

Time Relaxation of the Low-Temperature Modulated Structure of Thiourea

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Abstract

A conspicuous time variation of the diffraction diagram of thiourea in its incommensurate phase at 170 K is observed and characterized. The phenomenon is systematic and reproducible. Satellite intensities decrease according to linear laws, reaching in the case of third-order satellites up to a 28% reduction. Main reflections decrease or increase depending on the particular reflection. Sample degradation could be discarded as a possible cause. Through a rather complex procedure, which makes use of the structural data determined in previous studies, the kinetic process observed is shown to be fully consistent with a slow time relaxation of the soliton density of the incommensurate structural modulation from a value of 0.62 at the beginning of the measurement to 0.69 at the end of the main experiment, after 166 h. This variation represents a correlated decrease in the amplitudes of the harmonics of the modulation, with a reduction of its anharmonicity. Clearly, the structural modulation evolves with time towards a more sinusoidal regime. The origin of the phenomenon is unclear and its possible existence in other incommensurate materials is to be ascertained.

1. Introduction

A standard X-ray diffraction data collection intended for solving a crystal structure can take about 150 h or more. During this time, intensity of reflections is generally supposed to vary due to radiation damage, crystal degradation (long-term intensity decays) and X-ray beam instabilities (short-term intensity fluctuations). As each reflection is measured only once and all reflections at different times, intensities of different reflections are in general not comparable. These problems are palliated by measuring periodically some selected reflections (check reflections) during the data collection. Their average behaviour with time is later used to scale the whole data set on a comparable basis. In addition to this problem, which is inherent to any X-ray data collection,

incommensurate (IC) crystals seem to be particularly sensitive to the presence of defects and, therefore, sensible to radiation damage, as it implies a continuous defect creation. The defects present in the crystal can influence its structural evolution within the IC phase when the environmental conditions (normally the temperature) are varied. Also, related to the presence of defects, a great variety of kinetic phenomena appear: memory effects after annealing, pinning of the modulation, loss of correlation along the modulation direction, structural time relaxations at a fixed temperature *etc.* (Durand & Dénoyer, 1988; Leon-Gits, 1988). Some of these effects are apparently reinforced in those compounds that show a soliton regime. For example, if the discommensurations are pinned by randomly distributed defects, their periodic distribution (and, consequently, the long-range order of the modulation) would be destroyed giving rise to a broadening of the satellites.

The reported time scale for the kinetic phenomena mentioned above is of the order of hours (Schneck, Calvarin & Kiat, 1984) and the amount and type of defects present in a given crystal can be hardly controlled when the sample is being irradiated. Hence, for instance, time-relaxation effects are expected to be commonly present in IC structures during X-ray data collections at a fixed temperature. These effects are usually overseen or neglected. As changes in the structural modulation mainly affect satellite reflections, their presence among the check reflections is essential for having information about the way in which the IC structure has varied during experiment. However, because of their typical weakness, they are usually excluded from the set of check reflections or, when included, they are only used for routine scaling corrections (Gao, Gajhede, Mallinson, Petricek & Coppens, 1988), analogous to those used in 'normal' crystallography.

Relaxational effects in IC phases are, indeed, from the structural viewpoint rather weak and do not prevent, when neglected, accurate structural determinations. Thiourea, for instance, is expected to exhibit very strong kinetic effects, similarly to its deuterated compound (Durand & Dénoyer, 1988), although its structure was

very accurately determined at 168 K, in the vicinity of the lock-in transition, with a measurement that lasted about 10 d, taking no special account of the time behaviour of the sample (Zúñiga *et al.*, 1989). The atomic displacement fields could be parameterized in terms of rigid-body rotations and translations and include up to third-order harmonics.

If the behaviour of the check reflections (including satellites) is carefully analysed, time relaxation effects are strong enough to be easily detected during standard data collections of IC structures. This could be observed in a second measurement of the IC phase of thiourea at 170 K. The aim of this new data collection was to correct some experimental details that probably had reduced the accuracy of the structural determination of Zúñiga *et al.* (1989). The time behaviour evidenced by the check reflections in this new experiment was rather conspicuous; satellites of different order had very different decaying rates, while main reflections exhibited practically no decay or even increased with time (Aramburu & Madariaga, 1991). A significant degradation of the crystal could be discarded. These results induced us to perform an additional specific experiment, where 49 reflections were sequentially monitored over more than 100 h. This paper reports the results of this study. It will be shown that the time evolution of the reflections can be fully explained in terms of a certain variation of the form of the structural modulation. The previous knowledge of the incommensurate structure determined (Zúñiga *et al.*, 1989; Tanisaki, Mashiyama & Hasebe, 1988) and the assumption that the structural modulation approximately satisfies the sine-Gordon equation (Aramburu, Madariaga & Pérez-Mato, 1994, 1995) has been essential for a successful quantitative analysis of the results. The present study demonstrates that, when properly chosen and analysed, check reflections can provide a direct insight of the time relaxation of IC modulations. This relaxation is relatively small but clearly observable and its careful characterization can improve the accuracy of the structural analysis of these phases.

