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Modulated Structure of Thiourea

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Abstract

The modulated structure of $SC(NH_2)_2$ has been determined using the superspace-group formalism, in the superspace group $P(Pnma)$:$(s\bar{1}1)$. Data include main reflections and up to third-order satellite reflections. Three harmonics have been included in the modulation. The superspace description of the modulation is discussed in detail and compared with that using symmetry modes. The final agreement factors are $R = 0{\cdot}046$, $R_0 = 0{\cdot}038$, $R_1 = 0{\cdot}046$, $R_2 = 0{\cdot}089$ and $R_3 = 0{\cdot}115$, for all reflections, main reflections, and first-, second- and third-order satellites, respectively. The structure was investigated in the commensurate phase with modulation wavevector $\mathbf{q} = \frac{1}{5}\mathbf{b}^*$, but the analysis was performed considering the modulation as incommensurate. The results essentially agree with those recently obtained by Tanisaki & Mashiyama [*Acta Cryst.* (1988), B**44**, 441–445] using a standard commensurate approach for a ninefold structure. Other structural models proposed recently were checked with negative results. The atomic modulations could be interpreted in terms of rigid-body modulated motions. The anharmonicity of the modulation functions is considerable, with non-negligible contributions of second and third harmonics. The form of the rigid-body modulation functions indicates an incipient soliton regime. Crystal data of the average structure: $M_r = 76{\cdot}07$, orthorhombic, *Pnma*, $a = 7{\cdot}5429\ (8)$, $b = 8{\cdot}5422\ (7)$, $c = 5{\cdot}4647\ (4)$ Å, $V = 352{\cdot}10\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 59{\cdot}1$ cm^{-1}, $F(000) = 160$, $T = 168$ K, wavevector $\mathbf{q} = 0{\cdot}111\mathbf{b}^*$.

1. Introduction

Thiourea, $SC(NH_2)_2$, and its deuterated form exhibit rich phase diagrams under external variables such as temperature, pressure and electric field. At atmospheric pressure and zero electric field, thiourea

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undergoes a phase transition at 200 K from the room-temperature phase with space group *Pnma* to an incommensurate modulated phase along the *b* axis. In the interval 171–169 K the modulation locks into a commensurate form corresponding to a wavevector $\mathbf{q} = \frac{1}{9}\mathbf{b}^*$. Below 169 K, the crystal transforms into a nonmodulated ferroelectric phase ($\mathbf{q} = 0$) with space group $P2_1ma$ (Denoyer & Currat, 1986). The transition temperatures are approximate and are taken from Westrum & McCullough (1963). The corresponding temperatures for the deuterated compound are 218, 193 and 191 K (Denoyer, Mouden, Currat, Vettier, Bellamy & Lambert, 1982).

The symmetry and structure of the modulated phase of thiourea are still under discussion. Earlier structure analyses of the incommensurate phase have been reported by Futama (1970), Tanisaki & Nakamura (1970), Shiozaki (1971) and McKenzie (1975). In Shiozaki (1971), X-ray diffraction data from a monocrystal at 187 K were interpreted in terms of a transverse sinusoidal modulation. No assumption was made about the symmetry of the distorting mode, which was only constrained by means of qualitative and practical arguments. McKenzie (1975) reanalyzed the data of Shiozaki (1971) and also considered new neutron diffraction data for the deuterated compound. The modulation was also taken to be sinusoidal and transverse but the molecules were considered rigid units. The distortion was further restricted by symmetry arguments. The rotations and displacements of the molecules with respect to the high-temperature structure, of space group *Pnma*, were taken to transform according to the irreducible representation τ_4 with wavevector $\mathbf{q} = \delta\mathbf{b}^*$ (antisymmetric for the mirror plane σ_x and the binary rotation C_{2y}).

Based on the data of Shiozaki (1971), Yamamoto (1980) attempted a new structure determination using superspace formalism (de Wolff, 1977; Janner & Janssen, 1980; Yamamoto, 1982). Two harmonics were included in the modulation. He assumed that τ_4 was not only the symmetry of the first harmonic but also of the second one and this was determinant for the choice of the superspace group. It was argued that the presence of a second harmonic reduced the symmetry to the superspace group $P(P2_1/a)$:(11) from the more symmetric $P(Pnma)$:($s\bar{1}1$), which would correspond if only the first harmonic of symmetry τ_4 was present.

The relation between superspace symmetry and the symmetry restrictions of Landau theory for the primary and secondary distortions in a modulated phase was analyzed in a general context in Pérez-Mato, Madariaga & Tello (1984*a*,*b*). It was shown how the superspace group could be directly determined from a knowledge of the symmetry (and eventually the direction in multidimensional representation space) of the order parameter or primary distorting mode. If a continuous or quasi-continuous character is assumed for the phase transition to the incommensurate modulated state, the presence of secondary modes (higher harmonics) was demonstrated to be irrelevant for the superspace symmetry of the modulated phase. The secondary modes were shown to be compatible with the superspace group determined by the primary mode. Also the later work of Heine & Simmons (1987), which for simple cases reconsidered superspace symmetry in the frame of Landau theory, used this property of secondary modes as an implicit assumption.

According to these general properties, the superspace group $P(Pnma)$:($s\bar{1}1$) was proposed for the incommensurate modulated phase of thiourea (Pérez-Mato, Madariaga & Tello, 1984*c*). This proposal was at variance with the structure model of Yamamoto (1980). The constraints resulting from the proposed superspace group are equivalent to the assumption that the modulation is formed by the superposition of symmetry modes of wavevectors $n\mathbf{q} = n\delta\mathbf{b}^*$ with symmetries τ_4 and τ_1 for n odd and even respectively, provided that their relative global phases satisfy (9) (see §3).

Takahashi, Onodera & Shiozaki (1987, 1988) performed a new structural analysis at 175 K using a rigid-molecule model with a single harmonic. Besides the predominant transverse component, a longitudinal translational component was also included in the modulation. Symmetry-mode restrictions were used only partially. Some of the constraints resulting from the τ_4 symmetry of the first harmonic were confirmed by the results of the refinement.

