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Structure of the modulation in thiourea. II. Structure refinement

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Résumé. — Nous décrivons l'affinement structural de la phase commensurable \( q = b^*/9 \) de la thiourée, à partir de données de diffraction de neutrons et du modèle décrit dans un article antérieur. On a ajusté une onde de distorsion primaire et deux harmoniques aux intensités de 660 taches de diffraction fondamentales et satellites. La modulation est displacive, composée d'une rotation sinusoïdale autour de \( b \) (\( R_b = 0,116 \) rad), d'une translation sinusoïdale selon \( c \) (\( T_c = 0,03 \) c) et de petites composantes longitudinales et non sinusoïdales. Les amplitudes des harmoniques successives deux et trois sont \( |Q_3q| \sim |Qq|/10 \) ; \( |Qq|/100 \sim |Q_2q| \sim |Qq|/10 \). Un modèle ordre-désordre s'ajuste mal aux données expérimentales. L'information fournie par le développement de Landau de l'énergie libre est comparée à la description par les supergroupes d'espaces.

Abstract. — We describe structure refinement of the long-period, commensurate, \( q = b^*/9 \) phase of thiourea, using neutron diffraction data and the model derived in a previous paper. The primary distorsion wave and two harmonics are taken into account and fitted to 660 fundamental and satellite reflections. The displacive modulation is mainly a sinusoidal rotation around the \( b \) axis (\( R_b = 0,116 \) rad) and a sinusoidal translation along \( c \) (\( T_c = 0,03 \) c), with small longitudinal and non-sinusoïdal components. Amplitudes of harmonics two and three are \( |Q_3q| \sim |Qq|/10 \) ; \( |Qq|/100 \sim |Q_2q| \sim |Qq|/10 \). An order-disorder model does not fit the data. Information derived from the Landau free energy is compared to the superspace group approach.

1. Introduction.

The object of this paper is to describe the structure analysis of one of the modulated phases of thiourea SC(NH\(_2\))\(_2\). It follows reference [1], hereafter referred to as [1], which described the basic symmetry and structure of the modulation. The abundant literature dealing with thiourea attests to its importance as an incommensurate ferroelectric insulator with a great wealth of properties. Dielectric measurements, specific heat, birefringence, X-rays, elastic and inelastic neutron scattering and other techniques have been supplemented by extensive theoretical treatments in efforts to understand this more or less model system. [1] recalls the structures of the room temperature paraelectric phase and the low temperature, ferroelectric phase, as well as the phase diagrams as a function of pressure, external electric field and temperature. Here we shall describe crystallographic analysis of the modulation. Several such analyses of thiourea have been accomplished [2], and indeed, such microscopic information can be indispensable for characterizing the order parameter of a paraelectric-incommensurate phase transition, and as a starting point for the phenomenological models developed for this kind of system.

Generally speaking, knowledge of crystallographic structure will discriminate directly between order parameters of a displacive and order-disorder nature. It will also give the amplitudes of the successive Fourier components of the modulation. Standard theories of incommensurate systems make elaborate predictions concerning the development of higher harmonics in the modulation as the temperature is lowered towards a lock-in transition. This anharmonicity is related to the order and mechanism of the transition.

Crystallographic information can also be confronted with models, which make assumptions about the various microscopic interactions (dipolar forces and hydrogen bonds in thiourea) and which provide predictions for the variations of the wave-vector or order parameter.

These questions are particularly relevant in the case of thiourea. On the one hand, it is difficult to characterize the order parameter by dynamical
studies. For a long time, thiourea was thought to be an order-disorder type system, until a soft mode was found by Raman spectroscopy in the incommensurate and ferroelectric phases, and by infrared reflectivity in the paraelectric phase [3]. However, the complete observation of the dispersion branch is difficult because the mode is heavily damped, and many other low frequency branches are present. Thus, direct observation of the order parameter is important. On the other hand, early X-ray films showed the importance of satellite diffraction spots of orders two and three, in the lowest temperature part of the incommensurate phase [3] demonstrating the complexity of the modulation's structure. These are the reasons which motivated this work.

This paper is organized as follows.

We first review the specific problems of incommensurate structure analysis and recall the previous results on thiourea. Our experimental procedure is described. We then analyse qualitatively the diffraction pattern from an incommensurate structure. Finally, we describe our refinement procedure and discuss the results along the lines mentioned in this introduction.