2. Experimental

In the refinement of the modulated structure of thiourea performed by Zúñiga *et al.* (1989), a clear asymmetry was observed between the $m < 0$ and $m > 0$ satellite reflections. This was attributed to the data-collection sequence and the fact that only main reflections were used for the intensity-decay correction. Consequently, three independent scale factors were introduced: one for main reflections and the other two for satellite reflections with $m < 0$ and $m > 0$. In principle, this problem could have been avoided if satellite reflections had been included within the check reflections. To ascertain the significance of this shortcoming, a second data collection of the IC phase at 170 K was performed, taking this time both main and satellite reflections as check reflections.

Crystals were grown by slow evaporation of an aqueous solution of the purified compound. The X-ray measurements were performed with a CAD-4 diffractometer equipped with an open N₂-gas-flow cryostat (Cosier & Glazier, 1986). The temperature of the crystal was lowered from room temperature to 170 K at a rate of 6 K min⁻¹. The temperature stability was within ± 0.2 K. Radiation (Cu K α) was selected using a pyrolytic graphite monochromator. The modulus of the modulation wave vector ($\mathbf{q} = 0.116\mathbf{b}^*$) was determined from full profiles, along the modulation direction, of selected (by intensity) first-order satellites. Total time of data collection was 300 h. The chosen check reflections were (setting *Pnma* and four-integer indexing) 5450, 3220, 2001, 5321 and 4003. The relative weakness of second-order satellites prevented their systematic measurement. Once the data collection was complete, the changes with time of the check reflections were analysed. The detected behaviour was rather surprising, mainly among the satellite reflections. Fig. 1 shows the evolution with time of the raw integrated intensity of all check reflections. In order to compare their behaviours, the intensities have been normalized with respect to their value at $t = 0$ h. In the figure, it can be seen how the intensities of the satellites monotonically decrease with time. The decay is almost

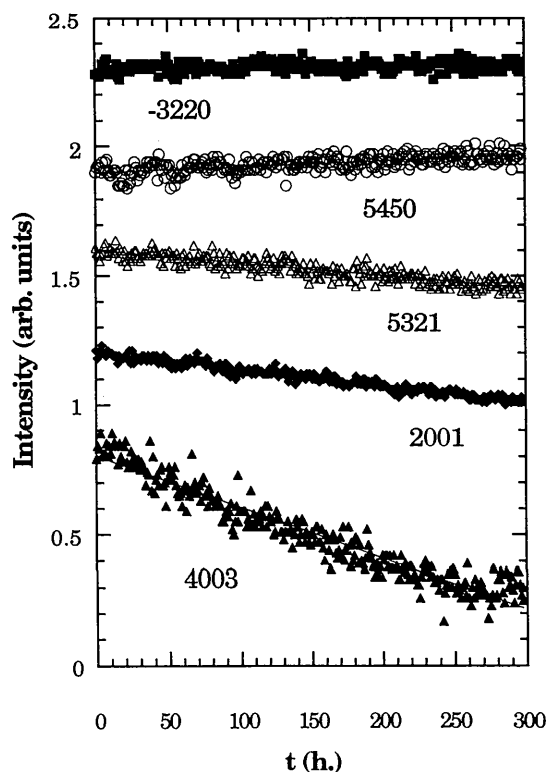


Fig. 1. Evolution with time of the integrated intensity of the check reflections. The intensities have been normalized with respect to their value at $t = 0$ and shifted an arbitrary distance.

linear for all satellites. Only for the third-order satellite can a slight exponential behaviour be inferred and only in this case does the relaxation seem to saturate at the end of the measurement. Hence, 300 h can be taken as a lower limit of the characteristic time associated with the observed kinetic process. The two first-order satellites show a similar decay, much less pronounced than that of the 4003 satellite. On the other hand, the intensity of the main reflection 5450 slightly increases with time while the intensity of the reflection $\bar{3}220$ remains practically constant. The experimental data were fitted to straight lines. An analysis of the obtained slopes clearly shows that the intensity decay of the third-order satellite is around three times greater than those of the first-order satellites. A loss of correlation in the sample as a possible origin for this behaviour can be disregarded. The full width at half-maximum (FWHM) of the reflections along the $\theta-2\theta$ reciprocal direction remains constant with time and even decreases slightly. This result is confirmed by the profile along \mathbf{b}^* of the most intense first-order satellite 2001 (see Fig. 2). Also, the modulation wave vector does not seem to vary significantly with time. Therefore, it should be concluded that the time variation of the reflection intensities has no relation to crystal degradation.

These results could be intuitively explained assuming a certain correlated decrease of the amplitude for all the harmonics contributing to the distortion, but a quantitative assertion and confirmation of this hypothesis requires the time monitoring of a much wider set of reflections, including second-order satellites. Hence, as mentioned in the *Introduction*, a new and specific experiment was performed with this purpose. For this measurement, a new crystal of thiourea was used. The cooling rate of the sample was again 6 K min^{-1} . The radiation was $\text{Mo K}\alpha$. The reflections selected were the check reflections from the previous measurement plus new main reflections and satellites of first, second and third order, up to a total of 49, 32 being symmetry independent (see Table 1). The

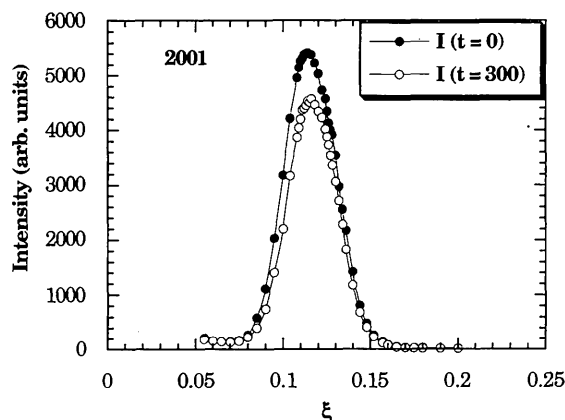


Fig. 2. Profile of the satellite reflection 2001 along $\xi\mathbf{b}^*$ at $t = 0 \text{ h}$ (●) and $t = 300 \text{ h}$ (○).

