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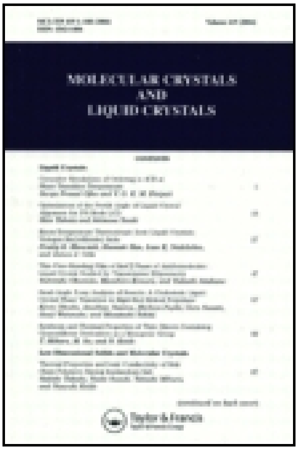

Molecular Crystals and Liquid Crystals

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Analysis of Multi-Wave Molecular Displacements in Modulated Crystals

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ANALYSIS OF MULTI-WAVE MOLECULAR DISPLACEMENTS IN MODULATED CRYSTALS

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Abstract A structure factor formalism for incommensurate modulated structures is described . It allows for several simultaneous translational and rotational displacements of molecules or molecular segments, which are considered as being rigidly displaced, and for the coexistence of several displacement waves in different parts of the crystal. Full use is made of the four-dimensional symmetry description of De Wolff, Janssen and Janner. Application to a data set on $(BEDT\text{-}TTF)_2 I_3$ is described briefly.

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INTRODUCTION

Scattering formalisms for modulated stru tures have been discussed by Overhauser[1], de Wolff[2], Axe[3], and Yamamoto et al.[4]. They take into account substitutional or displacive modulations of each of the atoms in the crystal. In molecular crystals, however, a translational or rotational displacement of a molecule, or one of its segments, is more likely because of the stiffness of the intramolecular linkages between atoms. Such a rigid body displacement analysis is related to the well-known treatments of thermal motion in crystal structure analysis. It has been applied to the molecular crystals of phenothiazine-7,7,8,8 tetracyanoquinodimethane (PTZ-TCNQ) by Kobayashi[5] and to the low temperature phase III of diphenyl by Baudour and Sanquer[6]. In both cases molecular displacement was dependent on the position of the origin of the unit cell. This choice is adequate when the number of molecules in the cell is limited to one per chain, but not sufficiently general when the cell contains more molecules, or several non-symmetry related chains. In the formalism discussed here the displacement center can be any point in the unit cell, such as the molecule's center of mass. It allows for several simultaneous translational and rotational displacements of the rigidly displaced body, and includes the possibility of several coexisting waves in different parts of the crystal. This latter feature is of particular importance for organic salts, in which cation and anion displacements will in general be different.

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SCATTERING FORMALISM

Let us consider a displacively modulated crystal in which the νth atom in the unit cell defined by $\underset{\sim}{n}$ is located at:

$$\underset{\sim}{r}_{n\nu} = \underset{\sim}{r}^{o}_{\nu} + \underset{\sim}{n} + u_{\nu}\{\underset{\sim}{q}.(\underset{\sim}{g}_{\nu} + \underset{\sim}{n})\} \quad (1)$$

where $\underset{\sim}{r}^{o}_{\nu}$ is the average position of atom ν, $\underset{\sim}{u}_{\nu}$ is the periodic vector field $\underset{\sim}{u}(x) = \underset{\sim}{u}(x+1)$, $\underset{\sim}{q}$ is the modulation vector and the vector $\underset{\sim}{g}$ determines the geometric center of the displaced entity.

In the molecular displacement model all atoms in the molecule share the same geometric center (in a variation of this model a "molecule" may be defined as a rigid group undergoing, for example, torsional displacements).

The model assumes a molecule to be displaced as a rigid unit. The displacement parameters are limited to translational and librational displacement coordinates. A convenient, but not unique, choice for the geometric center g is the center of mass of the rigidly displaced body: $\underset{\sim}{R} = \Sigma \underset{\sim}{m}_{i} \underset{\sim}{r}^{o}_{i} / \Sigma m_{i}$. For all atoms in the rigid body

$$\underset{\sim}{u}_{\nu} = \underset{\sim}{u}^{t}\{\underset{\sim}{q}.(\underset{\sim}{R} + \underset{\sim}{n})\} \quad (2a)$$

for translations, and :

$$\underset{\sim}{u}_{\nu} = \underset{\sim}{u}^{r}\{\underset{\sim}{q}.(\underset{\sim}{R} + \underset{\sim}{n})\} \times (\underset{\sim}{r}_{\nu} - \underset{\sim}{R}) \quad (2b)$$

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for rotations within a rectilinear approximation, where $\underset{\sim}{u}^{r}$ is a rotational displacive vector field which defines the direction and magnitude of the rotation.