The symmetry restrictions on the modulated structure of thiourea have been also discussed in terms of symmetry modes and Landau theory in Simonson, Denoyer & Currat (1985). The symmetry constraints on the symmetry modes contributing to the modulation were fully determined. The three first harmonics of the modulation were taken into account. It was argued that the superspace group of the incommensurate phase was not uniquely determined by the primary mode since the introduction of secondary modes in the Landau minimization procedure can lead to quite arbitrary relative shifts of the global phases of the different harmonics, so that the superspace group of the structure may be $P(Pn2_1a)$:($s11$) instead of $P(Pnma)$:($s\bar{1}1$). In the following, we will denote this particular noncentrosymmetric structural model as the 'free-harmonics' model. It was also claimed that the symmetry-mode description or 'Landau approach' leads to additional restrictions on the modulation, compared with the use of the superspace group. This work raised doubts about the comprehensiveness and limits of the superspace-symmetry description of modulated phases. The

weight of secondary modes in the global distortion of a modulated phase increases in a continuous manner as temperature is lowered. Thus, if the superspace symmetry of a modulated phase depends on the degree of relevance of secondary modes, the symmetry would not be unique for the whole range of the incommensurate phase, and the concept of superspace symmetry would be ill-defined.

The results of Simonson *et al.* (1985) were revised by Pérez-Mato & Madariaga (1987). It was shown that a correct minimization of the Landau potential, including the second and third harmonics, results in simple relations between the relative phases of the harmonics, maintaining $P(Pnma)$:$(s\bar{1}1)$ as the superspace group of the structure. A breaking of this superspace symmetry leading to the 'free-harmonics' model could only happen through an additional first-order phase transition to a new incommensurate phase, if higher-order terms in the Landau expansion eventually become relevant. But the observation of such an additional phase transition inside the range of the incommensurate phase has not been reported.

Simonson, Denoyer & Currat (1987) consider, however, that the minimum of the Landau free energy associated with the superspace group $P(Pnma)$:$(s\bar{1}1)$ represents only a 'good first approximation' (for small values of the order parameter) of the stable solution which should correspond to the 'free-harmonics' model. At the same time, in a parallel argument, they insist on the possibility of a phase transition between the two structural models corresponding to the two superspace groups discussed. The mechanism of such a transition is supposed to be present already in the Landau expansion up to sixth order in order parameter.

Recently, a refinement of the modulated structure of the deuterated compound in the $\delta = \frac{1}{9}$ phase has been reported (Simonson, Denoyer, Currat & Vettier, 1988) using neutron diffraction. First and third harmonics of symmetry τ_4 were included in the modulation. About 300 independent reflections were used in the refinement. The refined structure differs considerably from those reported previously but the agreement factor attained is only 0·28. Although this work was presented in support of the 'free-harmonics' model with $P(Pn2_1a)$:$(s11)$ as the most probable symmetry for the structure, the structure refinement was performed setting to zero the phases of both harmonics, so that in fact they were chosen to satisfy automatically the relation required for the structure to have the superspace symmetry $P(Pnma)$:$(s\bar{1}1)$. In any case, the accuracy of the refinement seems to be too low to distinguish the expected subtle differences on the diffraction diagram resulting from the different models.

Another recent analysis of the modulated structure of thiourea in the incommensurate phase has been reported by Gao, Gajhede, Mallinson, Petricek & Coppens (1988). In this work, a fourth superspace group, $P(P2_1ma)$:$(1\bar{1}1)$, was considered to describe the symmetry properties of the structure and the properties of its diffraction diagram. First and second harmonics were included in the modulation. The reported agreement factors, however, compare unfavorably with those attained with other models, like for instance that of Takahashi *et al.* (1988). In Table 1, a brief summary is given of the main characteristics of all these previous diffraction analyses of the modulated structure of thiourea.

Table 1. *Characteristic parameters of structure analyses of the modulated phase of thiourea*

T is the temperature and N_0, N_1, N_2, N_3 represent the number of independent observed reflections (main, first-, second- and third-order, respectively) included in the analysis. The global agreement factor R and the partial ones, R_m, corresponding to the different sets of reflections, are also listed.

T	N_0	N_1	N_2	N_3	R	R_0	R_1	R_2	R_3	Ref.
173	—	—	—	—	0·19	—	—	—	—	*a*
187	92	92	37	—	0·16	—	—	—	—	*b*
187	92	92	37	—	0·19	—	—	—	—	*c*
205	37	72	72	72	0·40	—	—	—	—	*d*
187	92	92	37	—	0·09	0·084	0·109	0·197	—	*e*
175	—	78	—	—	—	—	0·127	—	—	*f*
175	104	78	—	—	0·054	0·038	0·118	—	—	*g*
191	90	80	—	99	—	—	0·28	—	?	*h*
184	315	489	415	—	0·106	0·063	0·148	0·355	—	*i*
173	322	514	290		0·076	0·048	0·106	0·202	—	*i*
170	314	546	358	219	0·048	0·037	0·042	0·106	0·161	*j*
168	344	568	327	180	0·046	0·038	0·046	0·089	0·115	*k*

References: (*a*) Futama (1970); (*b*) Shiozaki (1971); (*c*) McKenzie (1975), data of Shiozaki (1971); (*d*) McKenzie (1975), deuterated compound; (*e*) Yamamoto (1980), data of Shiozaki (1971); (*f*) Takahashi *et al.* (1987); (*g*) Takahashi *et al.* (1988); (*h*) Simonson *et al.* (1988), deuterated compound; (*i*) Gao *et al.* (1988); (*j*) Tanisaki & Mashiyama (1988); (*k*) present results.

It is clear from the discussion above that some important questions remain to be clarified concerning the structure of the modulation in thiourea. Even its superspace symmetry is unclear, since up to now four different superspace groups have been proposed. The question of the comprehensiveness and coherency of the superspace description has also been raised. If different structure analyses are compared, the role played by second and third harmonics in the modulation is unclear. The existence of a longitudinal component and its importance compared with the transverse modulation requires further clarification. All these questions can be elucidated by means of an accurate structure diffraction analysis, which may allow discrimination between the different models. The hypothetical existence of an incommensurate–incommensurate phase transition can also be checked by this type of study. In the present paper, a new structure determination by X-ray diffraction of the modulated structure of thiourea is reported.

It has been argued (Simonson *et al.*, 1988) that X-ray diffraction may not be suitable for structural analysis in compounds like thiourea because of the

effects of radiation damage. However, these effects seem to be limited to an anomalous temperature variation of the modulation wavevector and eventually a decrease of long-range order in the modulation (André, Durand, Denoyer, Currat & Moussa, 1987; Durand & Denoyer, 1988). On the other hand, it is known that the atomic modulation in modulated structures is usually rather independent of the particular value of the modulation wavevector, being essentially the same even at successive commensurate lock-in values of the modulation wavevector. Therefore, it is expected that radiation damage effects have not essentially distorted the results of the present structural analysis. The high quality of the refinement results supports this assumption.