2. Structure analysis of modulated phases.

Structure analyses of incommensurate phases encounter specific difficulties. The modulation is a small perturbation of the mean structure. In terms of diffraction, it affects slightly the fundamental Bragg peaks and produces the much weaker satellite peaks. Typical intensities in this work were:

- $10^6$ counts for a fundamental peak
- $5 \times 10^4$ counts for a 1st order satellite peak
- $10^5$ counts for a 2nd order satellite peak
- $10^6$ counts for a 3rd order satellite peak.

Due to the long period of the structure, these diffraction peaks are close together and the strong fundamental peaks can easily contaminate their much weaker satellites. Also, the complete description of the symmetry of a modulated phase is rather complex and cumbersome: a physical description of the order parameter is required to exploit all the information contained in diffraction data.

An increasing number of modulated structures are being determined using the abstract supergroup formalism of de Wolff et al. [4], which is adapted to the development of standardized computer programs. However, this formalism cannot, as such, incorporate all the physical information.

3. Previous analyses of thiourea.

These difficulties account for the small number of modulated structures solved to date. In the case of thiourea, previous studies have used X-ray, electron and neutron diffraction. The most complete are those of Shiozaki (1971), McKenzie (1975) and Yamamoto (1979). Shiozaki used X-ray diffraction by a mono-crystal at 187 K, in the middle of the range of the incommensurate phase. He assumed transverse, sinusoidal displacements and used only the Bragg reflections in the planes $(h = 0)$ and $(\ell = 0)$ of reciprocal space. He concluded that the molecules rotate-translate rigidly with a rotation amplitude of $R_b = 0.119$ rad and a translation amplitude of $T = 0.025 a + 0.025 c$. McKenzie used neutron diffraction and a deuterated monocrystal, in the middle of the incommensurate phase. The use of neutron diffraction is important, because in the rotation around $b$, the deuterium atoms have the largest motions and convey much of the information about the modulation's amplitude. McKenzie assumed the molecule to be rigid and identical to its form in the paraelectric phase. He described the modulation as a basis vector of the appropriate soft mode. He worked with a 3-axis spectrometer, not a four-circle diffractometer, using as Shiozaki only the $(h = 0)$ and $(\ell = 0)$ planes. He found amplitudes of $R_b = 0.12$ rad and $T = 0.013 a + 0.020 c$. Finally Yamamoto used Shiozaki's data, superspacegroup formalism, and a model including two harmonics in the modulation. Unfortunately, the X-ray films misled him into wrong $(\tau_4)$ extinction rules for the second harmonic. The solution he found for the second harmonic is thus incorrect; but this does not affect significantly his results for the first harmonic. He found a slight distortion of the molecule and global rotation-translation of amplitudes $R_b = 0.087$ rad and $T = -0.01 a - 0.03 c$.

All of these models involve sinusoidal and transverse displacements. All of them are based on the sole $(h = 0)$ and $(\ell = 0)$ reflections, and the X-ray work ignores the important hydrogen atoms. More recent diffraction experiments showed the importance of higher distortion harmonics and the existence of small longitudinal displacements [3]. X-rays also create radiation damage in thiourea which interacts with the modulation, contributing to memory effects, hysteresis and pseudo-plateaux of the wave-vector, even doing away with the $\delta = 1/9$ phase [6]. Finally, the mutual agreement of these models is rather approximate. We felt that an additional, more complete analysis was thus necessary.

4. Experimental conditions.

Our analysis was done in the commensurate $\delta = 1/9$ phase using neutron diffraction. We chose to work in the $\delta = 1/9$ phase for several reasons. This phase is located between the incommensurate phase (above $T_i$) and the low-temperature ferroelectric phase.
(below $T_c$). It extends over only 2 K at ordinary pressure. This is where the amplitude of the modulation and its non-sinusoidal structure are strongest and best measurable. Crystallographic calculations are simplified by the translation symmetry of the commensurate phase. Most important, the structure of the modulation remains similar to that of the neighbouring incommensurate phase, as we observed experimentally: the diffraction pattern was seen to vary slowly and continuously throughout the whole modulated region. Also in an incommensurate phase, dynamic fluctuations of the phase and amplitude can have important effects on satellite intensities, whereas here the modulation is pinned down by Umklapp energy terms.