We assume that the displacement vector field $\underset{\sim}{u}_{\nu}^{t}$ is a harmonic function, so that

$$\underset{\sim}{r}_{\underset{\sim}{n}\nu} = \underset{\sim}{r}_{\nu}^{0} + \underset{\sim}{n} + \underset{\sim}{U}_{\nu}\sin\{2\pi \underset{\sim}{q}.\{\underset{\sim}{R}_{\nu} + \underset{\sim}{n}) - \psi_{\nu}\} \qquad (3)$$

where $\underset{\sim}{U}_{\nu}$ and ψ_{ν}, are the displacement wave's amplitude and r phase respectively. A parallel expression for rotations is obtained with (2b).

The contribution of the νth atom to the structure factor is described as

$$F_{\nu}(\underset{\sim}{Q}) = f_{\nu}(\underset{\sim}{Q})\sum_{\underset{\sim}{n}=(0,0,0)}^{(N_1,N_2,N_3)} \exp\{2\pi i \underset{\sim}{Q}.(\underset{\sim}{r}_{\nu}^{0} + \underset{\sim}{n} + \underset{\sim}{U}_{\nu}\sin[2\pi q.(\underset{\sim}{R}_{\nu} + \underset{\sim}{n}) - \psi_{\nu}]\} \quad (4)$$

where $f_{\nu}(\underset{\sim}{Q})$ is the atomic scattering factor and $\underset{\sim}{Q}$ the scattering vector.

As shown elsewhere[7] this leads to the following structure factor expression for an incommensurate modulation :

$$F_{\nu}(h,k,l,m) = f_{\nu}(\underset{\sim}{Q})\exp(2\pi i \underset{\sim}{Q}.\underset{\sim}{r}_{\nu}^{0})J_{m}(2\pi \underset{\sim}{Q}.\underset{\sim}{U}_{\nu})(-1)^{m}$$
$$\exp(-2\pi i m \underset{\sim}{q}.\underset{\sim}{R}_{\nu})\exp(im\psi_{\nu}) \qquad (5)$$

in which satellite reflections are defined by non-zero values of m.

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Phase and amplitudon temperature factors[1,3] can be readily introduced into this expression.

TREATMENT OF SYMMETRY

Incommensurate crystals with one-dimensional modulation can be described as periodic arrangements in four-dimensional space[2,8] In order to sum over all atoms related by the four-dimensional symmetry operations we must express the displacement $\underset{\sim}{u}_{\nu}{}^{j}$ of the atom generated by symmetry element S_j to that of the "source" atom $\underset{\sim}{u}_{\nu}$. From de Wolff et al[8] (expression 3.16) we have:

$$\underset{\sim}{u}^{j}_{\nu}(\underset{\sim}{q}.\underset{\sim}{g}_{\nu}{}^{j}) = \mathcal{R}^{j}\underset{\sim}{u}_{\nu}\{\varepsilon_j(\underset{\sim}{q}.\underset{\sim}{g}^{j}_{\nu} - \delta_j + \underset{\sim}{m}^{*}.\underset{\sim}{g}_{\nu})\} \qquad (6a)$$

where $\underset{\sim}{m}^{*}$ is a reciprocal lattice vector equal to $\varepsilon\underset{\sim}{q} - \mathcal{R}^{-1}\underset{\sim}{q}$, and $\mathcal{R}$ represents the rotation operator. Substitution of this expression in (6a) leads to

$$\underset{\sim}{u}^{j}_{\nu}(\underset{\sim}{q}.\underset{\sim}{g}_{\nu}{}^{j}) = \mathcal{R}^{j}\underset{\sim}{u}\{\underset{\sim}{q}.\underset{\sim}{g}_{\nu} + \varepsilon_j(\underset{\sim}{q}.\underset{\sim}{s}_j - \delta_j))\} \qquad (6b)$$

which is more suitable for computational purposes.

