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Structure Analysis of Modulated Molecular Crystals. III. Scattering Formalism and Symmetry Considerations: Extension to Higher-Dimensional Space Groups

By V. Petříček* and P. Coppens

Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, *USA*

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Abstract

Formalisms are developed for the scattering intensities of *d*-dimensional modulated molecular crystals, in which molecules or groups of atoms displace as rigid bodies. Expressions are given for the relation between the displacements of symmetry-related atoms, and phase restrictions are discussed that occur when rigid molecules are located at special positions. The formalisms have been incorporated into a computer program *JANA*5 applicable to the case of a two-dimensional modulation. The program allows inclusion of up to six higher harmonics of arbitrary order.

Introduction

In a previous paper (Petříček, Coppens & Becker, 1985; paper I) we developed formalisms to describe the scattering of modulated molecular crystals in which molecules or groups of atoms are displaced as rigid bodies. A computer program based on these formalisms has been applied to several molecular modulated crystals, including thiourea (Gao, Gajhede, Mallinson, Petříček & Coppens, 1987; paper II) and [bis(ethylenedithio)-TTF]$_2$I$_3$ (Leung, Emge, Beno, Wang, Williams, Petříček & Coppens, 1985). In more recent studies we have used the SUNY beamline at the National Synchrotron Light Source to measure the very weak $2k_F$ satellite reflections of TTF-TCNQ (tetrathiafulvalenium tetracyanoquinodimethanide) which occur below the metal-insulator transition (Coppens, Petříček, Levendis, Larsen, Paturle, Gao & LeGrand, 1987). The phase stable at the experimental temperature of 15 K is two-dimensionally modulated, with **q** vectors which are at an angle to the two fold axis of the monoclinic crystal class. In order to treat such two-dimensionally modulated molecular crystals we have extended our previous formalisms to the general *d*-dimensional case. We present here scattering expressions, relations between the displacements of symmetry-related atoms, and a discussion of general restrictions which apply to rigid molecules occupying special positions of the crystal's space group. Tables for symmetry restrictions in four-dimensional space groups will be presented in a subsequent publication.

Scattering formalism

Let us consider a *d*-dimensionally modulated crystal in which the νth atom in the unit cell defined by **n** is located at

$$\mathbf{r}_{\mathbf{n}\nu}=\mathbf{r}_\nu^0+\mathbf{n}+\mathbf{u}_\nu\{\mathbf{q}_1(\mathbf{g}_\nu+\mathbf{n}),\ldots,\mathbf{q}_d(\mathbf{g}_\nu+\mathbf{n})\} \qquad (1)$$

where $\mathbf{r}_\nu^0$ is the average position of atom ν, $\mathbf{u}_\nu$ is the *d*-dimensional periodic vector field $\mathbf{u}_\nu\,(x_1,\ldots,x_d)=\mathbf{u}_\nu\,(x_1+n_1,\ldots,x_d+n_d)$ ($n_1,\ldots,n_d$ being integers), $\mathbf{q}_1,\ldots,\mathbf{q}_d$ are incommensurate modulation vectors which are rationally independent in the basis $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$; $\mathbf{g}_\nu$ determines the phase reference point of the displaced entity (see paper I).

In the following we will confine ourselves to the case of several (say l) harmonic waves. This means a truncation of the infinite Fourier expression for $\mathbf{u}_\nu$:

$$\mathbf{u}_\nu=\sum_{i=1}^{l}\mathbf{U}_\nu^x(i)\sin\left[2\pi\bar{\mathbf{q}}_i\,.\,(\mathbf{n}+\mathbf{g}_\nu)\right]+\sum_{i=1}^{l}\mathbf{U}_\nu^y(i)\cos\left[2\pi\bar{\mathbf{q}}_i\,.\,(\mathbf{n}+\mathbf{g}_\nu)\right], \qquad (2)$$

where $\bar{\mathbf{q}}_i=\sum_{j=1}^{d}\alpha_{ij}\mathbf{q}_j$ (α_{ij} being integers) are the selected linear combinations of the modulation vectors and $\mathbf{U}_\nu^x(i)$ and $\mathbf{U}_\nu^y(i)$ are the amplitudes of the sin and cos displacement waves respectively.