We were especially interested to observe any deviation from the expected centrosymmetric superspace symmetry, $P(Pnma)$:$(s\bar{1}1)$. As these deviations, if they exist, are expected to increase with the modulation amplitude, the diffraction analysis was performed as close as possible to the ferroelectric ($\delta = 0$) phase, inside the range where the modulation is locked into the value $\delta = \frac{1}{9}$. As only a few harmonics (compared with the high order of the commensurate cell) are present in the modulation, this commensurate modulated structure and its symmetry can be described in the superspace formalism.

The present structural analysis indicates that the centrosymmetric superspace group $P(Pnma)$:$(s\bar{1}1)$ properly describes the symmetry properties of the modulated structure up to its low-temperature limit. Nevertheless, a refinement using the 'free-harmonics' model with superspace group $P(Pn2_1a)$:$(s11)$ was also attempted without success.

In the following section the experimental details of the X-ray measurements are described. Section 3 is dedicated to a description of the superspace symmetry and its consequences on the structural modulation and the diffraction diagram. The refinement procedure is then summarized (§4). Finally, the structure is described and compared with the results of previous studies (§5).

2. Experimental

High-purity thiourea, $SC(NH_2)_2$, was obtained after several recrystallizations of the commercial product in aqueous solution. Crystals suitable for X-ray diffraction were grown by slow evaporation at room temperature of an aqueous solution of the purified compound.

The X-ray measurements were performed with a CAD-4 diffractometer equipped with an open gas-flow cryostat (Cosier & Glazer, 1986). The temperature stability was within $\pm 0{\cdot}1$ K during short periods and $\pm 0{\cdot}2$ K during the collection of the intensities.

Preliminary studies of the stability range of the modulated structure and the characteristics of its diffraction diagram were first performed. In the present work, the crystallographic axes are referred to the setting in which the room-temperature space group is *Pnma*. Lattice constants at 293 K are $a = 7{\cdot}6633$ (4), $b = 8{\cdot}5598$ (4) and $c = 5{\cdot}4909$ (3) Å. The temperature dependence of the intensity and position of some satellite reflections were determined. Accurate values of the wavevector were obtained from the profile of scanned satellite reflections, along the $\mathbf{b}^*$ direction. At each temperature and before scanning the reflections, the orientation matrix of the crystal was refined from the angles of ten high-angle ($2\theta = 140°$) well-centered main reflections. The scans were performed with step-by-step (0·002) stationary measurements of the diffracted intensity along the k index. Once the wavevector was determined, the intensity of the satellite reflection was obtained from an ω scan. While first-order satellites were clearly detected at 200 K, satellites of second and third order could be clearly observed below 197 K. Fig. 1 shows the temperature dependence of the intensity of satellite $(1, 2 + 3\delta, 1)$ [(1, 2, 1, 3) in the four index notation]. This figure shows that the phase transition to the ferroelectric ($\delta = 0$) phase takes place at approximately 166 K. Above this value a narrow 'plateau' can be observed, which corresponds to the modulated commensurate phase with $\mathbf{q} = \frac{1}{9}\mathbf{b}^*$.

In order to analyze the modulated structure very near to the final lock-in transition, the collection of intensities was performed about 2 K above the observed transition. Accordingly, the temperature of the controller was fixed at 168 K. At this temperature, the modulation wavevector has the value $\mathbf{q} = 0{\cdot}111\mathbf{b}^* \simeq \frac{1}{9}\mathbf{b}^*$, as determined from the profiles of reflections (4, 0, 0, 3) and (3, 1, 2, 3) (Fig. 2). Similar good-quality profiles could be observed for other high-order satellite reflections.

The temperature measured for the ferroelectric lock-in phase transition differs by about 3 K from the values reported previously (see §1). The reason for such a difference is unclear. All our temperatures

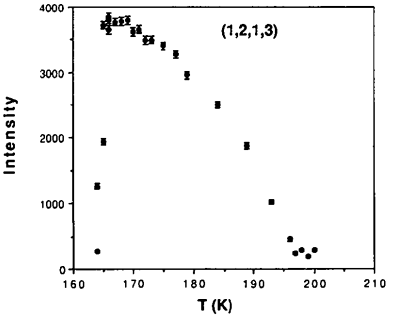

Fig. 1. Temperature dependence of the intensity of the satellite reflection $(1, 2 + 3\delta, 1)$.

refer to the values given by the controller and were measured a few millimeters away from the crystal in the nozzle of the cryostat. Although a small temperature gradient is expected with respect to the sample, previous calibrations of the cryostat indicate deviations smaller than 1 K.

The crystal data and the data-collection parameters are summarized in Table 2. The intensities were measured in the following sequence: first, satellite reflections with $m > 0$; next, the same sequence for $m < 0$; and finally, the main reflections. Only main reflections were used as check reflections. The reduction of the intensities to moduli of structure factors was performed by means of a local version of the program system *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), modified for one-dimensionally modulated structures. Intensities were corrected for absorption, intensity decay and Lorentz–polarization factors.

3. Symmetry of the modulated structure

Even if the modulated structure was measured at the $\delta = \frac{1}{9}$ commensurate phase, the refinement was performed considering the structure as incommensurate.

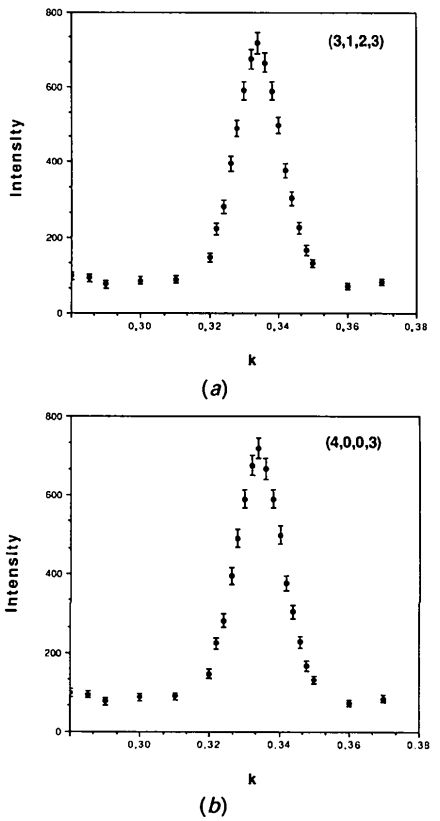

Fig. 2. Intensity profiles of the satellite reflections (*a*) (3, 1 + 3δ, 2) and (*b*) (4, 0 + 3δ, 0) at 168 K in the modulated phase. The modulation vectors calculated for both reflections are $\mathbf{q} =$ 0·334**b*** and 0·332**b***, respectively.