The experiments were carried out at the high-flux reactor of the Institut Laue Langevin. Single-crystal intensities were measured on the 4-circle diffractometer D10 at a wavelength $\lambda = 2.35 \, \text{Å}$ with a PG (002) monochromator and with a PG filter to reduce higher-order contamination. The sample was mounted in a full 4-circle continuous flow He cryostat designed for the temperature range of 3-300 K. At lower temperatures, measurements were performed in a fixed scattering plane geometry on D10. This instrument was then used in a 3-axis mode with a PG (002) analyser. The sample was a large, (3 mm x 4 mm x 5 mm) deuterated single-crystal of excellent optical quality, provided by Professor J. P. Chapelle. Its absorption was negligible.

The experiment was done at 191 K (in the middle of the $\delta = 1/9$ phase) with a stability of a few hundredths of K over two weeks, 660 reflections were recorded. The parameters of the mean structure were found to be:

$$a = 7.59 \, \text{Å} ; \quad b = 8.57 \, \text{Å} ; \quad c = 5.49 \, \text{Å}.$$ 

5. Extinction rules.

We recall the extinction rules observed in the modulated phases of thiourea: $Q = ha^* + kb^* + \ell c^* + nq$ is extinct if:

1. $h = 0$ and $k + f + n$ is odd, or
2. $f = 0$ and $h$ is odd.

This means that the odd harmonics of the modulation transform according to the $T_4$ irreducible representation of Pnma, and the even harmonics transform according to the $T_1$ irreducible representation (Tab. I).

(In a diffraction experiment, the extinctions of satellite reflections can be violated by various contaminating processes. Thus previous authors have occasionally claimed $T_4$ symmetry for the second harmonic. We recorded sixty-one satellites theoretically extinct, of which almost half had non-zero intensity. In every case, we were able to trace the intensity either to contamination from a strong neighbouring peak, or to multiple diffraction processes).

6. Diffraction by a modulated system.

Before discussing the approximations made during the structure refinement, it is worth making some additional comments on diffraction by a modulated system.

The structure factor of a modulated structure depends crucially on the nature of the modulation. Let us consider a displacive modulation of wave vector $q = 1/9 \, b^*$, and take into account the first three harmonics. Let $k$ be an atom in cell $\ell$. Its position, averaged over thermal fluctuations, is $F_k$. Averaging over the modulation displacements, we have its mean position $(\ell k)$. We may write:

$$F_k = \sum_{n} b_n e^{-\pi n} \sum_{n_1 + 2 n_2 + 3 n_3 + n} \sum_{n} \exp \left\{ -i \left( n_1 \phi_n^1 + n_2 \phi_n^2 + n_3 \phi_n^3 \right) \right\}$$

$k$ is summed over one cell of the mean structure ($e^{-\pi n}$ is a Debye Waller factor, $n = 0$ corresponds to a fundamental peak, $n = 1$ to a first order satellite, and so on).

The main contribution to the peak comes from the term $n_1 = n_2 = n_3 = 0$.

Even for a sinusoidal modulation, satellites of orders $n \gg 1$ appear. The fundamental peaks lose some intensity to satellites through the factor $J_0(Q \cdot U_0^{(1)}) \cdot J_0(Q \cdot U_0^{(2)}) \cdot J_0(Q \cdot U_0^{(3)})$; satellite peaks drop off with $n$ roughly as $J_n(Q \cdot U_0^{(1)}) \sim (Q \cdot U_0^{(1)})^n$.

An order-disorder modulation, on the other hand, in order to account for odd harmonics of $T_4$ symmetry and even harmonics of $T_1$ symmetry, would have to include two Ising variables and two ordering
positions at least. Assume, in other words, that each cell \( \ell \) is characterized by the Ising variables
\[
S(\ell) = \pm 1
\]
\[
S'(\ell) = \pm 1
\]
such that the position of atom \( k \) is
\[
\varphi_{tk} = \langle S\ell) + S(\ell) U_k^{(odd)} + S'(\ell) U_k^{(even)} \rangle;
\]
\( U_k^{(odd)} \) and \( U_k^{(even)} \) are the two ordering positions. \( \langle S(\ell) \rangle \) and \( \langle S'(\ell) \rangle \) are periodic functions of wave vectors \( q \) and \( 2q \) respectively (the average is over \( \ell \)):
\[
\langle S(\ell) \rangle = \sum_{n \text{ odd}} \alpha_n \exp(\text{i} nqr_1)
\]
\[
\langle S'(\ell) \rangle = \sum_{n \text{ even}} \beta_n \exp(\text{i} nqr_1)
\]
\( U_k^{(odd)} \) has \( \tau_4 \) symmetry, while \( U_k^{(even)} \) has \( \tau_1 \) symmetry. This model produces odd-order satellites proportional to \( a_n \) and even-order satellites proportional to \( \beta_n \), with the proper extinction rules.

