovicky & Hyde, 1981), the sublattices consist of interleaved planes of the two components. If the in-plane axes are labelled *a* and *b*, the $\boldsymbol{\sigma}$ matrix is given by

$$\boldsymbol{\sigma}=\begin{bmatrix}\sigma_{11} & \sigma_{12} & 0\\ \sigma_{21} & \sigma_{22} & 0\\ \sigma_{31} & \sigma_{32} & \sigma_{33}\end{bmatrix}, \qquad (6)$$

where the σ_{33} element is restricted to be an integer n by the space-fitting requirement. Several inorganic examples of such structures have been described by van Smaalen, Wiegers and collaborators (Wiegers, Meetsma, van Smaalen, Haange, Wulff, Zeinstra, de Boer, Kuypers, Van Tendeloo, Van Landuyt, Amelinckx, Meerschaut, Rabu & Rouxel, 1989; van Smaalen, 1989). Because both in-plane translation vectors of the two sublattices may differ, layer composite structures in general require a five-dimensional description. If, as seems generally to be the case, the *a* and *b* axes of the two sublattices can be selected to be parallel, the relation between the two lattices is given by

$$\boldsymbol{\sigma}=\begin{bmatrix}\sigma_{11} & 0 & 0\\ 0 & \sigma_{22} & 0\\ \sigma_{31} & \sigma_{32} & n\end{bmatrix}. \qquad (7)$$

The corresponding reciprocal-space interlattice matrix becomes:

$$\boldsymbol{\sigma}=\begin{bmatrix}1/\sigma_{11} & 0 & -\sigma_{31}/n\sigma_{11}\\ 0 & 1/\sigma_{22} & -\sigma_{32}/n\sigma_{22}\\ 0 & 0 & 1/n\end{bmatrix}. \qquad (8)$$

This expression corresponds to a five-dimensional description of the solid. In almost all cases described $n=1$, with the interesting exceptions of the minerals koenenite (Allmann, Lohse & Hellner, 1968) and valleriite (Evans & Allmann, 1968), and the intercalation compound $FeCl_3$/graphite (Cowley & Ibers, 1956), in which subsequent layers of one of the substructures have three times the translational period if the rhombohedral structure is described in a hexagonal unit cell.

An illustration of a layer composite structure is given in Fig. 1(*b*). The four-dimensional case is obtained when $\sigma_{11}=1$ and σ_{31} is rational (or $\sigma_{22}=1$ and σ_{32} is rational). Unlike the situation in column composite structures, there is no space-filling condition which forces layer composite structures to be four-dimensional.

Modulations

The interlattice interaction introduces a perturbing potential in each of the component lattices, which gives rise to a modulation with a **q** vector determined by the periodicity of the second lattice. For column structures the modulation in each of the lattices is one dimensional. In the general case of layer composite structures, the modulation in each of the sublattices is two dimensional, and five indices are needed to describe the full diffraction pattern. To our knowledge no examples of five-dimensional composite structures with modulations have been reported. van Smaalen (Wiegers *et al.*, 1989; van Smaalen, 1989) has derived the relations between the superspace group of composite solids and the superspace groups of each of the sublattices.

Scattering formalism for four-dimensional composite crystals

We will assume in the following discussion that the (*hk*00) plane is common to both reciprocal sublattices, in which case the main reflections have indices *hkl*0 and *hk*0*m*. A general *hklm* reflection is both an *m*th-order satellite of sublattice *A* and an *l*th-order satellite of sublattice *B*. Similarly, except for the *hk*00 reflections, each reflection with zero *l* or *m* index is simultaneously a main reflection of one sublattice and a satellite reflection of the second lattice. It follows that the X-ray scattering expression for each lattice point must contain contributions from two scattering processes.