Table 2. *Summary of experimental data*

Crystal form	Prismatic
Crystal size (cm)	0·015 × 0·0218 × 0·0243
Reflections for lattice constants	19 ($16 < \theta < 70°$)
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0·61
Check reflections	3 main reflections
*hkl*0 range	0/9 −10/10 −6/6 0/0
hklm range	0/8 0/9 0/6 −3/3
Scan width (°)	0·6 + 0·15tanθ
Scan speed (° min^{-1})	0·3 to 4·16
Number of reflections	
Total	4167
Main	1434
Satellite	2733
Independent reflections	
Main (observed $I > 3\sigma$)	359 (344)
First-order satellite	639 (568)
Second-order satellite	629 (327)
Third-order satellite	629 (180)
R_{int} without absorption	0·0297
R_{int} with absorption	0·0193
Transmission (max./min.)	0·0173/0·0105
Weights	$1/\sigma^2$
Max. (shift/e.s.d.)	0·06

The differences between a commensurate and an incommensurate description of the observed diffraction can be considered negligible in the present case. These possible differences would result from the coherent superposition of high-order satellites with the lower-order ones. In our case, for instance, satellites of ninth order will superpose with main reflections, satellites of eighth order with first-order satellites, seventh-order satellites with second-order ones, sixth-order satellites with third-order ones, and so on. Using an incommensurate model for the structure is equivalent to neglecting these superposition effects. As satellites beyond the third order are undetected in both the investigated commensurate phase and the contiguous incommensurate phase, it is reasonable to expect that these superposition effects are negligible.

If τ_4 (with $\mathbf{q} = \delta\mathbf{b}^*$) is taken as the irreducible representation corresponding to the order parameter of the modulated structure in thiourea, the superspace symmetry of this structure is expected to be described by the superspace group $P(Pnma)$:$(s\bar{1}1)$ (see §1). Therefore, this was our first choice for the structure refinement. The elements of this group (obviating the superlattice translations) are given in Table 3. The operations are indicated in the form $\{\mathbf{R}\,|\,\mathbf{t},\tau\}$, where $\mathbf{R}$ is the rotational operation, $\mathbf{t}$ indicates the fractional translation in the real space and τ is the shift along the internal space (Yamamoto, 1982, Pérez-Mato, Madariaga, Zuñiga & Garcia-Arribas, 1987). As can be seen in the table, the internal translation τ depends in general on the value of the modulation wavevector and on the arbitrary choice of origin along the internal space. The origin along the internal space is fixed by the value given to the phase φ in Table 3.

The extinction rules resulting from a given superspace-symmetry operation $\{\mathbf{R}\,|\,\mathbf{t},\tau\}$ can be

Table 3. *Representative elements of the superspace group P(Pnma):(s$\bar{1}$1) with* $\mathbf{q} = \delta\mathbf{b}^*$

The first four elements (with the same superlattice) generate the subgroup $P(Pn2_1a)$:(s11).

$\{E\|0,0,0,0\}$,	$\{I\|0,0,0,\varphi/\pi\}$
$\{\sigma_x\|\frac{1}{2},\frac{1}{2},\frac{1}{2},-\delta/2+\frac{1}{2}\}$	$\{C_{2x}\|\frac{1}{2},\frac{1}{2},\frac{1}{2},-\delta/2+\frac{1}{2}+\varphi/\pi\}$
$\{C_{2y}\|0,\frac{1}{2},0,-\delta/2+\frac{1}{2}\}$	$\{\sigma_y\|0,\frac{1}{2},0,-\delta/2+\frac{1}{2}+\varphi/\pi\}$
$\{\sigma_z\|\frac{1}{2},0,\frac{1}{2},0\}$	$\{C_{2z}\|\frac{1}{2},0,\frac{1}{2},\varphi/\pi\}$

Generators of the superlattice

$$\{E|1,0,0,0\},\ \{E|0,1,0,-\delta\},\ \{E|0,0,1,0\},\ \{E|0,0,0,1\}$$

easily deduced from the corresponding symmetry relation for the structure factor (Janner & Janssen, 1980, Pérez-Mato, Madariaga *et al.*, 1987):

$$F(\tilde{\mathbf{R}}\mathbf{H}) = F(\mathbf{H})\exp[-i2\pi(\mathbf{H}.\mathbf{t} + m\tau)], \qquad (1)$$

where $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ is any diffraction vector. For $\tilde{\mathbf{R}}\mathbf{H} = \mathbf{H}$, the extinction is then obliged if

$$\exp[-i2\pi(\mathbf{H}.\mathbf{t} + m\tau)] \neq 1. \qquad (2)$$

Accordingly, for the chosen superspace group, the following reflections are extinct:

$$\begin{aligned} &(0klm) \quad && k + l + m = \text{odd} \\ &(hk0m) \quad && h = \text{odd}. \end{aligned} \qquad (3)$$

These two extinction rules are caused by the symmetry operation $\binom{\sigma_x}{s}$ $(\{\sigma_x|\frac{1}{2},\frac{1}{2},\frac{1}{2},-\delta/2+\frac{1}{2}\})$ and $\binom{\sigma_z}{1}$ $(\{\sigma_z|\frac{1}{2},0,\frac{1}{2},0\})$ respectively, and include as subcases those resulting from the other operations. The same rules are also valid for the less-symmetric superspace group $P(Pn2_1a)$:(s11) since it also includes these two operations (see Table 2).

The reflections collected generally satisfy extinction conditions (3). Only a few forbidden reflections were detected as observed. Among them, the most remarkable cases were some main reflections. In Gao *et al.* (1988) a similar observation led the authors to discard the two mentioned superspace groups and to choose the superspace group $P(P2_1ma)$:(1$\bar{1}$1). In the present case, however, we investigated the particular characteristics of these reflections, and in general the extinction violation could be traced back to spurious intensity of neighboring strong main reflections. We therefore considered that the symmetry properties of the diffraction diagram are well described by either the superspace group $P(Pnma)$:(s$\bar{1}$1) or $P(Pn2_1a)$:(s11). The choice, between these two groups, of the centrosymmetric one was then made taking into account the prediction of Landau theory (Pérez-Mato *et al.*, 1984*a*,*c*). The present symmetry choice was confirmed by the refinement results.

In a modulated phase of wavevector $\mathbf{q}$, the atomic position, $\mathbf{r}(\mathbf{l},\mu)$, of atom μ in cell $\mathbf{l}$ can be described in the form:

$$\mathbf{r}(\mathbf{l},\mu) = \mathbf{l} + \mathbf{r}_0^\mu + \tfrac{1}{2}\sum_n \mathbf{u}_n^\mu \exp[i2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu)]. \qquad (4)$$

The vector $\mathbf{r}_0^\mu$ represents the average atomic position and $\mathbf{u}_n^\mu = \mathbf{u}_{-n}^{\mu\,*}$.