The structure factor expression (4) becomes, after summation over all symmetry related atoms N_s

$$F_{\nu}(\underset{\sim}{Q}) = \sum_{j=1}^{N_s} f_{\nu}(\underset{\sim}{Q})\sum_{n=(0,0,0)}^{(N_1,N_2,N_3)} \exp\{2\pi i\underset{\sim}{Q}.(\underset{\sim}{r}_{\nu}{}^{j} + \underset{\sim}{n} + \mathcal{R}^{j}U$$

$$\sin\{2\pi\underset{\sim}{q}.\underset{\sim}{g}_{\nu} + 2\pi(\varepsilon_j\underset{\sim}{q}.\underset{\sim}{n} + \varepsilon_j(\underset{\sim}{q}.\underset{\sim}{s}_j - \delta_j)) - \phi_{\nu}\} \qquad (7)$$

or after summation over all unit cells:

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$$F_\nu(\underset{\sim}{Q}) = \sum_{j=1}^{N_s} f_\nu(\underset{\sim}{Q})\exp(2\pi i\underset{\sim}{Q}.\underset{\sim}{r}_\nu{}^j)J_m(2\pi\underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^j)(-\varepsilon_j)^m$$

$$\exp(-2\pi im\varepsilon_j\underset{\sim}{q}.\underset{\sim}{g}_\nu)\exp\{im(2\pi(\delta_j-\underset{\sim}{q}.\underset{\sim}{s}_j)+\varepsilon_j\phi_\nu)\} \qquad (8)$$

COMBINATION OF SEVERAL DISPLACEMENT WAVES

In many structures encountered in practice, several modulation waves with the same $\underset{\sim}{q}$ are superimposed.

Let us have n modulation sinus waves for some atom in the structure:

$$\underset{\sim}{u}_\nu = \sum_{i=1}^{n} \underset{\sim}{U}_{\nu i}\sin(2\pi\underset{\sim}{q}.\underset{\sim}{R}_\nu - \psi_i) \qquad (9)$$

where $\underset{\sim}{u}_{\nu i}$, ψ_i are the amplitude and the phase of the i-th wave respectively. This equation can be rewritten as:

$$\underset{\sim}{u}_\nu = \underset{\sim}{U}_\nu{}^x\sin(2\pi\underset{\sim}{q}.\underset{\sim}{R}_\nu) - \underset{\sim}{U}_\nu{}^y\cos(2\pi\underset{\sim}{q}.\underset{\sim}{R}_\nu) \qquad (10)$$

with $\underset{\sim}{U}_\nu{}^x = \sum_i\underset{\sim}{u}_{\nu i}\cos\psi_i$ and $\underset{\sim}{U}_\nu{}^y = \sum_i\underset{\sim}{u}_{\nu i}\sin\psi_i$.

This means that the (3+1) x n (e.g. $\underset{\sim}{u}_{\nu i}$, ψ_i, i=1---n) parameters of (9) have been reduced to 6 parameters (e.g. components of $\underset{\sim}{U}_\nu{}^x$ and $\underset{\sim}{U}_\nu{}^y$).

For the structure factor expression (4) only the projection $\underset{\sim}{Q}.\underset{\sim}{u}_\nu$ is needed. From (10) we have:

$$(\underset{\sim}{Q}.\underset{\sim}{u}_\nu) = (\underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^x)\sin(2\pi\underset{\sim}{q}.\underset{\sim}{R}_\nu) - (\underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^y)\cos(2\pi\underset{\sim}{q}.\underset{\sim}{R}_\nu) \qquad (11)$$

Introducing U_ν and χ such that

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$$U_\nu = \{(\underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^{x})^2 + (\underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^{y})^2\}^{1/2} \qquad (12)$$

$\sin \chi_\nu = \underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^{x}/U_\nu$, $\cos \chi_\nu = \underset{\sim}{Q}.\underset{\sim}{U}_\nu{}^{y}/U_\nu$ we get

$$\underset{\sim}{Q}.\underset{\sim}{u}_\nu = U_\nu \sin(2\pi \underset{\sim}{q}.\underset{\sim}{g}_\nu - \chi_\nu) \qquad (13)$$

which is in particular convenient for calculational purposes. In expression (4) $\underset{\sim}{Q}.\underset{\sim}{U}_\nu$ and ψ_ν are replaced by U_ν and χ_ν respectively. This method represents a considerable simplification compared with expression containing products of Bessel functions. It can be understood in that a projection of the combination of waves with the same wavelength leads to a simple sine wave.