If atoms 1 through N_1 are in subsystem 1, and N_1+1 through N_2 in subsystem 2, the structure factor for the case of a harmonic modulation is given by

$$\begin{aligned} F(hklm) = & \sum_{\nu=1}^{N_1} f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{H}_1 . \mathbf{r}_\nu^0) \\ & \times J_m(2\pi \mathbf{Q}_1 . \mathbf{U}_\nu)(-1)^m \exp(im\varphi_\nu) \\ & + |\sigma|^{-1} \sum_{\nu=N_1+1}^{N_2} f_\nu(\mathbf{Q}) \exp(2\pi i \mathbf{H}_2 . \mathbf{r}_\nu^0) \\ & \times J_l(2\pi \mathbf{Q}_2 . \mathbf{U}_\nu)(-1)^l \exp(il\varphi_\nu), \end{aligned} \quad (9)$$

where $J_m(x)$ is the Bessel function of mth order, $\mathrm{f}_\nu(\mathbf{Q})$ is the thermally averaged atomic scattering factor of atom ν, $\mathbf{r}_\nu^0$, $\mathbf{U}_\nu$ are basic coordinates of the atom ν and the amplitude of its modulation, respectively, φ_ν is the phase of the modulation and

$$\mathbf{H}_1 = (h, k, l), \quad \mathbf{H}_2 = (h, k, m),$$
$$\mathbf{Q} = \mathbf{H}_1 + m\mathbf{a}_4^* = H_2 + l\mathbf{a}_3^*.$$

If higher harmonics are to be included, a sum over different contributions must be included in the scattering expression, as described elsewhere (Petricek & Coppens, 1988). The computer program *COMPREF* used in the refinements allows both displacive and occupational modulation. It incorporates the rigid-body displacement model of Petricek, Coppens & Becker (1985).

Expression (9) differs from the expression given recently by Kato (1990) which requires a numerical integration over the modulation.

Examples

Three examples are discussed below. The full analyses of the structures will be described elsewhere.

(1) *ET* $\mathrm{Hg_{0 \cdot 776}(SCN)_2}$

The HgSCN salt of ET [=3,4;3′4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene or BEDT-TTF], ET $\mathrm{Hg_{0 \cdot 776}(SCN)_2}$, was synthesized by Wang (Wang, Beno, Carlson, Thorup, Murray, Porter, Williams, Maly, Bu, Petricek, Coppens, Jung & Whangbo, 1991) using electrocrystallization methods. The composite structure, suggested by the non-stoichiometry as determined by chemical analysis, is confirmed by the diffraction pattern. Satellites up to order three were observed. A Fourier projection based on the *h*0*l*0 reflections, which are common to both reciprocal lattices, showed the Hg atoms at the origin and all the non-H atoms of the ET and SCN ions. Subsequent refinement of the substructures in space group $P\bar{1}$ showed the atoms of the SCN group to be located in the ET sublattice, while the Hg atoms form the second sublattice, with a *b*-axis translation vector parallel to, but incommensurate with, the *b* axis of the first lattice. The unit cells are as follows: ET+SCN, $a = 6{\cdot}746\,(2)$, $b = 4{\cdot}114\,(1)$, $c = 20{\cdot}580\,(3)$ Å, $\alpha = 83{\cdot}06\,(1)$, $\beta = 105{\cdot}93\,(2)$, $\gamma = 119{\cdot}01\,(2)^\circ$, $V_c = 480{\cdot}23$ Å^3, $Z = 1$; Hg, $a = 6{\cdot}758\,(2)$, $b = 5{\cdot}302\,(2)$, $c = 21{\cdot}352\,(6)$ Å, $\alpha = 73{\cdot}10\,(2)$, $\beta = 110{\cdot}44\,(3)$, $\gamma = 119{\cdot}17\,(3)^\circ$, $V_c = 618{\cdot}85$ Å^3, $Z = 1$. The σ matrix defined by $\mathbf{A}_{\mathrm{Hg}} = \boldsymbol{\sigma}\mathbf{A}_{\mathrm{ET+SCN}}$ is given by

$$\begin{bmatrix} 1{\cdot}0 & -0{\cdot}0077 & 0 \\ 0 & 1{\cdot}2903 & 0 \\ 0 & 0{\cdot}9083 & 1 \end{bmatrix}.$$

The ratio of the two unit-cell volumes $V(\mathrm{ET+SCN})/V(\mathrm{Hg})$ is $480{\cdot}23/618{\cdot}85 = 0{\cdot}776$, in agreement with the analytical results on the composition. The projection of the structure down the common *b* axis is shown in Fig. 2.