If two atoms, μ and ν, are related in the average structure by the symmetry operation $\{\mathbf{R}|\mathbf{t}\}$ ($\{\mathbf{R}|\mathbf{t},\tau\}$ being an operation of the structure superspace group), the complex Fourier vectorial amplitudes, $\mathbf{u}_n^\mu$ and $\mathbf{u}_n^\nu$, describing their modulations according to (4), satisfy the following relation (Pérez-Mato, Madariaga & Tello, 1986; Pérez-Mato, Madariaga *et al.*, 1987):

$$\mathbf{u}_n^\nu = \mathbf{R}\mathbf{u}^\mu{}_{\Gamma(\mathbf{R})n}\exp(-i2\pi n\tau_0), \qquad (5)$$

where $\Gamma(\mathbf{R})$ is $+1$ (-1) if $\mathbf{Rq} = +\mathbf{q}$ $(-\mathbf{q})$ and $\tau_0 = \tau + \mathbf{q}.\mathbf{t}$. If atom μ is in a special position so that $\mu = \nu$, (5) becomes a symmetry restriction for the corresponding Fourier amplitudes:

$$\mathbf{u}_n^\mu = \mathbf{R}\mathbf{u}^\mu{}_{\Gamma(\mathbf{R})n}\exp(-i2\pi n\tau_0). \qquad (6)$$

In the case of superspace group $P(Pnma)$:(s$\bar{1}$1), a symmetry restriction of this type results from the superspace-group operation $\{\sigma_y|0\frac{1}{2},0,-\delta/2+\frac{1}{2}+\varphi/\pi\}$ for atoms or rigid bodies lying on the plane m in the average structure. If we define a new phase ψ, so that $\varphi = \pi/2 - \psi$, the value of τ_0 for the mentioned operation reduces to $-\psi/\pi$ (mod Z). The corresponding condition (6) reduces to $u_{n,x,z} = u_{-n,x,z}\exp(i2n\psi)$ and $u_{n,y} = u_{-n,y}\exp(i2n\psi + i\pi)$. Considering the complex conjugation relation between u_n and u_{-n}, the modulation in (4) for these atoms can then be put in the simple form:

$$\begin{aligned} &\sum_{n>0} A_{n,x}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi] \\ &\sum_{n>0} A_{n,y}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi + \pi/2] \\ &\sum_{n>0} A_{n,z}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi], \end{aligned} \qquad (7)$$

where the amplitudes $A_{n,i}$ $(i = x, y, z)$ are real quantities.

Obviously, a symmetry relation analogous to (5) exists for small rotational degrees of freedom, if rigid bodies centered on the plane m are considered. Consequently, a symmetry restriction of the Fourier amplitudes, R_n^μ, describing the rotational modulation and similar to (6), must also be introduced, taking into account that the three rotational components transform as a pseudovector. This means that inversely to the translational modulation, the rotational modulation can be described by:

$$\begin{aligned} &\sum_{n>0} R_{n,x}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi + \pi/2] \\ &\sum_{n>0} R_{n,y}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi] \\ &\sum_{n>0} R_{n,z}\cos[2\pi n\mathbf{q}.(\mathbf{l} + \mathbf{r}_0^\mu) + n\psi + \pi/2]. \end{aligned} \qquad (8)$$

The restrictions on the harmonics of the structural modulation, given by (5), (7) and (8) are equivalent

to those obtained by the symmetry-mode approach of Simonson *et al.* (1985). It can be easily checked that relation (5), together with the restrictions (7) and (8), is enough for atoms or rigid bodies lying on the plane m to ensure that the odd and even harmonics of the modulation have τ_4 and τ_1 symmetry, respectively, as required in the Landau model. Equations (7) and (8) also introduce a fixed relation between the global phases ψ_n of the different harmonics:

$$\psi_n = n\psi(\mathrm{mod}\,\pi). \qquad (9)$$

Thus, the mode approach is fully equivalent to the superspace description in the superspace group $P(Pnma)$:$(s\bar{1}1)$, if the global phases of the different harmonics are assumed to satisfy (9). From a simple Landau model, relation (9) can be expected to be satisfied in the modulated phase of thiourea, so that the superspace group $P(Pnma)$:$(s\bar{1}1)$ also describes the symmetry of the structure if higher harmonics are relevant in the modulation (Pérez-Mato & Madariaga, 1987). In general, the breaking of relation (9) can only happen through a further hypothetical first-order phase transition into a new incommensurate phase, if very high-order terms in the Landau expansion become relevant; this possibility has not been detected experimentally.

Simonson *et al.* (1985, 1987) argue that relation (9) is not satisfied in general and the superspace symmetry reduces to the superspace group $P(Pn2_1a)$:$(s11)$. As can be seen from the preceding analysis, a structural modulation of the type described above but excluding the phase relation (9) (what we called in §1 the 'free-harmonics' model) introduces additional structural restrictions to those resulting from the superspace group $P(Pn2_1a)$:$(s11)$. The validity of this model was investigated with negative results, by means of an additional refinement process in the superspace group $P(Pn2_1a)$:$(s11)$, introducing the additional restrictions mentioned above through linear constraints of the refined structural parameters.

4. Structure refinement

Structure refinement was performed by means of a new version of the program described in detail in Paciorek & Kucharczyk (1985) and Paciorek & Uszyński (1987). This last version has been updated and now the user can select one of two possible parametrizations of the atomic modulation functions:

$$u(t) = \sum_{n>0} A_n\cos[2\pi(nt + \phi_n)] \qquad (10)$$

$$u(t) = \sum_{n>0} [a_n\cos(2\pi nt) + b_n\sin(2\pi nt)] \qquad (11)$$

where u is a modulation function related to any structural parameter to be refined, and t is the internal (continous) coordinate ranging from 0 to 1, which corresponds to the dense set of fractional values $\mathbf{q}.(\mathbf{l} + \mathbf{r}^{\mu})$ in (4). Although both parametrizations are equivalent, the first one may be important for cases when the constraint equations between amplitudes and/or phases should be included during structure refinement. These constraint equations are nonlinear when the second parametrization is selected. Furthermore, when only one harmonic is considered, the amplitudes can be refined using only main reflections at the first stage of the refinement (phases are fixed at arbitrary values). This approach also gives the correct (in the least-squares method sense) values of the standard deviations of amplitudes and phases (Pérez-Mato, Madariaga & Zuñiga, 1989).