Table 1. Reflections periodically measured over 166 h at 170 K

Main reflections (10 independent reflections)	
5320	8400
4000	7520
0040	3120
0200	5450
0400	3220
First-order satellites (13 reflections: 3 independent)	
200 $\bar{1}$	532 $\bar{1}$
2001	532 $\bar{1}$
200 $\bar{1}$	532 $\bar{1}$
532 $\bar{1}$	532 $\bar{1}$
5321	
532 $\bar{1}$	
5321	
Second-order satellites (12 reflections: 11 independent)	
4002	3122
400 $\bar{2}$	4202
6442	615 $\bar{2}$
7122	5322
7522	8402
3122	8202
Third-order satellites (14 reflections: 8 independent)	
4003	840 $\bar{3}$
400 $\bar{3}$	8403
4003	312 $\bar{3}$
400 $\bar{3}$	8203
6003	820 $\bar{3}$
6203	8203
8403	
840 $\bar{3}$	

intensity of these reflections were measured periodically (every 1.5 h) over 166 h at 170 K. The evolution with time of the integrated intensity of some representative reflections is shown in Fig. 3. Table 2 shows the values of the slopes resulting from the fitting of the experimental data to straight lines. Only the most significant (within the estimated errors) have been included. The main features observed can be summarized as follows:

(i) The variation of the integrated intensity with time corresponding to the reflections $\bar{3}220$, 5450, 5321, 2001 and 4003 was the same as in the previous experiment. That is to say, the results seem to be independent of the crystal and the type of radiation used.

(ii) The intensity of main reflections can increase, decrease or remain constant depending on the particular reflection considered.

(iii) The satellite intensities always show a monotonically decreasing behaviour with time.

(iv) The dispersion in the values of the slopes resulting from a fitting of the experimental data to straight lines is small for satellites of the same order.

(v) The average value of the decay slope for the n th-order satellites (\bar{S}_n) is proportional to their order (n)

within the experimental accuracy:

$$\overline{S_2}/\overline{S_1} \approx 1.8 \pm 0.7$$

$$\overline{S_3}/\overline{S_1} \approx 2.7 \pm 1.0.$$

(vi) The FWHM of the measured θ - 2θ scans remain practically constant, indicating that the variations in intensity cannot be only due to a loss of correlation in the sample (radiation damage, degradation of the crystal *etc.*).

3. The diffraction diagram as a function of the soliton density

Points (iii), (v) and (vi) in the previous section seem to indicate an evolution with time of the static structure towards a more sinusoidal regime, *i.e.* a decrease in amplitude of the harmonics contributing to the IC distortion with a relatively higher decrease for harmonics of higher order. The atomic modulations measured in thiourea are in general highly anharmonic and this anharmonicity could be described with a soliton density of the order-parameter modulation (Bruce, Cowley & Murray, 1978) of about 0.6 (Zúñiga *et al.*, 1989). It is, therefore, tempting to consider that the observed

Table 2. Most significant slopes resulting from a linear regression of the integrated intensities versus time at 170 K

Intensities were corrected for absorption. Before the fitting, the intensity of each reflection has been divided by its value at $t = 0$. E.s.d.'s are given in parentheses.

Reflection	Slope
$\bar{3}220$	$8 (300) \times 10^{-7}$
7520	$4.6 (6) \times 10^{-4}$
5450	$1.0 (9) \times 10^{-4}$
4000	$-1.22 (9) \times 10^{-3}$
5321	$-3.3 (4) \times 10^{-4}$
$532\bar{1}$	$-3.6 (4) \times 10^{-4}$
2001	$-5.6 (3) \times 10^{-4}$
3122	$-8 (1) \times 10^{-4}$
4002	$-7.3 (9) \times 10^{-4}$
5322	$-7.3 (8) \times 10^{-4}$
4003	$-1.7 (2) \times 10^{-3}$
6003	$-1.2 (2) \times 10^{-3}$
$6\bar{2}0\bar{3}$	$-1.1 (3) \times 10^{-3}$

structural relaxation is the result of a time variation of this soliton density, the particular details of each atomic modulation being kept unchanged. It is, however, not obvious that this hypothesis can explain the variety of behaviours observed in main reflections [point (ii)]. In order to check it, we proceeded with a quantitative analysis of the influence of the modulation changes on the reflection intensities.