The Hg atoms have four S and four N nearest neighbors. Because of the incommensurability the separation along the *b* axis of the Hg atoms and its neighbors is continuously variable and equal to zero in some of the unit cells (Fig. 3*a*). In these cells, the Hg–S distance in the average structure is only 1·90 Å, which is physically unreasonable given the typical Hg–S coordination distance of 2·40 Å. This strong interaction between the two lattices leads to each being modulated to relieve the Hg–S repulsions and satisfy the coordination of otherwise unbound ligands (Fig. 3*b*). An analysis of the modulational displacements using the rigid-body model for the ET and SCN ions (Coppens, Maly & Petricek, 1990) shows large displacements of both SCN and Hg, with significant higher harmonic contributions to the Hg displacements. Since the SCN ion is linear only two rotations around axes perpendicular to the molecule are considered. A description of the modulation by

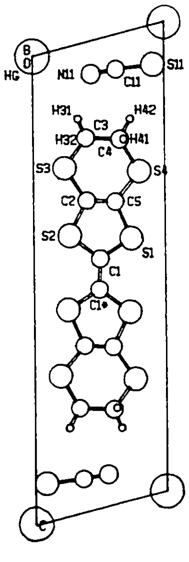


Fig. 2. The projection of the structure of ET $\mathrm{Hg_{0 \cdot 776}(SCN)_2}$ down the common *b*-axis direction.

a superposition of three harmonics gives a lengthening of the shortest distance from 1·90 to 2·25 Å, mainly due to very large displacements of the Hg atoms, as illustrated in Fig. 3. The ET translational and rotational amplitudes are 0·103(3) Å and 0·5(1)°, respectively. Numerical information on the refinement is given in Table 2.

Table 2. *Numerical information on the refinements*

	N_0*	N_ν†	$R_{\rm all}$	$R_{\rm main}$	$R_{\rm satellite}$
ET $Hg_{0\cdot776}(SCN)_2$	3318	154	9·2	8·7	16·7
$BO_{2\cdot4}I_3$	2173	117	5·5	4·6	14·1
$M_{10}Cu_{17}O_{29}$	666	57	6·5	6·3	10·7

* Number of unique reflections with $I > 3\sigma(I)$.
† Number of variables.

(2) $BO_{2\cdot4}I_3$ (*Wudl, Yamochi, Suzuki, Isotalo, Fite, Kasmai, Liou, Srdanov, Coppens, Maly & Frost-Jensen*, 1990)

BO [=3,4;3′4′-bis(ethylenedioxy)-2,2′,5,5′-tetrathiafulvalene or BEDO-TTF] was first synthesized by Wudl and co-workers (Suzuki, Yamochi, Srdanov, Hinkelmann & Wudl, 1989). Its triiodide salt has a composite structure with different periodicities of the BO and triiodide components along the *b* axis. First-order satellites are observable. Cell dimension are: BO, $a = 5\cdot3269\,(1)$, $b = 4\cdot029\,(1)$, $c = 16\cdot885\,(2)$ Å, $\alpha = 88\cdot29\,(2)$, $\beta = 83\cdot45\,(1)$, $\gamma = 81\cdot21\,(2)$°; I, $a = 5\cdot840\,(1)$, $b = 9\cdot620\,(2)$, $c = 17\cdot115\,(2)$ Å, $\alpha = 99\cdot55\,(1)$, $\beta = 80\cdot19\,(1)$, $\gamma = 115\cdot67\,(1)$°. The *b* axes of the two component structures are parallel, while $\mathbf{a}_{\rm I}$ is in the plane of $\mathbf{b}_{\rm BO}$ and $\mathbf{a}_{\rm BO}$, and $\mathbf{c}_{\rm I}$ in the plane of $\mathbf{b}_{\rm BO}$ and $\mathbf{c}_{\rm BO}$, as evident from the $\boldsymbol{\sigma}$ matrix defined by $\mathbf{A}_{\rm BO} = \boldsymbol{\sigma}\mathbf{A}_{\rm I}$:

$$\begin{bmatrix} 1 & 0\cdot3476 & 0 \\ 0 & 0\cdot4188 & 0 \\ 0 & 0\cdot3476 & 1 \end{bmatrix}.$$