The contribution of the νth atom to the structure factor is given by

$$F_\nu(\mathbf{Q})=f_\nu(\mathbf{Q})\sum_{\mathbf{n}=(0,0,0)}^{N_1N_2N_3}\exp\left[2\pi i\mathbf{Q}\,.\left(\mathbf{r}_\nu^0+\mathbf{n}+\sum_{i=1}^{l}\{\mathbf{U}_\nu^x(i)\sin\left[2\pi\bar{\mathbf{q}}_i\,.\,(\mathbf{n}+\mathbf{g}_\nu)\right]+\mathbf{U}_\nu^y(i)\cos\left[2\pi\bar{\mathbf{q}}_i\,.\,(\mathbf{n}+\mathbf{g}_\nu)\right]\}\right)\right], \qquad (3)$$

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* Permanent address: Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 Praha 8, Czechoslovakia.

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where $f_\nu(\mathbf{Q})$ is the atomic scattering factor containing the unmodulated temperature factor, $\mathbf{Q}$ is the scattering vector and the summation runs over a parallelepiped with edges $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$, $N_3\mathbf{a}_3$. We assume that the effect of the modulation of the temperature parameters is negligible.

An important simplification of (3) follows from the fact that the part representing the modulation contains only the projections $\mathbf{Q}\,.\,\mathbf{U}^x_\nu(i)$ and $\mathbf{Q}\,.\,\mathbf{U}^y_\nu(i)$. Introducing $U_\nu(i)$ and $\chi_\nu(i)$ such that

$$\begin{aligned} U_\nu(i) &= \{[\mathbf{Q}\,.\,\mathbf{U}^x_\nu(i)]^2+[\mathbf{Q}\,.\,\mathbf{U}^y_\nu(i)]^2\}^{1/2}, \\ \sin\chi_\nu(i) &= \mathbf{Q}\,.\,\mathbf{U}^y_\nu(i)/U_\nu(i), \\ \cos\chi_\nu(i) &= \mathbf{Q}\,.\,\mathbf{U}^x_\nu(i)/U_\nu(i), \end{aligned} \tag{4}$$

we get from (3)

$$F_\nu(\mathbf{Q}) = f_\nu(\mathbf{Q})\exp(2\pi i\mathbf{Q}\,.\,\mathbf{r}^0_\nu)\sum_{\mathbf{n}=(0,0,0)}^{N_1N_2N_3}\exp\Big(2\pi i\{\mathbf{Q}\,.\,\mathbf{n} + \sum_{i=1}^{l} U_\nu(i)\sin[2\pi\bar{\mathbf{q}}_i\,.\,(\mathbf{n}+\mathbf{g})+\chi_\nu(i)]\}\Big). \tag{5}$$

With the Jacobi–Auger expansion

$$\exp(iz\sin\alpha) = \sum_{m=-\infty}^{\infty} J_{-m}(z)\exp(-im\alpha),$$

(5) becomes

$$\begin{aligned} F_\nu(\mathbf{Q}) &= f_\nu(\mathbf{Q})\exp(2\pi i\mathbf{Q}\,.\,\mathbf{r}^0_\nu) \\ &\times \sum_{m_1,\ldots,m_l=-\infty}^{\infty}\prod_{i=1}^{l}\{J_{-m_i}[2\pi U_\nu(i)] \\ &\times\exp(-2\pi i m_i\bar{\mathbf{q}}_i\,.\,\mathbf{g}_\nu)\exp[-im_i\chi_\nu(i)]\} \\ &\times\sum_{\mathbf{n}=(0,0,0)}^{N_1,N_2,N_3}\exp\Big[2\pi i\Big(\mathbf{Q}-\sum_{i=1}^{l} m_i\bar{\mathbf{q}}_i\Big)\,.\,\mathbf{n}\Big]. \end{aligned} \tag{6}$$

For $N_i \gg 1$ the sum over $\mathbf{n}$ leads to principal maxima at every point $\mathbf{H}=h\mathbf{a}^*_1+k\mathbf{a}^*_2+l\mathbf{a}^*_3$. This means that reflections occur for $\mathbf{Q}=\mathbf{H}+\sum_{i=1}^{l} m_i\bar{\mathbf{q}}_i$.

We can describe the different models through selection of the vectors $\bar{\mathbf{q}}$:

(a) $l=d$; $\alpha_{ij}=\delta_{ij}$. This is the d-dimensional harmonic model, and leads to the non-overlapping of contributions from different $\mathbf{q}$ vectors. The summation in (6) over $m_1,\ldots,m_l$ is reduced to one term.