7. Structure refinement and results.

We are now in a position to discuss the actual fitting of the model exposed in [1] to the data collection.

The displacements of the four molecules of the unit cell of the mean structure were derived in [1]. The molecules are treated as rigid, their displacements described by four symmetry-related six-vectors. For molecule 1 of cell \( \ell \), displacements associated with the distortion mode \((q \tau_4)\) are
\[
U(\ell, 1) = \begin{pmatrix}
T_1^{(1)} \cos(q \ell + \varphi(q, \tau_4)) \\
T_2^{(1)} \cos(q \ell + \varphi(q, \tau_4) + \pi/2) \\
T_3^{(1)} \cos(q \ell + \varphi(q, \tau_4)) \\
R_4^{(1)} \cos(q \ell + \varphi(q, \tau_4)) \\
R_5^{(1)} \cos(q \ell + \varphi(q, \tau_4)) \\
R_6^{(1)} \cos(q \ell + \varphi(q, \tau_4) + \pi/2)
\end{pmatrix}
\]

For the other molecules \( j = 2, 3, 4, U(\ell, j) \) is obtained by replacing \( (T_1, T_2, T_3, R_4, R_5, R_6, \varphi, \tau_4) \) from [1] by \( \varphi(q, \tau_4) \) from table III of [1].

For the second and third distortion harmonics, we do the same, using \( (2q, \tau_4) \) and \( (3q, \tau_4) \) from [1]. For each distortion harmonic there are seven real, adjustable constants \( T_1, T_2, T_3, R_4, R_5, R_6, \) and \( \varphi(q, \tau_4) \). If we accept the rigid molecule hypothesis, then these are the most general displacements possible compatible with the extinction rules recalled above. Thanks to the commensurate wavevector, we have no need to calculate structure factors with series of Bessel functions, but simply sum \( b_{j(k)} \exp(\text{i} Q \cdot R_{j(k)}) \) over nine cells (one supercell).

7.1 Mean structure refinement. — The simplest way to treat the mean structure is to fix the molecule in the configuration it adopts in the paraelectric phase, and to refine only its position and orientation, either by themselves or together with the modulation amplitudes.

This procedure did not converge to a realistic solution. If, however, we did not maintain the molecule in a rigid form, we obtained satisfying results for the first harmonic, despite slightly artificial deviation of the molecule from its paraelectric form. This distortion is not expected to affect the validity of the solution found for the amplitudes of the harmonics. Therefore, our first step was to refine the mean structure alone using the fundamental Bragg peaks and allowing for the modulation only through the Debye-Waller factor.

In other words, the terms \( I_0(Q \cdot U_1^{(1)}) I_0(Q \cdot U_1^{(2)}) \) \( J_0(Q \cdot U_1^{(3)}) e^{-w_k} \) in \( F(Q) \) are replaced by simply \( e^{-w_k} \), an effective Debye-Waller factor.

From the Landau theory approach of the paraelectric-modulated phase transition, it follows that in the modulated phases the mean structure has the same space group as the parent, paraelectric phase, namely \( \text{Pnma} \). The mean structure was refined by a standard least-squares procedure, with the paraelectric structure as a starting point, using the crystallographic program SHEXL [7]. Only 90 non-extinct fundamental reflections were measured. In the least-squares refinement, these were given the weight \( 1/(\sigma(F) + 0.07 F) \), except for reflections with zero intensity, to which we attributed half the intensity of the smallest observed peak, as well as its weight. With one isotropic Debye-Waller factor per atom, there were 18 free variables, and the value of \( R = 18 \% \) was reached (including reflexions of zero intensity). The resulting thiourea molecule is slightly different from the paraelectric form found by Elcombe and Taylor [8] due to an unrealistic distortion of the N-D bonds. Figure 1 shows the resulting molecule ; its coordinates are given in table II. The observed and calculated structure factor amplitudes are given in the appendix (A.1).

It is unreasonable to expect an actual distortion of the N-D bonds in the modulated phases. As pointed out in [1], almost no distortion is observed in the low temperature, ferroelectric phase. Also, the internal degrees of freedom of the molecule have no reason to couple to the modulation, since there is a large frequency gap between the internal vibration frequencies and the frequency of the \( \tau_4 \) soft mode.