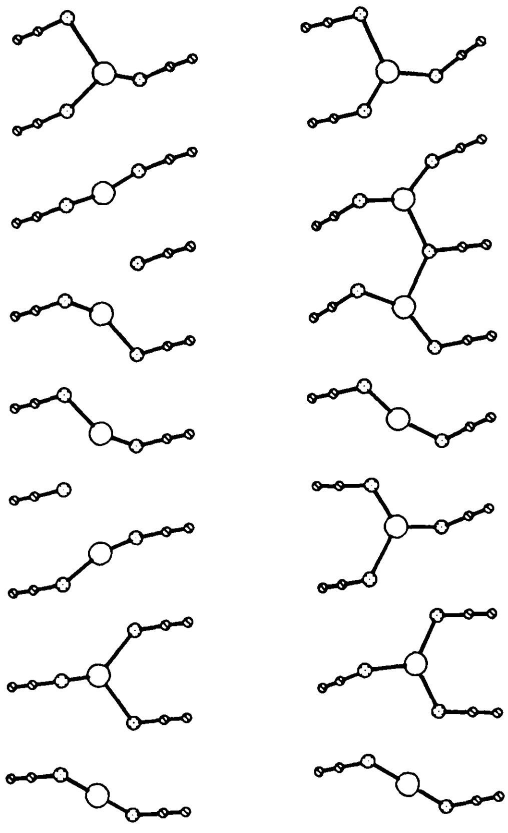

(*a*) (*b*)

Fig. 3. (*a*) The coordination of Hg and SCN in the average structure of ET $Hg_{0\cdot776}(SCN)_2$ as projected on the *ab* plane. The *b* axes of the two sublattices are vertical. The lack of commensurability leads to a continuously varying coordination. Connected atoms are at distances less than 3·0 Å. Large circles: Hg, intermediate size circles: S. (*b*) As for (*a*) but including the modulation.

The component cell volumes have a ratio $V(\mathrm{I})/V(\mathrm{BO}) = 2\cdot4$, implying the stoichiometry. This corresponds to an average net charge on the BO cations of 0·42 e, indicating that neutral BO molecules and BO^+ monocations coexist in the solid. There is one BO in the BO unit cell, which at the corners is bounded by columns of linear I_3^- ions. The *b*-axis projection of the average structure of the two lattices is shown in Fig. 4.

The BO molecules are treated as rigid bodies in the analysis of the modulation. The rigid-body displacements of BO are directed along the molecule's long molecular axis, with significant amplitudes of 0·049 and 0·071 Å for the first and third harmonic respectively. The direction of this displacement appears controlled by the short S · · · S contacts of

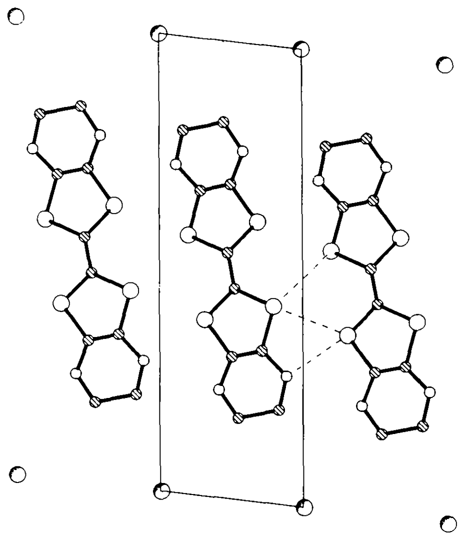


Fig. 4. Projection of the structure of $BO_{2\cdot4}I_3$ down the common *b*-axis direction.

only 3·402 Å, perpendicular to both the stacking axis and the long molecular axis. The I atoms show large translational and rotational rigid-body displacements, with amplitudes of up to 0·12 Å and 6·7°, respectively. Similar large displacements of the I_3^- ions were observed in the modulated structure of $(ET)_2I_3$ (Leung, Emge, Beno, Wang, Williams, Petricek & Coppens, 1985).

(3) $(Bi, Sr, Ca)_{10}Cu_{17}O_{29}$ (*Frost-Jensen*, 1990; *Frost-Jensen, Larsen, Johannsen, Cisarova, Maly & Coppens*, 1991)

$(Bi, Sr, Ca)_{10}Cu_{17}O_{29}$ is a byproduct of the synthesis of the high-T_c Bi cuprates. The structure of the Bi-free and (Bi, Ca)-free phases has been analyzed in an approximate supercell by McCarron *et al.* (McCarron, Subramanian, Calabrese & Harlow, 1988), while a composite structure analysis of $Bi_{0.31}Ca_{5.64}Sr_{4.05}Cu_{17}O_{29}$ has been described by Kato (1990). Neither of these two analyses includes the satellite reflections; 68 such reflections with $I > 3\sigma(I)$ were included in a more recent study of $Bi_{0.55}Ca_{5.60}Sr_{3.85}Cu_{17}O_{29}$ by Frost-Jensen *et al.* (1991) using the program *COMPREF*.