(b) $l>d$ and $\alpha_{ij}=\delta_{ij}$ for $i\le d$, and α_{ij} has integer components for $i>d$. This model describes the anharmonic approach where the effect of anharmonicity is described by $l-d$ terms. The summation over $m_1,\ldots,m_l$ is restricted by the conditions

$$\sum_{i=1}^{l} m_i\bar{\mathbf{q}}_i = \sum_{i=1}^{d} M_j\mathbf{q}_j,$$

where M_j ($j=1,\ldots,d$) are satellite indices of reflection to be calculated. The m_i and M_j are related by $\mathbf{m\alpha}=\mathbf{M}$. Note that $\bar{\mathbf{q}}_i$ must be a complete basis set which can represent all reflections to be calculated.

We obtain for the contribution of atom ν to the scattering amplitude

$$\begin{aligned} F_\nu(\mathbf{Q}) &= f_\nu(\mathbf{Q})\exp(2\pi i\mathbf{Q}\,.\,\mathbf{r}^0_\nu) \\ &\times\exp\Big(-2\pi i\sum_{i=1}^{d} M_i\mathbf{q}_i\,.\,\mathbf{g}_\nu\Big) \\ &\times\sum_{\substack{m_1,\ldots,m_l=-\infty \\ (\mathbf{m\alpha}=\mathbf{M})}}^{\infty}\prod_{i=1}^{l}\{J_{-m_i}[2\pi U_\nu(i)] \\ &\times\exp[-im_i\chi_\nu(i)]\}. \end{aligned} \tag{7}$$

This expression is essentially equivalent to that given by Perez-Mato, Madariaga & Tello (1986), except for the use of the phase reference point g_ν, common to a group of atoms, which is typical for the molecular model. An analogous expression suitable for numerical integration over the internal coordinates has been derived by Yamamoto (1982).

Treatment of symmetry

Incommensurate crystals with d-dimensional modulation can be described as periodic arrangements in $(3+d)$-dimensional space (Janner & Janssen, 1979; Janner, Janssen & de Wolff, 1983). The reciprocal base $\mathbf{b}^*_1,\ldots,\mathbf{b}^*_{3+d}$ in $(3+d)$-space was chosen in order to describe satellite reflections. The real diffraction pattern is a projection of the $(3+d)$-dimensional lattice onto R_3. The reciprocal base can be described as

$$\begin{aligned} \mathbf{b}^*_i &= \mathbf{a}^*_i \qquad (i=1,2,3); \\ \mathbf{b}^*_{i+3} &= \mathbf{q}_i+\mathbf{e}^*_i \qquad (i=1,\ldots,d). \end{aligned} \tag{8}$$

The additional $\mathbf{e}^*_i$ vectors are perpendicular to R_3; they are in general not an orthogonal set.

The basis dual to the basis (8) in the $(3+d)$-dimensional space is

$$\begin{aligned} \mathbf{b}_i &= \mathbf{a}_i-\sum_{j=1}^{d}(\mathbf{q}_j\,.\,\mathbf{a}_i)\mathbf{e}_j \qquad (i=1,2,3); \\ \mathbf{b}_{i+3} &= \mathbf{e}_i \qquad (i=1,\ldots,d) \end{aligned} \tag{9}$$

where $\mathbf{e}_i$ is dual to $\mathbf{e}^*_i$ ($i=1,\ldots,d$) in the internal space.

The generalized periodic electron density $\tilde{\rho}$ can be defined as the Fourier transform of the $(3+d)$-dimensional diffraction pattern (see de Wolff, 1974). The real electron density in R_3 is the section of the $(3+d)$-dimensional function $\tilde{\rho}$ defined by conditions $(\mathbf{r}\,.\,\mathbf{e}^*_i)=0$, where $\mathbf{r}\in R_{3+d}$. The coordinates of the positional vector $\mathbf{r}$ with respect to base $\mathbf{b}_1,\ldots,\mathbf{b}_{3+d}$ are

$$\begin{pmatrix}\mathbf{r}_E \\ \mathbf{r}_I\end{pmatrix},$$

where $\mathbf{r}_E$ is a column of three coordinates with respect to $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$, and $\mathbf{r}_I$ is a column of d coordinates with respect to $\mathbf{b}_4, \ldots, \mathbf{b}_{3+d}$.