Two types of errors can perhaps account for an artificial distortion. On the one hand, our description of the modulation is simplistic at this stage, because the approximation \( J_0(Q \cdot U_1^{(1)}) J_0(Q \cdot U_1^{(2)}) J_0(Q \cdot U_1^{(3)}) \times e^{-w_k} \approx e^{-w_{k\text{eff}}} \) (3) amounts to assuming an isotropic modulation.
Indeed, to the second order in \( u_k^{(1)} \), (3) may be written

\[
(Q \cdot u_k^{(1)})^2 + 2 \pi^2 \langle u_k^{(2)} \rangle_T Q^2 = 2 \pi^2 \langle U_k^{2\text{eff}} \rangle Q^2
\]

(with the notations of Tab. I), or:

\[
\frac{1}{2} U_k^{(1)2} = \langle U_k^{2\text{eff}} \rangle \text{eff} - \langle U_k^{2\text{eff}} \rangle_T.
\]  

\( 3' \)

The deuterium positions are particularly sensitive to this approximation, since they are most affected by the strong \( R_b^{(1)} \) displacement. (In fact, their root mean square displacements due to the modulation determined in this work are 0.28 Å and 0.16 Å respectively — more than the artificial distortion of their mean position.)

If we anticipate the results of our refinement of \( U_k^{(1)} \), we may compare the terms of equation \( 3' \). The results are listed in table III.

The agreement may be considered quite good, attesting to the consistency of our successive approximations.

However, the anisotropy of the modulation remains, and limits the quality of our mean structure.

The second error inherent to our procedure comes from the small amount of data. The 90 reflections used for the mean-structure do not provide a reliable averaging over reciprocal space of experimental errors.

7.2 REFINEMENT OF THE FIRST HARMONIC. — With the scale-factor and mean structure fixed as above, we replaced the artificial Debye-Waller factors de-

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Table II. — The mean structure refined from our data: coordinates of the asymmetric unit and mean square thermal vibrations. The first set (a) of temperature factors, called \( \langle u_k^{2\text{eff}} \rangle \), are the effective thermal factors refined from our data (which include the effect of the modulation). The second set (b) called \( \langle u_k^{2} \rangle_T \), was found by interpolating the data of the paraelectric and ferroelectric phases (Elcombe and Taylor) to the temperature of our experiment.

<table>
<thead>
<tr>
<th></th>
<th>( x/a )</th>
<th>( y/b )</th>
<th>( z/c )</th>
<th>( \langle u_k^{2\text{eff}} \rangle )</th>
<th>( \langle u_k^{2} \rangle_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>-0.061</td>
<td>0.25</td>
<td>0.1261</td>
<td>0.026</td>
<td>0.013</td>
</tr>
<tr>
<td>C</td>
<td>0.0818</td>
<td>0.25</td>
<td>-0.1511</td>
<td>0.048</td>
<td>0.013</td>
</tr>
<tr>
<td>N</td>
<td>0.1301</td>
<td>0.3975</td>
<td>0.2706</td>
<td>0.089</td>
<td>0.020</td>
</tr>
<tr>
<td>D</td>
<td>0.1799</td>
<td>0.4010</td>
<td>-0.4761</td>
<td>0.096</td>
<td>0.032</td>
</tr>
<tr>
<td>D'</td>
<td>0.0759</td>
<td>0.4505</td>
<td>-0.2064</td>
<td>0.051</td>
<td>0.020</td>
</tr>
</tbody>
</table>

---
Table III. — Comparison between our effective Debye-Waller factor (found refining the mean structure) and the displacements associated with the first harmonic of the modulation (found at the next stage of our refinement).

<table>
<thead>
<tr>
<th></th>
<th>$U_{k}^{(1)}$</th>
<th>$\langle u_{k}^{2} \rangle_{\text{eff}}$</th>
<th>$\langle u_{k}^{2} \rangle_{\tau}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.013</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.016</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>0.037</td>
<td>0.069</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.075</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>D'</td>
<td>0.024</td>
<td>0.031</td>
<td></td>
</tr>
</tbody>
</table>

obtained above by taking the ones from the paraelectric and ferroelectric structures, interpolating them to the temperature of our experiment and taking their isotropic part. We made no attempt to refine the phase value $\phi(q, \tau_d)$ which only contributes to the modulus $|F(Q)|$ through minute terms. The fundamental reflections and the 80 first-order satellites were used, and the second and third distortion harmonics neglected at this stage. The amplitudes were adjusted using a least-squares routine.