According to Zúñiga *et al.* (1989), the atomic modulations describing the modulated structure of thiourea can be in general reduced to expressions of the form

$$u_{\alpha}^{\mu}(v) = u_{\alpha,0}^{\mu} \cos[2\pi\theta(v) + \psi_{\alpha,0}^{\mu}], \quad \alpha = x, y, z, \quad (1)$$

where μ labels the atoms and v is the internal coordinate ($v \equiv \mathbf{q} \cdot \mathbf{l}$ with \mathbf{l} the cell vector and \mathbf{q} the wave vector of the modulation). In fact, this description of the atomic modulation functions can also be obtained when an appropriate thermodynamic potential is used (Aramburu, Madariaga & Pérez-Mato, 1994). In this context, the amplitudes $u_{\alpha,0}^{\mu}$ are proportional to the amplitude of the order parameter, ρ , which is assumed to be independent of v (constant-amplitude approximation), and $\theta(v)$ is the inhomogeneous phase of the order parameter. As the temperature decreases, ρ , and therefore $u_{\alpha,0}^{\mu}$, increase, and the shape of the function $\theta(v)$ (linear in the sinusoidal limit) becomes progressively more step-like (Aramburu, Madariaga & Pérez-Mato, 1994). According to (1), these changes describe the progressive appearance of quasi-commensurate regions separated by discommensurations (or solitons) as a previous state to the lock-in phase (McMillan, 1976; Bak & Emery, 1976; Bruce *et al.*, 1978). It can be demonstrated that in thiourea $\theta(v)$ satisfies approximately the sine-Gordon equation (Aramburu, Madariaga & Pérez-Mato, 1994), although this material does not belong to the type of IC compounds for which the sine-Gordon equation can be derived from a

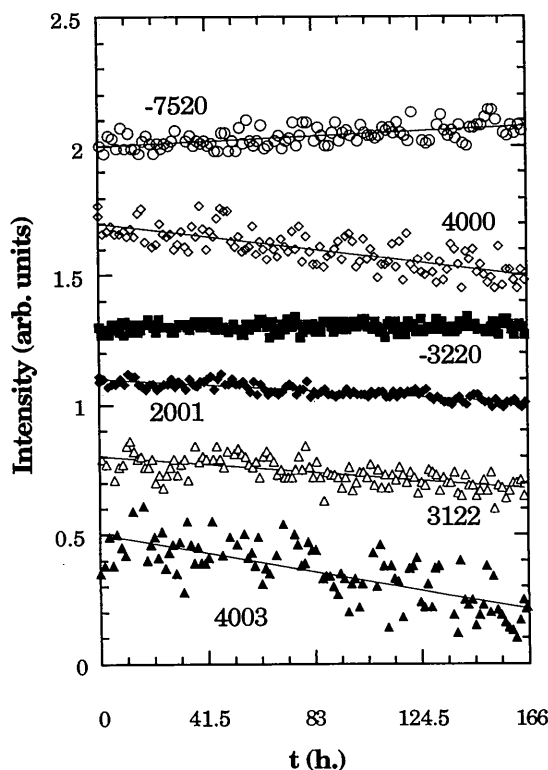


Fig. 3. Evolution with time of the integrated intensity of several reflections. In order to compare their different kinds of behaviour, the intensities have been again normalized at $t = 0$ h and shifted arbitrarily.

straightforward Landau analysis (Bak & Emery, 1976; Bruce *et al.*, 1978; Tolédano & Tolédano, 1987). In the case of thiourea, the equation can be put in the form

$$(d\theta/dv)^2 = [4K^2(k)/\pi^2][1 - k^2 \cos^2(\theta)], \quad (2)$$

$K(k)$ being the complete elliptic integral of the first kind and $\theta(v+1) = \theta(v) + 1$. Therefore, with $\theta(0) \equiv 0$, the configuration of $\theta(v)$ at each temperature within the IC phase will be determined only by the value of the parameter k . In the sinusoidal limit, $k = 0$ and $\theta(v) = v$, whereas in a perfect solitonic limit $k = 1$ and $\theta(v)$ acquires a perfect step-like shape. This parameter, k , is directly related to the soliton density $n_s = \pi/[2K(k)]$ (Blinc, Rutar, Topic, Milia & Rasing, 1986), with the limiting values 1 and 0 in the sinusoidal and solitonic limits, respectively. As in other compounds, in the case of thiourea, the dependence of the amplitude of the order parameter ρ with k is also given by the expression (Golovko, 1980; Sannikov, 1981; Blinc *et al.*, 1986; Aramburu, Madariaga & Pérez-Mato, 1994):

$$\rho(k) = \rho_{\max}[k/E(k)]^{1/2}, \quad (3)$$

ρ_{\max} being the value of ρ at the solitonic limit ($k = 1$) and $E(k)$ the complete elliptic integral of the second kind. Therefore, thermal changes in $\theta(v)$ are related to the changes of ρ through the parameter k (or n_s). Equation (1) can be rewritten as

$$u_{\alpha}^{\mu}(k, v) = u_{\alpha, \max}^{\mu}[k/E(k)]^{1/2} \cos[2\pi\theta(k, v) + \psi_{0\alpha}^{\mu}], \quad (4)$$

showing explicitly that, in principle, the variation of the atomic modulations when temperature is varied is governed by the thermal change of the parameter k (or the soliton density n_s). We will assume that (4) is also valid in the detected relaxation process, the time variation being restricted to the parameter k or n_s . The quantities $\{u_{\alpha, \max}^{\mu}, \psi_{0\alpha}^{\mu}\}$ describe the particular characteristics of each atomic modulation function that define the eigenvector or polarization vector of the mode associated with the order parameter. This eigenvector is supposed to be invariant, while only the global amplitude of the mode and its degree of anharmonicity vary through the parameter k . By definition, when decomposed in harmonics, (4) only contains harmonics having the same symmetry as the first one, *i.e.* the symmetry of the order parameter. In the case of thiourea, these harmonics are the odd ones. Since a second harmonic of different symmetry has been detected in the static modulation (Zúñiga *et al.*, 1989), one should expect that the model may not be enough to explain the intensities of second-order satellites essentially associated with secondary weak modes, but in principle could be sufficient for a description of the main reflections and first- and third-order satellites.