A $(3+d)$-dimensional symmetry operation $\hat{S}^j$,

$$\hat{S}^j \begin{pmatrix} \mathbf{r}_E \\ \mathbf{r}_I \end{pmatrix} = \begin{pmatrix} \mathbf{r}^j_E \\ \mathbf{r}^j_I \end{pmatrix}, \text{ with } \tilde{\rho}(\mathbf{r}^j_E, \mathbf{r}^j_I) = \tilde{\rho}(\mathbf{r}_E, \mathbf{r}_I),$$

is described by

$$\begin{pmatrix} \boldsymbol{\Gamma}^j_E & \mathbf{0} \\ \boldsymbol{\Gamma}^j_M & \boldsymbol{\Gamma}^j_I \end{pmatrix} \begin{pmatrix} \mathbf{r}_E \\ \mathbf{r}_I \end{pmatrix} + \begin{pmatrix} \mathbf{s}^j_E \\ \mathbf{s}^j_I \end{pmatrix} = \begin{pmatrix} \mathbf{r}^j_E \\ \mathbf{r}^j_I \end{pmatrix}, \tag{10}$$

where $\boldsymbol{\Gamma}^j_E$, $\boldsymbol{\Gamma}^j_M$ and $\boldsymbol{\Gamma}^j_I$ are 3×3, $d\times3$ and $d\times d$ matrices respectively, describing the rotational part of $\hat{S}^j$, and $\mathbf{s}^j_E$ and $\mathbf{s}^j_I$ are columns of dimensions (3×1) and $(d\times1)$ respectively describing the translational part of $\hat{S}^j$. The connection with the notation of paper I and de Wolff, Janssen & Janner (1981) is given by the following equivalences:

$$(\boldsymbol{\Gamma}^j_E \leftarrow R^j, \boldsymbol{\Gamma}^j_I \leftarrow \varepsilon^j, \boldsymbol{\Gamma}^j_M \leftarrow -m^*_j, \mathbf{s}^j_E \leftarrow \mathbf{s}^j \text{ and } \mathbf{s}^j_I \leftarrow \delta^j).$$

All combinations of $\boldsymbol{\Gamma}^j_E$, $\boldsymbol{\Gamma}^j_M$ and $\boldsymbol{\Gamma}^j_I$ are restricted by the equation (Janner & Janssen, 1979)

$$\boldsymbol{\sigma}\boldsymbol{\Gamma}^j_E - \boldsymbol{\Gamma}^j_I\boldsymbol{\sigma} = \boldsymbol{\Gamma}^j_M$$

where the σ_{ij} are the components of $\mathbf{q}_i$ with respect to $\mathbf{a}^*_1$, $\mathbf{a}^*_2$ and $\mathbf{a}^*_3$, such that $\mathbf{q}_i = \sum \sigma_{ij}\mathbf{a}^*_j$.

In order to evaluate the scattering of symmetry-related atoms according to (7) the displacement $\mathbf{u}^j_\nu$ of the atom generated by $\hat{S}^j$ must be related to that of the 'source' atom $\mathbf{u}_\nu$. Similarly to de Wolff, Janssen & Janner [(1981), expression (3.16)], we have the transformation law

$$\mathbf{u}^j_\nu(\mathbf{g}^j_{I\nu}) = \boldsymbol{\Gamma}^j_E\mathbf{u}_\nu[(\boldsymbol{\Gamma}^j_I)^{-1}(\mathbf{g}^j_{I\nu} - \mathbf{s}^j_I - \boldsymbol{\Gamma}^j_M\mathbf{g}_{E\nu})], \tag{11}$$

where $\mathbf{g}_{I\nu}$ and $\mathbf{g}_{E\nu}$ are respectively the internal and external coordinates of the vector $\mathbf{g}_\nu$.

Application of (7) requires the displacement of the symmetry-related atom in R_3. Use of the d conditions $(\mathbf{g}^j_\nu \,.\, \mathbf{e}^*_i) = 0$ and (9) gives

$$\mathbf{g}^j_{I\nu} = \boldsymbol{\sigma}\mathbf{g}^j_{E\nu}.$$

Substitution in (11) finally leads to

$$\mathbf{u}^j_\nu(\boldsymbol{\sigma}\mathbf{g}^j_{E\nu}) = \boldsymbol{\Gamma}^j_E\mathbf{u}_\nu[\boldsymbol{\sigma}\mathbf{g}_{E\nu} + (\boldsymbol{\Gamma}^j_I)^{-1}(\boldsymbol{\sigma}\mathbf{s}^j_E - \mathbf{s}^j_I)], \tag{12}$$

in which each displacement is referred to its own phase reference point [this is a generalization of equation (12b) from paper I].