We found the amplitudes:

$$T_{a}^{(1)} = -0.002a$$

$$T_{b}^{(1)} = -0.002b$$

$$T_{c}^{(1)} = -0.029c$$

$$R_{a}^{(1)} = -0.016 \text{ rad}$$

$$R_{b}^{(1)} = 0.116 \text{ rad}$$

$$R_{c}^{(1)} = 0.009 \text{ rad}$$

in agreement with earlier work.

The observed and calculated structure factors were in reasonable qualitative agreement ($R = 28\%$) and are given in the appendix (A.2).

7.3 REFINEMENT OF THE SECOND HARMONIC. — The second-order satellites were extremely weak and many were contaminated by strong, neighboring, first-order satellites. (Only 56 were exploitable; of these, 36 had zero-intensity.) Only an order of magnitude could be estimated for $Q_{q \tau_4}$, $\tau_1$.

$$|Q_{q \tau_4}|_{100} > |Q_{q \tau_1}| = |Q_{q \tau_4}|_{100}^2.$$

7.4 REFINEMENT OF THE THIRD HARMONIC. — Third-order satellites were more intense and reliable. The third harmonic could be determined while neglecting the second, because the two diffract very much independently. The phase of $\psi(3q, \tau_d)$ was set to zero, which did not affect the amplitudes $T_{a}^{(3)}, T_{b}^{(3)}, \ldots, T_{c}^{(3)}$.

Using the 99 third-order satellites along with the fundamental and 1st-order reflections, we found (Appendix A.3):

$$T_{a}^{(3)} = 0.003a$$

$$T_{b}^{(3)} = 0.00$$

$$T_{c}^{(3)} = 0.004c$$

$$R_{a}^{(3)} = 0.006 \text{ rad}$$

$$R_{b}^{(3)} = 0.002 \text{ rad}$$

$$R_{c}^{(3)} = -0.002 \text{ rad}.$$

These results are summarized in table IV, along with the results of previous authors.

Order disorder model: Despite the complications involved in an order-disorder model (particularly when several harmonics are present), we did consider a sinusoidal order-disorder model, neglecting harmonics two and three. We fitted the probability amplitude $a_1$, and the ordering positions $U_{k}^{(\text{odd})}$ to our diffraction data.

Because of the poor fit and unrealistic ordering positions which resulted, we consider the model very unlikely.

Table IV. — Amplitude of the various components of the modulation. Our results and those of previous authors. The diffraction technique used and the temperature of each experiment are given. Temperatures of experiments done on SC(NH$_2$)$_2$ and SC(ND$_2$)$_2$ are not directly comparable. When SC(NH$_2$)$_2$ was used, we give in parentheses an "equivalent" SC(ND$_2$)$_2$ temperature, at which the modulation in SC(ND$_2$)$_2$ would have approximately the same amplitude as in the actual experiment.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_a$</td>
<td>0.025</td>
<td>0.013</td>
<td>0.010</td>
<td>- 0.002</td>
<td>0.003</td>
</tr>
<tr>
<td>$T_b$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>- 0.002</td>
<td>0</td>
</tr>
<tr>
<td>$T_c$</td>
<td>0.025</td>
<td>0.020</td>
<td>0.030</td>
<td>- 0.029</td>
<td>0.004</td>
</tr>
<tr>
<td>$R_a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>- 0.016</td>
<td>0.006</td>
</tr>
<tr>
<td>$R_b$</td>
<td>0.119</td>
<td>0.12</td>
<td>0.087</td>
<td>0.116</td>
<td>0.002</td>
</tr>
<tr>
<td>$R_c$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>- 0.002</td>
</tr>
</tbody>
</table>
8. Discussion.

Figure 2 shows the shape of the most important, transverse parts of the modulation. The transverse displacements of molecule $j = 1$ of cell $f$ are shown as a function of $f$; neglecting the second harmonic, we have:

$$T_x(f) = T_x^{(1)} \cos qf + T_x^{(3)} \cos 3qf$$
$$T_y(f) = T_y^{(3)} \cos qf + T_y^{(3)} \cos 3qf$$
$$R_y(f) = R_y^{(3)} \cos qf + R_y^{(3)} \cos 3qf.$$

Fig. 2. — The $T_x$, $T_y$, and $R_y$ components of the displacement of molecule one of cell $f$, taking into account harmonics one and three. The non-transverse components $T_y$, $R_y$, and $R_z$ are much smaller than the ones shown.