As before, zero-order harmonics are not included. Instead, the average structure parameters are simultaneously refined. The program also refines scale factors and the extinction correction in the form $F_c^{\mathrm{corr}} = F_c/(1 + 10^{-5}\mathrm{ext}F_c^2/\sin\theta)^{1/4}$, where ext is the refined quantity. The quantity minimized is the weighted R factor. The refinement is based on F values and the program always works in the full-matrix mode.

The structure refinement of thiourea was performed in several steps. The average structure was first refined using only main reflections. Starting parameters were taken from Elcombe & Taylor (1968). Subsequently, the displacive modulation (as described in §3) was introduced and the whole structure was refined using all observed reflections. The arbitrary global phase ψ in (7) was set to zero. According to the highest order of observed satellite reflections, the maximum number of harmonics in the modulation functions was set to three. The temperature factors (anisotropic for non-H atoms and isotropic for H atoms) were assumed to be unmodulated. At the end of the refinement process, extinction corrections were introduced. The final R factors are presented in Table 4.

Although the refinement results are satisfactory, the partial agreement factors and the scaling ratios indicated a clear asymmetry of the refinement between the $m < 0$ and $m > 0$ satellite reflections. For instance, in the case of first-order satellites, the partial R factors were 0·044 and 0·060, respectively. The intensity decay of satellite reflections was usually observed to be faster than that of main reflections (Gao *et al.*, 1988). Taking into account the data-collection sequence indicated in §2, the main reason for this asymmetry is probably the fact that only main reflections were used for the intensity decay correction. Consequently, at this stage of the refinement, three independent scale factors, for main

Table 4. *Partial R factors of the modulated structure of thiourea*

m is the order of satellite reflections, *N* is the number of observed reflections and *R* is the agreement factor.

	N	*R*	*R**	*R*†
All observed reflections	1419	0·046	0·050	0·060
$\|m\| = 0$	344	0·038	0·041	0·037
$\|m\| = 1$	568	0·046	0·052	0·050
$\|m\| = 2$	327	0·089	0·091	0·184
$\|m\| = 3$	180	0·115	0·124	0·471

* *R* factors for the refinement with a single scale factor.
† *R* factors for the model with only first-order harmonics.

reflections, satellite reflections with $m < 0$, and satellite reflections with $m > 0$, were intrduced. By this means, these decay effects were taken into account, at least partially. In the subsequent refinement process, the asymmetry decreased considerably and the fit improved significantly. The average structure and the modulation parameters are presented in Tables 5 and 6.* The strongest main reflection (0200) was marked as non-observed owing to high extinction effects and was not taken into account in the least-squares refinement (but it contributes to the *R* factor for all reflections).

A parallel refinement, with only a first-order harmonic in the modulation, was also performed in order to establish the importance of higher harmonics. The agreement factors for this model are also presented in Table 4. Refinement results were not satisfactory, especially for second- and third-order satellite reflections, which are obviously more affected by the higher-order harmonics of the displacive modulation.

Additional calculations were performed to check the 'free-harmonics' model of Simonson *et al.* (1985, 1987). The symmetry of the structure was lowered to the noncentrosymmetric superspace group $P(Pn2_1a)$:-$(s11)$, but according to the model, the average structure was maintained centrosymmetric and the modulation functions for atoms lying on the plane *m* were constrained to form (7), with the global phases, ψ_n, in the second and third harmonics as free parameters to be refined, instead of satisfying (9). The arbitrary global phase of the first harmonic was kept zero. All these structual restrictions were introduced by means of linear constraint equations on the phases of the different atomic modulation functions. In addition, the amplitudes and phases of the modulations, corresponding to pairs of atoms related by the plane *m* in the average structure, had to be constrained by means of (5) to maintain the required symmetry mode. The resulting phase shift between the modulation harmonics was of the order of magnitude of the standard deviation for the phase parameters. No improvement of the agreement with the high-symmetry model was obtained. Full refinement within the noncentrosymmetric superspace group $P(Pn2_1a)$:$(s11)$ was also attempted with similar negative results.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52127 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Average structure of thiourea*

$U_{eq} = \frac{1}{3}\sum_i U_{ii}$ for non-H atoms. Standard deviations are given in parentheses.

	x	*y*	*z*	U_{eq} (or *U*) (Å²)
S	−0·00760 (5)	0·25000	0·11473 (7)	0·029
C	0·08812 (20)	0·25000	−0·16772 (30)	0·028
N	0·12754 (14)	0·38277 (16)	−0·27982 (20)	0·040
H1	0·1606 (23)	0·3796 (24)	−0·4266 (29)	0·031
H2	0·0921 (20)	0·4699 (25)	−0·2145 (27)	0·013

Table 6. *Amplitudes* ($\times 10^5$) *and phases* ($\times 10^3$) *of the modulation functions of thiourea*

Modulating functions are: $u_i(t) = \sum_{n=1\ldots3} a_{i,n}\cos[2\pi(nt + \varphi_{i,n})]$, $i = x, y, z$. Standard deviations are given in parentheses. Starred parameters are fixed.

		First harmonic		Second harmonic		Third harmonic	
		$a_{i,1}$	$\varphi_{i,1}$	$a_{i,2}$	$\varphi_{i,2}$	$a_{i,3}$	$\varphi_{i,3}$
S	*x*	3418 (19)	0*	139 (8)	500*	150 (6)	500*
	y	40 (6)	250*	28 (7)	750*	5 (3)	750*
	z	1204 (11)	500*	128 (7)	500*	97 (12)	0*
C	*x*	1201 (29)	0*	135 (25)	500*	24 (26)	0*
	y	107 (24)	750*	1 (30)	750*	42 (34)	250*
	z	2758 (39)	500*	67 (35)	500*	235 (45)	0*
N	*x*	320 (21)	28 (11)	168 (18)	431 (18)	105 (20)	957 (33)
	y	318 (15)	733 (8)	15 (18)	620 (216)	74 (22)	241 (63)
	z	3406 (31)	493 (1)	33 (27)	240 (103)	343 (36)	983 (17)
H1	*x*	688 (233)	65 (62)	212 (234)	825 (151)	96 (249)	849 (401)
	y	346 (196)	734 (88)	220 (243)	835 (188)	163 (296)	472 (287)
	z	4384 (217)	504 (13)	712 (274)	934 (71)	820 (412)	962 (90)
H2	*x*	653 (196)	64 (49)	176 (176)	382 (155)	111 (216)	129 (304)
	y	209 (160)	372 (121)	386 (193)	404 (86)	346 (230)	164 (141)
	z	3662 (281)	469 (13)	325 (299)	515 (126)	322 (310)	144 (151)

5. Concluding remarks

The consistency of the determined structure model with a rigid-body picture of the thiourea molecules (see Fig. 3) was investigated by means of a least-squares fitting program. An optimal rigid-body structural model consistent with the observed individual atomic modulations was searched. The fit was satisfactory if H atoms were excluded. The resulting model is shown in Table 8. The agreement factor *D* in this table corresponds to the average value in a representative number of basic cells of $[\sum(\mathbf{d}_c - \mathbf{d}_o)^2/\sum\mathbf{d}_o^2]^{0.5}$, where $\mathbf{d}_o$ are the 'observed' atomic displacements in the free-atom model and $\mathbf{d}_c$ the calculated ones in the rigid-body approximation.