For the case of l waves (and d modulation vectors), the structure-factor formula (7) becomes, after summation over all symmetry-related atoms N_s,

$$\begin{aligned} F_\nu(\mathbf{Q}) = \sum_{j=1}^{N_s} f_\nu(\mathbf{Q}) &\exp(2\pi i\mathbf{Q}\mathbf{r}^j_{E\nu}) \\ &\times \exp(-2\pi i\mathbf{M}\boldsymbol{\Gamma}^j_I\boldsymbol{\sigma}\mathbf{g}_{E\nu}) \\ &\times \exp[-2\pi\mathbf{M}i(\boldsymbol{\sigma}\mathbf{s}^j_E - \mathbf{s}^j_I)] \\ &\times \sum_{\substack{m_1,\ldots,m_l=-\infty \\ (\mathbf{m}\boldsymbol{\alpha}=\mathbf{M}\boldsymbol{\Gamma}^j_I)}}^{\infty} \prod_{i=1}^{l} \{J_{-m_i}[2\pi U^j_\nu(i)] \\ &\times \exp[-im_i\chi^j_\nu(i)]\} \end{aligned} \tag{13}$$

where the superscript j for $U^j_\nu(i)$ and $\chi^j_\nu(i)$ implies use of (4) with symmetry-related amplitudes.

Symmetry restrictions resulting from special positions

For an atom at $\mathbf{r}_{E\nu}$ with its phase reference point at a special position such that

$$\mathbf{g}_{E\nu} = \boldsymbol{\Gamma}^j_E\mathbf{g}_{E\nu} + \mathbf{s}^j_E, \tag{14}$$

restrictions follow from the condition that the displacements must be invariant under the symmetry operation. Application of the transformation law (11) to the expression for the displacement (2) gives the following equation which leads to restrictions for $\mathbf{U}^x_\nu(i)$ and $\mathbf{U}^y_\nu(i)$:

$$\begin{aligned} &\sum_{i=1}^{l} [\mathbf{U}^x_\nu(i)\sin x_i + \mathbf{U}^y_\nu(i)\cos x_i] \\ &\quad = \sum_{i=1}^{l} \boldsymbol{\Gamma}^j_E[\mathbf{U}^x_\nu(i)\sin x'_i + \mathbf{U}^y_\nu(i)\cos x'_i], \end{aligned} \tag{15}$$

where the following abbreviations have been used:

$$\begin{aligned} x_i &= 2\pi\boldsymbol{\alpha}_i\mathbf{g}^j_{I\nu} \\ x'_i &= 2\pi\boldsymbol{\alpha}_i(\boldsymbol{\Gamma}^j_I)^{-1}(\mathbf{g}^j_{I\nu} - \mathbf{s}^j_I - \boldsymbol{\Gamma}^j_M\mathbf{g}_{E\nu}). \end{aligned} \tag{16}$$

Here $\boldsymbol{\alpha}_i$ is the ith row of the matrix $\boldsymbol{\alpha}$ defined previously.

Symmetry restrictions applying to atoms in special positions have been used in previous studies (*e.g.* Yamamoto, 1983; Kucharczyk, Paciorek & Uszynski, 1986). For the molecular displacement model special positions lead to further restrictions owing to the rigidity of the molecules. According to this model the atomic displacements may be described in terms of the translations and rotations of the rigid molecules,

$$\mathbf{u}_\nu = \mathbf{u}^t + \mathbf{u}^r \times (\mathbf{r}_{E\nu} - \mathbf{R}), \tag{17}$$

where $\mathbf{R}$ is the center of mass of the molecule which may be used as the phase reference point. For a molecule in a special position the symmetry element $\hat{S}^j_E$ transforms every atom of the molecule into some (not necessarily the same) atom of the molecule. There are two ways to derive the displacement of the transformed atom. The transformation law (11) may be applied directly, or the rigid-body condition (17) may be applied to the transformed position of the atom. The requirement of uniqueness and the condition $\hat{S}^j_E\mathbf{R}=\mathbf{R}$ leads to the following conditions for translations and rotations respectively:

$$\begin{aligned}\sum_{i=1}^{l}[\mathbf{U}^x_t(i)\sin x_i+\mathbf{U}^y_t(i)\cos x_i]&=\sum_{i=1}^{l}\boldsymbol{\Gamma}^j_E[\mathbf{U}^x_t(i)\sin x'_i+\mathbf{U}^y_t(i)\cos x'_i]\\ \sum_{i=1}^{l}[\mathbf{U}^x_r(i)\sin x_i+\mathbf{U}^y_r(i)\cos x_i]&=\sum_{i=1}^{l}(\det\boldsymbol{\Gamma}^j_E)\boldsymbol{\Gamma}^j_E[\mathbf{U}^x_r(i)\sin x'_i+\mathbf{U}^y_r(i)\cos x'_i],\end{aligned}\tag{18}$$

where $\mathbf{U}^x_t$, $\mathbf{U}^y_t$ are translational and $\mathbf{U}^x_r$, $\mathbf{U}^y_r$ rotational amplitudes. The restrictions for the translational part of the molecular displacement are the same as those for atoms in special positions (15).

Two examples will illustrate the use of these conditions:

(1) *Thiourea* [atomic model: Yamamoto (1980); Kucharczyk, Paciorek & Uszynski (1986); molecular model: Gao, Gajhede, Mallinson, Petříček & Coppens (1987)], superspace group $P{:}nma{:}s\bar{1}1$, $d=1$.

(*a*) *Atomic model.* Atoms S and C are located on the mirror plane

$$m_y|(0,\tfrac{1}{2},0)\text{ with }\Gamma_I=-1.$$

Because of the non-uniqueness of s_I for elements with $\Gamma_I=-1$ [see de Wolff, Janssen & Janner (1981) and paper I], only the most convenient choices will be discussed, namely $s_I=0$ and $\frac{1}{2}$. The latter means that the center of symmetry is located at the origin of four-dimensional space. Let us select l harmonics. This means that $\alpha_n=n$, $x_1=nx$ and $x'_1=-nx+2\pi ns_I$ where n stands for the order of the harmonic. From (15) we have

$$\begin{pmatrix}U^x_\nu(n)_a\\U^x_\nu(n)_b\\U^x_\nu(n)_c\end{pmatrix}\sin(nx)=\begin{pmatrix}U^x_\nu(n)_a\\-U^x_\nu(n)_b\\U^x_\nu(n)_c\end{pmatrix}\times(-1)\sin(nx-2\pi ns_I)$$

$$\begin{pmatrix}U^y_\nu(n)_a\\U^y_\nu(n)_b\\U^y_\nu(n)_c\end{pmatrix}\cos(nx)=\begin{pmatrix}U^y_\nu(n)_a\\-U^y_\nu(n)_b\\U^y_\nu(n)_c\end{pmatrix}\cos(nx-2\pi ns_I).$$

For $s_I=0$ we have $U^x_\nu(n)_a=U^x_\nu(n)_c=0$ and $U^y_\nu(n)_b=0$; for $s_I=\frac{1}{2}$, $U^y_\nu(n)_a=U^y_\nu(n)_c=0$ and $U^x_\nu(n)_b=0$ for odd-order harmonics, and $U^x_\nu(n)_a=U^x_\nu(n)_c=0$, $U^y_\nu(n)_b=0$ for even-order harmonics.

(*b*) *Molecular model.* In the molecular model the translational part is restricted in the same way as in the atomic model, but there are reverse conditions for components of rotational displacements because $\det(\boldsymbol{\Gamma}^j_E)=\det(m_y)=-1$.

(2) *TTF-TCNQ* (Coppens, Petříček, Levendis, Larsen, Paturle, Gao & LeGrand, 1987), superspace group $P{:}P2_1/c{:}cmm$, $d=2$.

The TTF and TCNQ molecules are located at the centers of symmetry at (0, 0, 0) and ($\frac{1}{2}$, 0, 0) for which we have $(\boldsymbol{\Gamma}_I)_{ij}=-\delta_{ij}$. The simple harmonics with $\mathbf{q}_1$ and $\mathbf{q}_2$ were used for a description of the modulation. For a choice of origin at the center of symmetry in five-dimensional space, application of (17) leads to the conclusion that the translational and rotational waves are pure sin and cos waves, respectively ($\mathbf{U}^y_t=0$, $\mathbf{U}^x_r=0$).