Using (4), the variation of the diffraction diagram of thiourea with the soliton density as single parameter

has been investigated. As amplitudes and phases $\{u_{\alpha, \max}^{\mu}, \psi_{0\alpha}^{\mu}\}$, those associated with the first harmonic in the modulated structure determined by Zúñiga *et al.* (1989) were introduced. H atoms were not considered and isotropic thermal parameters were also extracted from Zúñiga *et al.* (1989). The change of the static modulation towards a more sinusoidal regime was simulated by introducing in (4) several values of k in the interval $[0, 1)$. For each k , the $|F_c(k)|^2$ of the measured reflections (see Table 1) were determined with the REMOS program (Yamamoto, 1982) after decomposing equations (4) into Fourier expansions. Figs. 4(a) and (b) show the evolution of $|F_c|^2$ with n_s for several reflections. To allow a comparison of the relative changes for different reflections, the structure factors of each reflection have been divided by their value in a regime near the sinusoidal limit ($n_s \simeq 0.997$). The intensity behaviour of the satellites appearing in Fig. 4(b) can be considered as representative for all satellites of the same order. Nevertheless, as shown in Fig. 4(a), main reflections exhibit a variety of behaviours: the change of the static modulation towards a more

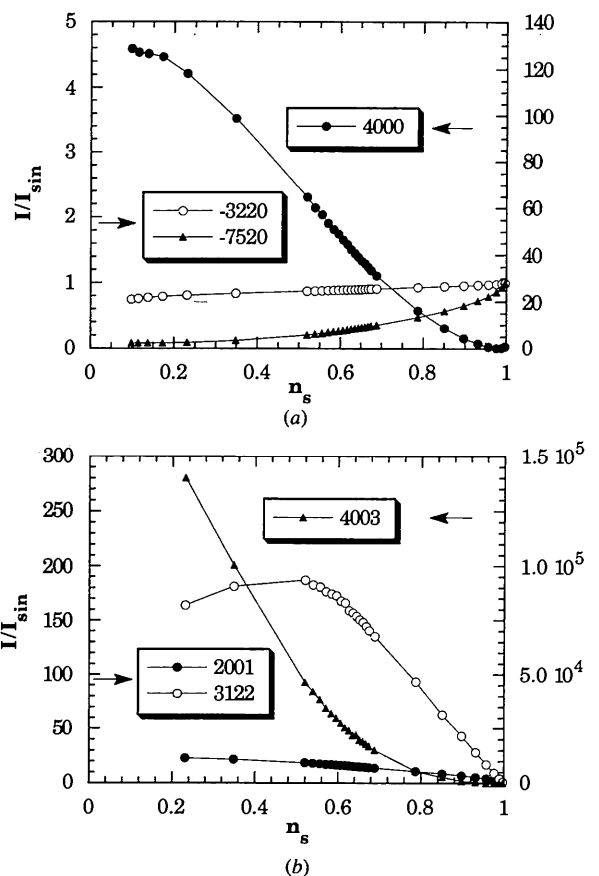


Fig. 4. Evolution of $|F_c|^2$ with n_s for (a) the three main reflections represented in Fig. 3; (b) one satellite representative of the behaviour for each order. The magnitudes of $|F_c|^2$ have been normalized by the value corresponding to $n_s \simeq 0.997$.

sinusoidal regime can imply an intensity increase for some reflections [see the reflection 7520 in Fig. 4(a)], a decrease (4000) or practically no effect (3220). Indeed, the general trends of the structure factors for n_s values around 0.56 [the soliton density proposed for the structure by Zúñiga *et al.* (1989)] confirm the hypothesis of a structural evolution towards a more harmonic regime (limited to a small variation of the soliton density to larger values) as a possible explanation of the time behaviour of the measured intensities [compare Figs. 4(a), (b) with Fig. 3]. Furthermore, if the calculated structure factors are normalized with respect to their value at $n_s \simeq 0.5$, the qualitative relations 'greater than' or 'less than' between the slopes of different reflections also agree with the experiment.

4. Time relaxation of the soliton density

For a quantitative determination of the variation of n_s during the time of the experiment, the full structural data of Zúñiga *et al.* (1989) were considered, *i.e.* the modulations of the H atoms, anisotropic thermal parameters for S, C and N atoms and fixed isotropic temperature factors for H atoms were included in the structure-factor calculations. Instead of identifying directly the first-harmonic amplitudes $\{u_{\alpha,1}^{\mu}\}$ of the experimental structure with the amplitudes $\{u_{\alpha,max}^{\mu}\}$, a more precise estimate of the latter was obtained using (4) and an approximate value of k (n_s) for the determined structure.