The modulation is intermediate between a sinusoidal and a step-wise form. This can be characterized by the amplitudes of the successive components of the order-parameter: $|Q_{q1}|$, $|Q_{3q1}|$, $|Q_{q2}|$, $|Q_{3q2}|$.

We find:

$$|Q_q| = 3.7 \, \text{Å} \, g^{1/2}$$
$$|Q_{3q}| = 0.46 \, \text{Å} \, g^{1/2}$$

$|Q_{3q}|$ is estimated to be somewhat smaller than $|Q_{3q}|$.

For a step-wise modulation one would have

$$|Q_{3q}| = 0$$
$$|Q_{3q}| = \frac{1}{3} |Q_q|.$$ 

A step-wise domain structure of the modulation is thus excluded. The large rotation around the $b$-axis is accompanied by a large translation along the $c$-axis (Fig. 2), as had been observed by the previous authors. The longitudinal components are quite small — of the same importance as the third harmonic, in fact.

As we mentioned, the form of the modulation varies slowly and continuously as temperature is raised up through the incommensurate phase. Below $T_c$, in the ferroelectric phase, the tilt between the two molecules is $2R_y = 2 \times 0.098$ rad at $120$ K.

Landau theory analyses of the phase diagram of thiourea have been done with a one-harmonic model by Levanyuk and Sannikov, Ishibashi and Dvorak, Barreto et al. [9]. We see that this approximation is partly justified. Parlinski and Michel have done calculations taking into account three harmonics of the modulation [10]. It has been shown that higher harmonics are particularly important in explaining the form of the dielectric susceptibility as a function of temperature [11].

As seen from figure 3, the first harmonic polarizes the unit cell by rotating molecules 1 and 4 (respectively 2 and 3) around $b$, in opposite directions, away from their mean direction, so that their dipole moments no longer compensate each other. Thus, $P_{q1} \propto R_y^{(3)}(1 + \cos (qb/2)).$

Fig. 3. — Schematic representation of the displacement associated with the first harmonic of the modulation. A unit cell of the mean structure is shown projected onto the $(a, c)$ plane, with the symmetry planes $n = (\sigma_x, (b+c)/2)$ and $a = (\sigma_x, a/2)$. Molecules 1 and 2 are in the plane $y = 0$; 3 and 4 are in the plane $y = b/2$. The most important, transverse, components $T_x$, $T_y$, and $R_y$ are shown. The polarization associated with this wave is seen to be proportional to $R_y^{(3)}(1 + \cos (qb/2)).$

The second harmonic (Fig. 4) rotates molecules 1 and 4 (respectively 2 and 3) in the same direction around $b$. However, the phase difference $q \cdot b$ between the two molecules of a pair leads to a net polarization, albeit a reduced one compared to the preceding mechanism:

$$P_{2q1} \propto R_y^{(5)}(1 - \cos (qb)).$$

In the presence of an external electric field along $a$, an additional component is present in the form of a second harmonic of $\tau_4$ symmetry, proportional to $E_x: P_{2q1}$. We want to emphasize the coexistence of two distinct contributions to the second harmonic and the fact that theoretical calculations of $|P_{2q1}|$
Fig. 4. — Schematic representation of the $R_b$ component of the second harmonic. One can see that due to the phase difference of $2 \theta \cdot b/2$ between molecules 1 and 4 (respectively 2 and 3), this wave is polarized. Its polarization is proportional to $R_b^{(2)}(1 - \cos (\theta \cdot b))$. Thus the polarizations of the first and second harmonics are related by:

$$\left| P_{2qT_1}/P_{qT_4} \right| = 0.12 R_b^{(2)}/R_b^{(1)}.$$}

by Parlinski and Michel, taken with our estimate of $|P_{2qT_1}|$, suggest that $P_{2qT_1}$ is probably as large as $P_{2qT_4}$ in parts of the incommensurate phase. Following calculations by Montambaux et al., it is easily shown that:

$$P_{2qT_1} \propto P_{qT_4}^2 \left( 1 - \lambda P_0^2 \right)$$

$$P_{2qT_4} \propto P_0^2 P_{qT_4}$$

$$P_{3qT_4} \propto P_{qT_4}^2$$

($P_0$ is the net overall polarization, proportional to $E_0$).

Thus, $P_{2qT_1}$ is expected to subsist in the absence of an external field.