For symmetry related atoms $\underset{\sim}{U}_\nu{}^{x}$ and $\underset{\sim}{U}_\nu{}^{y}$ in (13) are replaced by $\underset{\sim}{U}_\nu{}^{x}$ and $\underset{\sim}{U}_\nu{}^{y}$ before substitution into (8).

APPLICATION

Analysis of $(BEDT\text{-}TTF)_2I_3$; (ET_2I_3)

Crystals of the ambient pressure superconductor BEDT-TTF[9,10] show strong first order satellite reflections below 200K with a $\underset{\sim}{q}$ vector of $0.08\,\underset{\sim}{a}^* + 0.27\,\underset{\sim}{b}^* + 0.205\,\underset{\sim}{c}^*$ at 125K and super spacegroup $P^{P\bar{1}}_{\bar{1}}$.

In a first model, applied to a set of 3346 main and 1041 strong sattellite reflections one translational wave of variable amplitude $\underset{\sim}{U}_\nu$ was introduced for each of the

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molecular species I_3^- and ET. This treatment showed large modulations of I_3^- ($|U_\nu|$ = 0.281(1)Å directed along $\underset{\sim}{a}$ and ET ($|U_\nu|$ = 0.124(3)Å directed almost exactly along one of the inertial axes in the average plane of the ET (molecule).

Since the R factor on the satellite intensities (R(F)= 0.036 and 0.163 for the main and satellite reflections respectively) was higher than expected from the estimated accuracy of the intensities, the constraints of the model were relaxed by 1) introducing separate motion of the two independent atoms in I_3^-, 2) using both sine and cosine terms as in (11) for the terminal I atom (the phase of the central I atom is fixed by the center of symmetry) and the ET molecule and 3) introducing rotational displacements for ET.

A final refinement included 3209 satellite reflections with $I>3\sigma(I)$ gave R factors of 0.034 and 0.098 for the two groups of reflections.

The results summarized in table 1 show a significant deviation from pure translational displacement for I_3^-, which in part rotational, in part due to internal distortions. For ET a small but significant rotational displacement with amplitude equal to 1.24 degrees is observed.

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TABLE I. Modulation parameters in $(BEDT\text{-}TTF)_2I_3^-$

refinement 1 Rigid-body translations only

	Magnitude	x	y	z	ψ
I_3^-	0.281(1)	0.0428(2)	0.0008(2)	-0.022(1)	0°
ET	0.124(3)	0.0151(3)	-0.0047(3)	0.0022(1)	13.8(9)°

refinement 2, non-rigid iodide ion, both translations and rotations for ET, using combination of waves expression (19)

translations (in fractions of the unit cell edge)

(a)	U^x	U^y
$I_1^{(a)}$	0.0392(2)	-
	0.0009(2)	-
	-0.0039(2)	-
magnitude	0.271Å	
$I_2^{(a)}$	0.0431(2)	0.0030(2)
	0.0022(1)	-0.0076(2)
	-0.0003(1)	-0.0030(2)
magnitude	0.277Å	0.088Å
$ET^{(b)}$	0.0143(2)	0.0017(2)

	-0.0042(1)	-0.0021(1)
	-0.0013	0.0021(1)
magnitude	0.113Å	0. 41Å
rotation		
ET(b)	0.00232(6)	
	0.00172(5)	
	-0.00067(5)	
magnitude	1.24°	

(a) $\phi=0$ at the origin of the cell, which is the position of the central iodine atom. (b) $\phi=0$ at ET molecular center.

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