Implementation of the expressions

A least-squares program, *JANA*5, has been written for two-dimensionally modulated crystals, using expression (13). It is based on the one-dimensional version *JANA* described earlier (paper I; Petříček, Coppens & Becker, 1985). The infinite summation (for the anharmonic case) is truncated by the additional condition $|m_i|\leq 4\,(i=1,\ldots,d)$. Similarly the satellite index is limited to 4. The displacements of the atoms can be refined individually or as a part of a rigid molecule. The program allows simultaneous refinement of atomic positional and thermal parameters and extinction parameters, in addition to the displacement coordinates. Up to eight waves can be selected as linear combinations of $\mathbf{q}_1$ and $\mathbf{q}_2$, which enables refinement of six higher-order harmonic contributions.

The program has been successfully tested with the 15K data on the insulating phase I of TTF-TCNQ, which is two-dimensionally modulated (Coppens, Petříček, Levendis, Larsen, Paturle, Gao & LeGrand, 1987). Additional applications to the insulating phases of low-dimensional organic solids are being planned.

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Small-Single-Crystal Diffractometry with Monochromated Synchrotron Radiation – the Wavelength-Dispersion Minimum Condition for Bragg Reflection Profile Measurement

BY A. McL. MATHIESON

Chemistry Department, La Trobe University, Bundoora, Victoria, Australia 3083

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Abstract

The interaction of a synchrotron beam incident on a 'perfect' monochromator crystal, M, and then on a small single crystal, c, is examined and the resultant 2D shape in $\Delta\omega$, $\Delta 2\theta$ space of Bragg reflections from c is deduced. This allows (a) identification of the components intrinsic to M which contribute to the shape, namely its effective aperture and angular bandpass, and (b) prediction of the change of shape with θ_c. Projection of the 2D shape onto the $\Delta\omega$ axis yields the corresponding 1D 'counter' profile and shows that, for Gaussian-like components, the full width at half maximum (FWHM) of the profile is $[p^2+q^2(t-t_{\min})^2]^{1/2}$ where p and q are constants, $t=\tan\theta_c/\tan\theta_M$ and $t_{\min}$ corresponds to the minimum dispersion condition. It is suggested that, for similar conditions, the relationship determining scan range should be of a similar functional form rather than the conventional linear relationship.

Introduction

The angular divergences involved in synchrotron beam lines are considerably smaller than those associated with conventional X-ray sources. Indeed, one might be inclined to conclude, following the discussion in Willis (1960), relating to divergence (a) ~ 0°, that this near-parallelism could lead to the minimum dispersion condition for the 'counter' profile in the synchrotron-radiation (SR) case occurring nearer $t=-2$ than $t=-1$, t being $\tan\theta_c/\tan\theta_M$. However, as we will show, this does not appear to be the case.

Nevertheless, the smaller divergence does provide a greater possibility, in single-crystal diffractometry on a beam line, of deriving quantitative estimates of the reflectivity curves of specimen crystals which, for 'imperfect' crystals, is closely allied to the mosaic spread, Mathieson (1984a). Even so, the influence of components intrinsic to the system, such as the effective aperture (illuminated length) of the monochromator crystal and the corresponding angular bandpass, cannot be ignored. It is therefore useful to establish their influence on the shape of Bragg reflections, especially in respect of change with scattering angle of the specimen crystal. This information can then be used to derive realistic estimates of reflectivity curves by deconvolution of experimental data, *cf.* Schneider (1977).

For the combination of a 'perfect' monochromator crystal, M, and a specimen crystal, c, of nominally zero mosaic spread, the 2D shape in $\Delta\omega$, $\Delta 2\theta^{(0)}$ space (for terminology, see Mathieson, 1983) of the Bragg reflection from c is deduced and its change with θ_c is studied. The corresponding change in the more generally used 1D 'counter' profile is then derived and compared with published data.

From the conclusions concerning counter profile width, observations are offered on a form of relationship, different from the accepted linear one, which would appear to be appropriate to determine scan range for small-crystal measurement on synchrotron sources. Use of this relationship should ensure uniform rather than variable truncation, *e.g.* Denne (1977), and hence estimates of integrated intensity which are consistent from reflection to reflection.

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