9. Conclusion.

We have presented the structural analysis of the non-sinusoidal modulation of thiourea in the commensurate $\delta = 1/9$ phase. The amplitude of the modulation and its non-sinusoidal character are close reflections of the competing interactions which give rise to the modulation. Structure refinement of this kind of system is difficult because of the complex symmetry of the modulation, its long period, and the weak intensity of satellite reflections. In many cases — including thiourea — X-ray diffraction is not suitable because modest doses of irradiation create drastic defects in the modulation. Our work was done with neutron diffraction.

Fitting the displacements derived in [1] to our neutron diffraction data showed that the modulation is mainly composed of a sinusoidal rotation around $b$ and translation along $c$, with small longitudinal components and higher harmonics. Conceivably, a quantitative microscopic model would be able to interpret the coupling between $R_b$ and $T_1$ in terms of local and long-range interactions. The second distortion harmonic is estimated to be an order of magnitude weaker than the third harmonic, which is equal to $|Q_3|/10$. This is in qualitative agreement with the theoretical calculations of Parlinski and Michel.

A general consequence of this work is a demonstration of the relationship between the Landau theoretical approach to modulated phases, and their superspace description. In conclusion, we want to summarize this relationship, starting from the practical point of structure refinement.

For a displacive transition, Landau theory assumes that the modulation is an eigen-vector of the dynamic matrix so that we can: 1) write the displacements in terms of irreducible representations of the parent space group; 2) think of higher harmonics as powers of the primary order parameter; 3) write the appropriate form of the free energy functional. Each point gives information about the others. We saw in [1] that in thiourea, a harmonic modulation minimizes its energy for particular, non-zero values of its phases $\varphi(q)$, $\varphi(2q)$, $\varphi(3q)$, ... which depend on a series of terms in the free energy. (This prediction was made simultaneously by Aizu [12]; it refutes, on the other hand, some prior results [13].) We should emphasize that it holds in the case of thiourea because the third harmonic is fairly large; if $|Q_3| < |Q_2| < |Q_q|$ were true then all three phases would be 0 or $\pi$. We saw that time-inversion symmetry of the dynamic matrix reduces the number of degrees of freedom by one half. This information can be generalized to any modulated system. On the other hand, sole consideration of the system’s crystallographic symmetry, as derived from the satellite extinction rules, will not give phase information or exploit time-inversion symmetry (at least until after structure refinement), since both are explicitly related to the system’s free energy. This is just to repeat the obvious fact that symmetry alone never gives the full physical information. Failure to incorporate the requirements of time-inversion symmetry into superspace description of NaN02, biphenyl, Rb2ZnBr4(Cl8) and thiourea led to erroneous symmetry groups and erroneous conclusions (as shown by Heine [5]; see also our remarks above concerning the work of Yamamoto on thiourea). Heine has in fact described a simple ad hoc way to incorporate time-symmetry requirements into a superspace description.

Another limitation of superspace theory is the difficulty it has to describe a non-sinusoidal modulation when the phase differences between successive harmonics are not 0 or $\pi$ (see [1]). We saw that thiourea has the superspace group $P_{31}$ if the second harmonic is neglected, and the superspace
If it is taken into account. This is due to the phase difference between harmonics one, two and three. However, the crystallographic symmetry contained in this second superspace group obviously gives an incomplete picture of the physical symmetry of the system (just as in an ordinary 3-dimensional crystal, to decide what atomic displacement is responsible for the absence of a symmetry element, structure refinement — or theoretical assumptions — are necessary).

For future studies of modulated phases in which several harmonics are present, these distinctions will be of importance.

Acknowledgments.

Discussions with L. Bernard, P. Lederer and G. Montambaux are acknowledged.

Appendix.

Tables A.1, A.2, A.3.

Observed and calculated structure factor amplitudes.
The reflections are indexed in the unit cell of the $\delta = 1/9$ phase. (Thus for example $1 \ 10 \ 1$ is a first order satellite of the fundamental reflection $1 \ 9 \ 1$). The three tables A.1, A.2 and A.3 are all on the same scale.

References


Table A.1. — The mean structure: observed and calculated $F$s of the fundamental reflections.

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Table A.1. — The mean structure: observed and calculated $F$s of the fundamental reflections.
Table A.2. — The first harmonic of the modulation: observed and calculated F’s of the first-order satellite reflections.

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Table A.3. — The third harmonic of the modulation: observed and calculated F’s of the third-order satellite reflections (the structure factors calculated for the fundamental and first-order peaks are hardly affected by including the third harmonic in the model).

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