An accurate determination of the value of n_s corresponding to the structure of thiourea reported by Zúñiga *et al.* (1989) required a rather complex procedure. Firstly, for each value of k from a selected set in the range [0,1), a corresponding value of $\{u_{\alpha,max}^{\mu}\}$ was calculated with the restriction that their associated first harmonics $u_{\alpha,1}^{\mu}$ were always identical to the ones determined by Zúñiga *et al.* (1989). Then, for each pair $\{k, u_{\alpha,max}^{\mu}\}$, the structure factors corresponding to the 32 independent reflections of Table 1 were generated. The best k (and, therefore, the corresponding $u_{\alpha,max}^{\mu}$) was selected as the one for which a minimum was achieved in the partial R factors* for the corresponding observed structure factors. According to this method, R_1 should be approximately 0 and independent of k , since the first harmonic of the model, which essentially determines the first-order satellites, coincides, by definition, with the experimentally determined one. On the other hand, the second-order satellites will be strongly influenced by second-order harmonics, not considered in the model. Therefore, the partial R factor that determines the value of k will be essentially that corresponding to the third-order satellites. A deep minimum for R_3 at $k = 0.915$ (see Fig. 5) was obtained, which corresponds to

*The partial R factors are defined as $R_m = \sum_{i_m} |F_{o,i_m}| - |F_{c,i_m}| / \sum_{i_m} |F_{o,i_m}|$, where m ($= 0, 1, 2, 3$) indicates the reflection order.

$n_s \simeq 0.67$. This value can, therefore, be taken as the soliton density characterizing the modulated structure determined by Zúñiga *et al.* (1989), to be compared with a rough estimation of 0.56 given in the mentioned reference. In other words, the intensity observed for the selected first- and third-order satellites requires a relation between the first and third harmonics of the modulation similar to that obtained through the sine-Gordon equation for $n_s \simeq 0.67$. A graphical comparison between a theoretical modulation of type (4) corresponding to this soliton density value and one of the atomic modulations determined by Zúñiga *et al.* (1989) is shown in Fig. 6.

Once the approximate values of $\{u_{\alpha,max}^{\mu}\}$ are obtained (in fact of ρ_{max}), the limit values (at $t = 0$ and $t = 166$ h) of the soliton density in the measurement at 170 K reported here can be determined. The extreme extrapolated values at $t = 0$ and $t = 166$ h for the 32

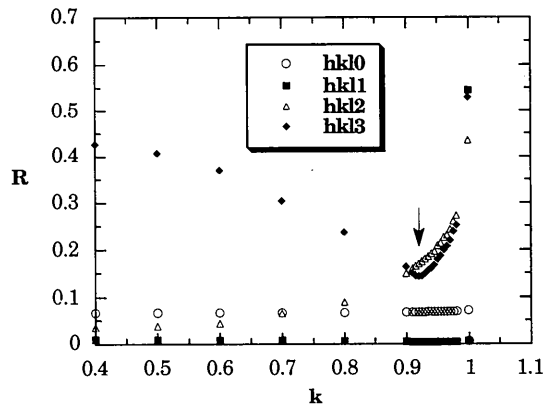


Fig. 5. Partial R factors plotted as functions of k . The values of $|F_c|^2$ have been obtained according to the method described in the text. The corresponding $|F_o|^2$ are those of Zúñiga *et al.* (1989) at 168 K. The agreement factors have been calculated for the 32 independent reflections listed in Table 1.

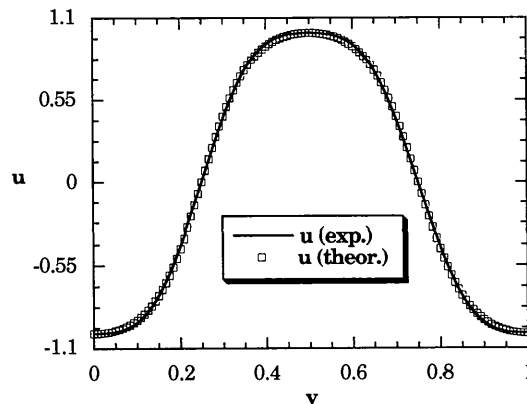


Fig. 6. Comparative plot showing the displacement obtained from the sine-Gordon equation for $n_s \simeq 0.67$ (\square) and that corresponding to the rigid-body translation along z (continuous line) extracted from Zúñiga *et al.* (1989). v is the internal coordinate defined as $v \equiv \mathbf{q} \cdot \mathbf{l}$, where \mathbf{l} is the cell index and \mathbf{q} the wave vector of the modulation.

independent reflections (corrected for absorption and Lorentz-polarization) were taken as $|F_o|^2$ and compared with the calculated structure factors for different values of k . The partial R factors are represented as a function of k in Fig. 7. At $t = 0$ (see Fig. 7a), the value of k for which R_1 and R_3 present a minimum is $k \simeq 0.945$ ($n_s \simeq 0.62$). That is to say, at the beginning of the measurement the structural modulation was approximately characterized by a soliton density of 0.62. It can be observed that the minima for R_1 and R_3 occur practically at the same value of k , showing the forced (by the sine-Gordon equation) correlation between the first and third harmonics of the structural modulation. On the other hand, a correct explanation of the intensity observed in the second-order satellites would require a primary distortion of greater amplitude and/or the introduction of an additional secondary distortion. With the same calculations carried out for the $|F_o|^2$ at $t = 166$ h (see Fig. 7b), the soliton density [$n_s \simeq 0.69$] ($k \simeq 0.9$) at the end of the measurement was obtained. It is worth noting that the correlation between first- and third-order satellites remained approximately valid, showing their corresponding agreement factors were a

minimum for, approximately, the same value of k . Furthermore, the value of the soliton density of the structure determined at 168 K (Zúñiga *et al.*, 1989) was within the range of variation obtained for the soliton density at 170 K:

$$[n_s(170 \text{ K}, t = 0) \simeq 0.62] < [n_s(168 \text{ K}) \simeq 0.67] \\ < [n_s(170 \text{ K}, t = 166 \text{ h}) \simeq 0.69].$$