The cell dimensions of the two sublattices at 292K are

MCu_2O_3

$a = 11{\cdot}3819\,(15),\quad b = 12{\cdot}959\,(3),\quad c = 3{\cdot}9155\,(5)$ Å

and

CuO_2

$a = 11{\cdot}3788\,(13),\quad b = 12{\cdot}961\,(2),\quad c = 2{\cdot}7522\,(4)$ Å.

Superspace group $P{:}F222{:}\bar{1}\bar{1}1$.

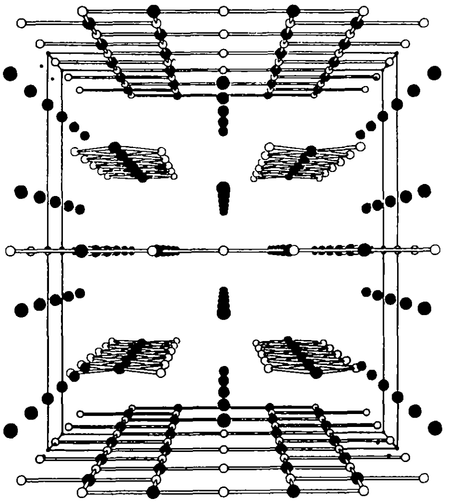


Fig. 5. Structure of $M_{10}Cu_{17}O_{29}$ viewed down the c axis. The b axis is in the vertical direction. The CuO_2 ribbons are at $y = \frac{1}{4}, \frac{3}{4}$. The M atoms are in columns between the CuO_2 ribbons and the Cu_2O_3 sheets at $y = 0, \frac{1}{2}$.

The interlattice matrix of this orthorhombic crystal is particularly simple and given by

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & c_I/c_{II} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1{\cdot}423 \end{bmatrix}.$$

This matrix conforms to the column interlattice matrix (4) with $\sigma_{13} = \sigma_{23} = 0$ as well as to the layer interlattice matrix (7) with $\sigma_{31} = \sigma_{32} = 0$. The CuO_2 ribbons which form the second sublattice may be considered as columns, or alternatively as an infinite layer of nonconnected ribbons (Fig. 5). In such a case, the distinction between the two classes is no longer obvious.

The refinement shows that the modulation consists mainly of a c-axis displacement of the Cu atoms of the CuO_2 component of about 0·1 Å, a b-axis displacement (in the direction perpendicular to the Cu_2O_3 sheets) of Cu by about 0·07 Å, and an a-axis displacement by about 0·06 Å of the metal atoms.

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Ab Initio Phase Determination for X-ray Diffraction Data from Crystals of a Native Protein

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Abstract

An efficient algorithm for the determination of an everywhere positive electron-density distribution that agrees with observed structure amplitudes has been used to determine the phases of X-ray diffraction data from recombinant bovine chymosin, a protein with 323 amino-acid residues in the molecular chain whose structure was recently determined using molecular replacement methods. A systematic procedure for testing the signs of centric reflections, using the total entropy of the map as a figure of merit, was used to produce a low-resolution map. The phases of acentric and additional centric reflections were then chosen by adding them to the map with various possible phases and computing the total entropy of the resulting map. Of 159 centric reflections whose phases were chosen by this procedure, 141 had the same phase as in the refined structure. The median absolute phase difference for 1811 acentric reflections was 32°. A map produced from these 1970 reflections, out of 12 346 reflections in the data set, showed a remarkable agreement with the refined structure. This molecule is many times larger than any whose structures have previously been determined without the use of isomorphous replacement, molecular replacement or anomalous dispersion, and the map demonstrates the potential of maximum-entropy methods in macromolecular structure determination.

Introduction

Direct methods of phase determination rely on the fact that, although diffraction intensities are proportional to the squared moduli of the structure factors, which are the complex values of the Fourier transform of the electron density in the unit cell, and thus contain no phase information, the non-negativity of the electron-density places restrictions on the possible values of the phases. Karle & Hauptman (1950) expressed these restrictions in the form of determinantal inequalities, which imply that the modulus of the difference between a structure factor and another complex number that is a function of other

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