There are two reasons why H atoms could not be included in the rigid-body fitting. On one hand, the

possibility of rotations of the NH_2 groups (see Fig. 3) with respect to the rest of the molecule is plausible. On the other hand, given the small weight of the H atoms on the diffraction diagram, the harmonics determined for the H atoms may have little physical significance. This is clearly demonstrated when the interatomic distances are calculated. In Table 7, the average, maximum and minimum values of the interatomic distances along the modulation are shown. The bond distances are typically maintained up to 0·01–0·02 Å, except for the N—H bond which takes unrealistic values. The cause of such unphysical behaviour can be traced back to the second- and third-order harmonics of the hydrogen-modulation functions. These can therefore be considered an artifact of the refinement process. However, the results of the refinement hardly depend on these structural parameters. The agreement factors obtained for the same structure, restricting the hydrogen modulation to their first harmonic, do not differ significantly from those given above.

The modulation functions corresponding to the fitted rigid-body model are given in Table 8 and shown in Figs. 4 and 5. A clear step-like form can be observed in two of the three transverse components (R_y and T_z). In the case of T_x, the third harmonic is too small for such an effect, but is adequately in antiphase to introduce the step-like form for larger amplitudes. These three transverse components are clearly predominant in the modulation. In the first harmonic, their amplitudes are one order of magnitude larger than those of the longitudinal components. The amplitudes of the third harmonic are in general comparable to those of the second harmonic or even larger. In the case of the transverse components, the third-harmonic amplitudes are typically one order of magnitude smaller than those of the first harmonic and therefore comparable to the values of the first-harmonic longitudinal components. The form of the modulation functions for these longitudinal components (see Fig. 5) is especially significant. The phase relations between the first and third harmonics define a characteristic form. The displacements concentrate in the internal coordinate interval around 0·25 and 0·75, while the modulation tends to become zero at the intervals where the transverse components have their steps (see Fig. 4). This typical form of the transverse and longitudinal components can also be clearly distinguished in the individual atomic modulations. This behaviour can be understood, if we consider that when the modulation wavevector q becomes null the transverse components merge into the homogeneous mode B_{3u}, and this mode is responsible for the primary distortion in the ferroelectric nonmodulated phase of symmetry $P2_1ma$. On the other hand, the longitudinal components correspond, when the modulation is eliminated, to the symmetry B_{1g} and are therefore forbidden in the $P2_1ma$ phase (the labels of the irreducible representations depend on the choice of setting).

The theoretical models proposed so far for thiourea do not predict in principle the existence of a soliton regime as a previous stage to the transition into the ferroelectric nonmodulated phase (Bruce, Cowley & Murray, 1978; Denoyer & Currat, 1986). In fact, the relative maximum amplitude for the third-order harmonic has been estimated to be smaller than 3·5% (Bruce *et al.*, 1978). However, the third harmonic determined in the present analysis surpasses in some cases 10 and 25% of the first-

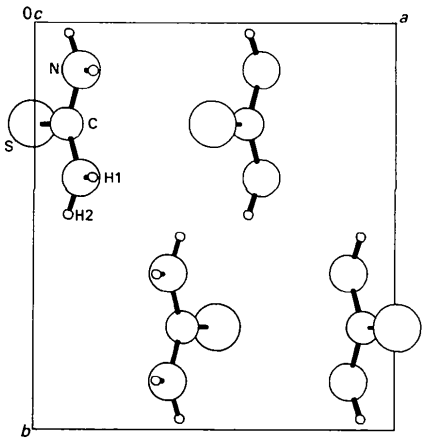

Fig. 3. Projection of the average structure of thiourea on the *ab* plane. Rigid-body units refer to individual $SC(NH_2)_2$ molecules.

Table 7. *Interatomic distances* (Å) *and angles* (°) *of thiourea*

Standard deviations are given in parentheses.

	Average	Min.	Max.	Max. − min.
S—C	1·704 (1)	1·704 (1)	1·715 (2)	0·01141
C—N	1·3228 (8)	1·314 (2)	1·338 (2)	0·02388
N—H1	0·84 (1)	0·77 (3)	0·93 (3)	0·16453
N—H2	0·87 (1)	0·79 (3)	0·92 (3)	0·13528
S—C—N	121·0 (1)	120·7 (3)	121·6 (3)	0·63
H1—N—H2	121 (2)	120 (4)	122 (4)	1·96

Table 8. *Amplitudes and phases* ($/2\pi$) *of the modulation functions corresponding to the fitted rigid-body model of the modulated structure of thiourea*

The rotational (R) and translational (T) amplitudes are given in sexagesimal degrees and relative units ($\times 10^4$), respectively. D is the agreement factor described in the text.

		First harmonic		Second harmonic		Third harmonic	
		a	φ	a	φ	a	φ
R	x	0·552	0·75	0·101	0·25	0·169	0·25
	y	6·326	0·00	0·031	0·50	0·552	0·50
	z	0·364	0·75	0·150	0·75	0·000	0·75
T	x	0·0185	0·00	0·0015	0·50	0·0003	0·50
	y	0·0012	0·75	0·0002	0·75	0·0003	0·25
	z	0·0234	0·50	0·0005	0·50	0·0022	0·00
D		0·05		0·24		0·10	

harmonic amplitude for the transverse and longitudinal components respectively. Figs. 4 and 5 clearly show the existence of an incipient soliton regime which is caused essentially by the contribution of this third harmonic. The two steps in the modulation of the transverse components correspond to the two domains in the ferroelectric phase, while the longitudinal component of the modulation tends to be zero in the commensurate domains and concentrated in the discommensuration regions, in agreement with the fact that the longitudinal components should disappear in the ferroelectric phase.