This probably indicates that the same kind of structure relaxation occurred at 168 K during the data collection and, in consequence, the published structural model represents an average between two limiting states.

Under the assumption of a linear time decay of n_s between the two estimated extreme values, the square of the structure factors was calculated along the time interval of the experiment. As in the experimental case, the calculated intensities were normalized by their value at $t = 0$. The results showed a good agreement with the experimental decay of the intensities for first- and third-order satellites (see §2):

$$(\overline{S_2}/\overline{S_1})_{\text{simul}} \simeq 1.2 \\ (\overline{S_3}/\overline{S_1})_{\text{simul}} \simeq 2.8.$$

The higher disagreement in the case of the second-order satellites should be expected as no second-order harmonic has been allowed in the modulation. Another limitation that can influence the results is that all modulations have been forced to have the same degree of anharmonicity (*i.e.* the same value of n_s). Such strict regularity is not exactly true: Among the six modulation functions obtained in a rigid-body approximation of the molecule, there is one that remains almost sinusoidal, the one corresponding to the translation along the a axis (Zúñiga *et al.*, 1989; Tanisaki, Mashiyama & Hasebe, 1988). The reason for this exception is well understood (Aramburu, Madariaga & Perez-Mato, 1994) but for simplicity this feature has been neglected in the calculations above. In any case, the observed time behaviour of first- and third-order satellites is satisfactorily described with this simplified model, at least on average.

The model used above correlates the changes in ρ and θ , that is to say, the changes in the amplitude of the first harmonic are correlated with the changes in the modulation anharmonicity (ratio between the amplitudes of the third and first harmonics). It could be argued that other alternative simple relaxation processes could be possible; for instance, a change in ρ without any change of θ or, conversely, only changes in θ while ρ remains constant. In order to elucidate among these three possibilities, a comparative study of the evolution of $|F_c|^2$ predicted in such different cases between $n_s = 0.62$ and $n_s = 0.69$ was carried out. In the case of the third-order satellites, that should be the most influenced by the changes in the phase θ , the observed evolution with time

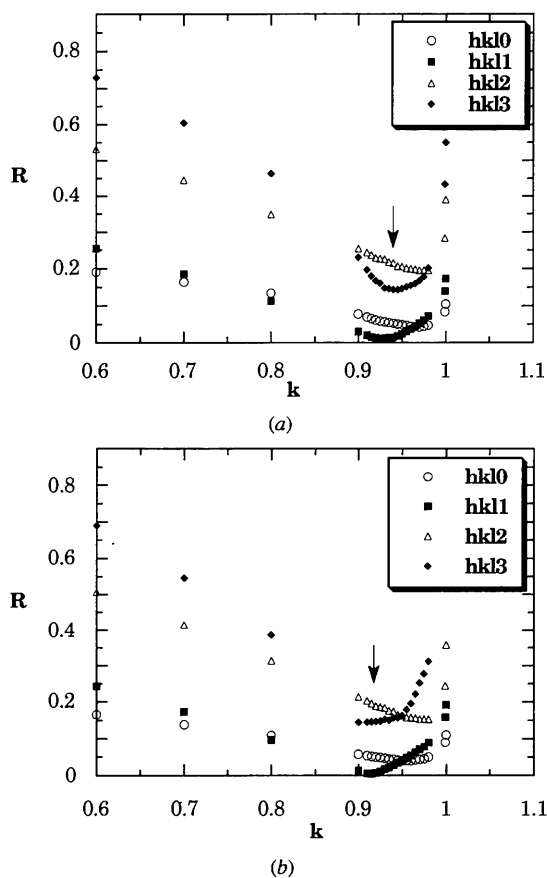


Fig. 7. Partial R factors plotted as functions of k corresponding to the reflections listed in Table 1: (a) at $t = 0$ h; (b) at $t = 166$ h.

can be mainly explained changing only the phase θ (see Fig. 8a). Nevertheless, an adequate explanation of the behaviour of the first-order satellites needs a change in ρ (see Fig. 8b). In consequence, an adequate explanation of the evolution with time of all reflections observed would require a change of both amplitude and degree of anharmonicity of the modulation. According to the values of n_s determined for $t=0$ and $t=166$ h, the relative changes in ρ and anharmonicity are about 2.4 and 22%, respectively.

Finally, Fig. 9 schematizes the change in a given atomic modulation associated with the change of the soliton density detected during the experiment, from $n_s \simeq 0.62$ ($t=0$ h) to $n_s \simeq 0.69$ ($t=166$ h).