In broad terms the determined modulation seems to correspond to a soliton density n_s (Blinc, Prelovsek, Rutar, Seligar & Zumer, 1986) of about 0·5. For comparison, we show in Fig. 6 the general form of the theoretical modulation functions for the transverse and longitudinal components:

$$u_t(t) = A\cos[\theta(t)]$$
$$u_l(t) = A\cos[\theta(t) + \pi/2], \qquad (12)$$

with the phase function $\theta(t)$ having a 'soliton' form corresponding to a soliton density of approximately 0·56. The essential features of the experimental modulation functions can be identified in this simulation. Although they do not correspond to what can be called the 'narrow' soliton regime, a soliton density as low as 0·5 is quite remarkable, if we consider that in compounds like Rb_2ZnCl_4, which are considered as prototype examples of materials having a soliton regime, the soliton density has been reported to decrease only to values of about 0·3 (Blinc, Lozar, Milia & Kind, 1984; Blinc *et al.*, 1986)

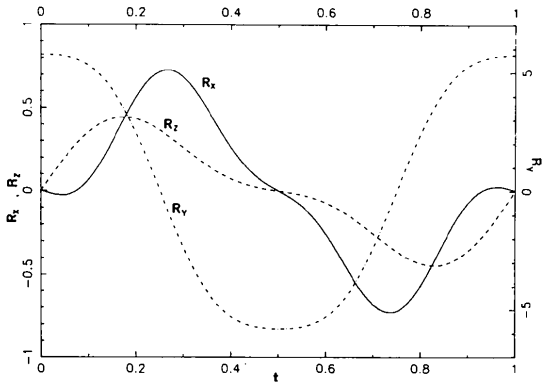

Fig. 4. Rotational modulation functions, R_x, R_y and R_z, obtained by fitting the independent atomic displacements of Table 6 to a rigid-body model. t refers to the internal coordinate and rotations are given in °.

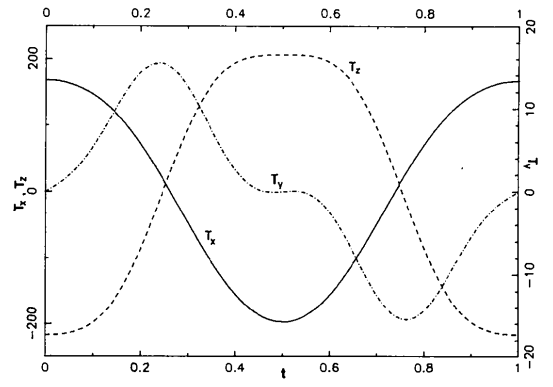

Fig. 5. Translation modulation functions, T_x, T_y and T_z ($\times 10^4$), obtained as in Fig. 4.

However, the experimental results do not agree completely with a soliton regime picture, because a unique soliton density is not consistent with the form of all the determined modulation functions. In particular, that corresponding to the x translations is practically sinusoidal and in this sense differs appreciably from the rest. These deviations from a common behaviour may be due to the accuracy limits of the structural analysis (which are especially critical for the third-harmonic parameters) and the errors introduced by rigid-body fitting.

The first harmonic in Table 8 is comparable with the results of Takahashi *et al.* (1988). The amplitudes are in the present case a little larger, as expected because of the different temperatures investigated, while the relative phases coincide. An exception is T_z which is seemingly smaller. On the other hand, the structural model in Table 8 differs considerably from that proposed in Simonson *et al.* (1988), especially the transverse component T_x and the longitudinal ones R_x and R_z. Also the relative phases do not coincide in general.

The reported structure can also be compared with the ferroelectric structure at 110 K, determined by Elcombe & Taylor (1968). The atomic displacements relating the ferroelectric structure with the average structure of the modulated structure have been fitted to a rigid-body model. A distorting mode corresponding to the symmetry B_{3u} is predominant. Its amplitudes, $R_y = 8{\cdot}02°$ and $T_z = -0{\cdot}0294$ relative

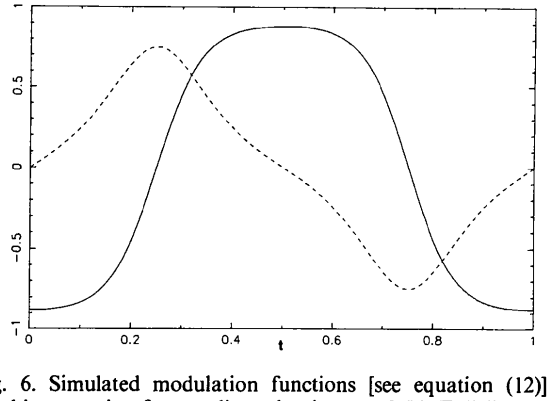

Fig. 6. Simulated modulation functions [see equation (12)] in arbitrary units, for a soliton density $n_s = 0{\cdot}56$. Full line: $u_t(t)$, dashed line: $u_l(t)$.

units, are consistent with those of the first harmonic in the modulated phase (see Table 8), but about 25% larger. Given the arbitrary choice of origin along the x coordinate in the ferroelectric space group, a similar comparison for the x translation T_x is not possible.

Recently, Tanisaki & Mashiyama (1988) have reported a structural analysis of the same modulated phase using a standard refinement procedure. The structure was taken as a ninefold commensurate structure and refined in the space group *Pnma*. A commensurate approach to this type of structure implies in general a larger number of refinement parameters than the superspace analysis (if in this latter refinement the number of harmonics in the modulation is truncated). In the present case, the number of positional and thermal parameters is reduced from 109 and 128, respectively, in Tanisaki & Mashiyama (1988), to 85 and 16 in the present study. Nevertheless, taking into account the differences between the two descriptions, the results of both studies essentially coincide. In particular, a soliton-like form for the atomic modulation functions can also be observed in Tanisaki & Mashiyama (1988). The rigid-body translation along x is also an exception in their model, being essentially sinusoidal.

It should be noted that the incommensurate description used in the present work implies that the phase ψ in (7) is considered irrelevant and arbitrary. In fact, the expression used for the structure-factor modulus is independent of ψ. On the other hand, the choice of the space group *Pnma* in a commensurate description is equivalent to an *a priori* restriction on the value of ψ. The two strictly different commensurate models obtained by Tanisaki & Mashiyama (1988) correspond to the only two possible nonequivalent ψ values which lead to commensurate phases with *Pnma* symmetry, if the modulation wavevector takes the value $\frac{1}{5}\mathbf{b}^*$ (see Table 3). The fact that the fit was of similar quality for both commensurate models indicates that the diffraction diagram is essentially insensitive to the value of the modulation phase, and confirms the validity of an incommensurate description.

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