5. Conclusions

A systematic and reproducible change with time in the diffracted intensities by the IC phase of thiourea has been

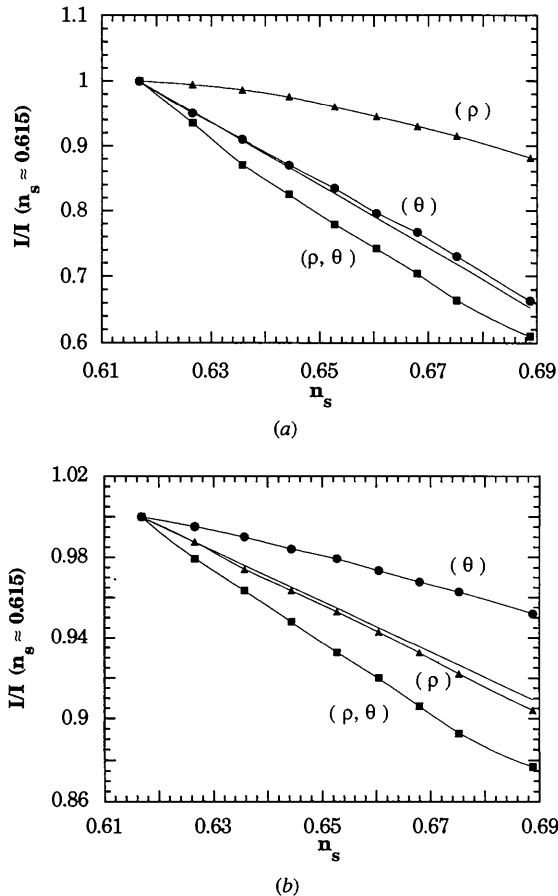


Fig. 8. Evolution with n_s of the square of the structure factors calculated considering a change in both amplitude (ρ) and phase (θ) of the order parameter (■), only in θ (●) or only in ρ (▲) for the reflections (a) 4003 and (b) 2001. The continuous line represents the experimental evolution assuming a linear relation between n_s and time. n_s has been varied within the range assigned at 170 K.

observed at 170 K. Intensities decrease in the case of satellites (up to 28% in the case of the third-order satellite 4003 after 166 h). In the case of main reflections, the time behaviour strongly depends on the value of the indices. In all cases, the FWHM remains constant, indicating that the changes in intensities were not related to degradation phenomena. The time of measurement must be at least 300 h to see a possible end of the process (see the behaviour of the intensity of reflection 4003 in Fig. 1). The kinetic process observed can be modelled within the Landau framework and is consistent with a correlated decrease in the amplitudes of the harmonics of the modulation, reducing its anharmonicity. Clearly, the structural modulation evolves with time towards a more sinusoidal regime. Quantitatively, the average evolution of the intensities of the first- and third-order satellites can be explained by correlated changes in the amplitude for the first and third harmonics of 4.6 and 25.6% in 166 h, respectively. In terms of the soliton density, this corresponds to a change from $n_s \simeq 0.62$ at the beginning of the measurement to $n_s \simeq 0.69$ at the end. In the case of second-order satellites and main reflections, these changes are not sufficient to explain quantitatively what is observed, which is reasonable if we consider that the second harmonic in the modulation was not included in the structural model.

The present work demonstrates that, if data are carefully analysed, X-ray diffraction is sensitive enough, to detect very small variations (see Fig. 9) of the soliton density associated with IC structures, at least when the number of solitons is small.

The reason for the soliton density of the modulation changing with time is not clear. On one hand, the time evolution of the structural modulation towards a more sinusoidal regime could indicate a response of the modulation to a too fast decrease of the temperature and its accommodation to a more sinusoidal defect wave with more thermal inertia. But, on the other hand, this evolution of the structural modulation seems to be very

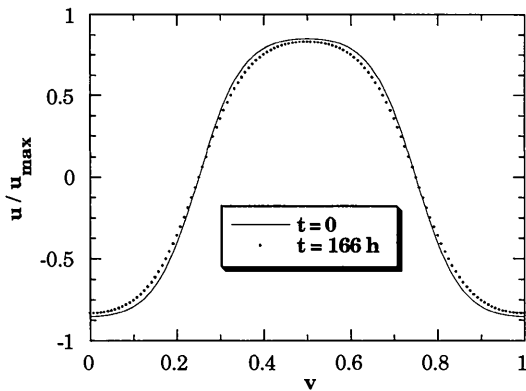


Fig. 9. Change of an atomic modulation at 170 K from $t=0$ h (continuous line, $n_s \simeq 0.62$) to $t=166$ h (●, $n_s \simeq 0.69$).

slow compared with other compounds where structure relaxations have also been detected. It remains to be explained, for instance, why such slow relaxation has not been reported in dielectric measurements of thiourea or its deuterated isomorph, or if the fact that the sample is being continuously irradiated in the X-ray experiment plays a role.

The relaxation phenomenon that has been characterized here, if general among IC material, evidences a limitation in the acquisition and treatment of diffraction experimental data for this type of system. A more sophisticated internal scaling than the usual ones, including also satellites as check reflections, can easily complement the structure determination with some information about the structure-time evolution during the data collection (Madariaga & Aramburu, 1996), facilitating the access to a noticeable amount of additional information that is, until now, routinely wasted. If this information were carefully analysed, the accuracy of the structural studies of IC materials could be further improved.

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