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X-ray study of the modulation-wave structure in thiourea

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A longitudinal component of the modulated structure of thiourea $SC(NH_2)_2$ which corresponds to the translational mode transformed under the irreducible representation B_{3g} in D_{2h} has been observed by x-ray diffraction. The parameters including the longitudinal component are examined. The longitudinal component accounts well for the asymmetry of pairs of the satellite intensities ($hkl \pm \delta$). The phase of the longitudinal wave differs by $\pi/2$ from those of the transverse waves of B_{2u} symmetry, which corresponds to the ferroelectric soft mode. The amplitude of the longitudinal wave is as small as 10^{-1} times those of the transverse waves. A possible interpretation on the longitudinal mode is given by considering the short-range interaction between molecules: It suggests that the longitudinal component, as well as the transverse components, plays an important role in the occurrence of the incommensurate phase of thiourea.

I. INTRODUCTION

Thiourea is a well-known molecular ferroelectric compound, which displays several intermediate incommensurate (IC) and commensurate (C) phases in the temperature–pressure–dc-bias-field phase diagram. Since the phase transitions in this substance are very attractive, many experimental and theoretical studies have been performed.¹ Three important phases exist at the atmospheric pressure: paraelectric (P) phase ($> -71^\circ C$, $Pbnm$), ferroelectric (F) phase ($< -104^\circ C$, $Pb2_1m$), and IC phase (between the P phase and the F phase). The F phase arises as the result of the condensation of the B_{2u} mode in D_{2h} .² The IC phase is characterized by the wave vector $q = \delta c^*$, where δ varies from $\frac{1}{7}$ to $\frac{1}{9}$. If we assume that the molecules are rigid units, only the three modes are allowed in the B_{2u} symmetry. However, at $q = \delta c^*$ another three modes are added, which correspond to the B_{3g} symmetry at $q = 0$ (Table I).^{3,4} Several workers have shown that only three modes of the B_{2u} symmetry sufficiently describe the modulated structure even at $q = \delta c^*$.^{3,5} However, Denoyer *et al.* pointed out the existence of a longitudinal component in deuterated thiourea by means of neutron diffraction.⁶ Nevertheless, no analysis of this longitudinal component

has been performed yet. It is very interesting to consider the role of the longitudinal mode in the successive phase transitions of thiourea.

We report here on the observation of the longitudinal mode by x-ray diffraction and the analysis of the structure of the modulation wave in $SC(NH_2)_2$.

II. EXPERIMENTS AND RESULTS

Cylindrical specimens parallel to the a and b axes were prepared, of which lengths and diameters were about 0.5 and 0.3 mm, respectively. They were mounted in a cryostat which controlled the temperature of the sample within $\pm 0.5^\circ C$. A $2\theta - \omega$ step scanning method was adopted for measuring the integrated intensities of ($h 0 l \pm \delta$) and ($0 k l \pm \delta$) satellite reflections using a four-circle diffractometer. Thus we have 78 independent integrated intensities of the first satellite reflections.

The most important facts are the existence of the weak ($0 0 7 \pm \delta$) reflections, and their temperature dependence different from the ordinary satellite reflections (Fig. 1). This is the first direct evidence of an appearance of a longitudinal component in the IC phase of natural thiourea. There is no extinction rule on ($0 0 l$) reflections in the F phase; however, at $-148^\circ C$ (in the F

TABLE I. The symmetry coordinates for the molecules of thiourea for $q = (0, 0, 2\pi\delta/c)$ ($0 < \delta < \frac{1}{2}$). For example, the amplitude of the translational mode along the a axis for molecule 2 is obtained as $T_{a2} = -T_a$. The molecules are labeled as in Ref. 5.

Molecule	$\delta = 0$				$\delta \neq 0$			
	1	2	3	4	1	2	3	4
T_a		$-T_a$	$-T_a$	T_a	T_a	$-T_a$	$-T_a$	T_a
T_b		T_b	T_b	T_b	T_b	T_b	T_b	T_b
					T_c	T_c	$-T_c$	$-T_c$
					R_a	R_a	R_a	R_a
					R_b	$-R_b$	$-R_b$	R_b
R_c		$-R_c$	R_c	$-R_c$	R_c	$-R_c$	R_c	$-R_c$

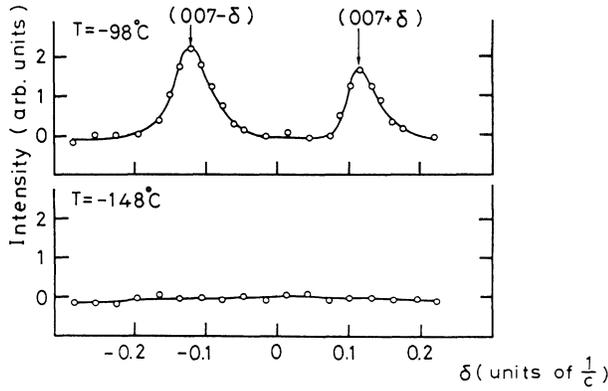


FIG. 1. Satellite reflections of $(007\pm\delta)$. $T = -98$ and -148°C .

phase) the main reflection of (007) does not appear. Thus these facts suggest that the longitudinal component is induced by the ferroelectric soft mode only in the IC phase. There are several representations that contain the translational T_c mode; however, only the B_{3g} representation allows the $(007\pm\delta)$ reflections. Therefore, it is concluded that this longitudinal component (the z component) of the modulation wave corresponds to the

translational T_c mode transformed under the B_{3g} representation.

Therefore, we can describe the modulated structure as a superposition of the soft modes and the translational mode T_c of the B_{3g} symmetry.

The position of the j th atom in the i th molecule of the L th cell is given as

$$\mathbf{r}_{Lij} = \mathbf{r}_{0ij} + \mathbf{U}_{Lij}, \quad (1)$$

where

$$\begin{aligned} \mathbf{U}_{Lij} = & R_{ci} \sin(q\xi) \mathbf{e}_c \times (\mathbf{r}_{0ij} - \mathbf{r}_{Gi}) + T_{ai} \sin(q\xi + \phi_a) \mathbf{e}_a \\ & + T_{bi} \sin(q\xi + \phi_b) \mathbf{e}_b + T_{ci} \sin(q\xi + \phi_c) \mathbf{e}_c, \\ & \xi = Lc + z_{Gi}. \quad (2) \end{aligned}$$

\mathbf{r}_{0ij} stands for the atomic position of the average structure and $\mathbf{r}_{Gi} = (x_{Gi}, y_{Gi}, z_{Gi})$ the position of the center of mass of the i th molecule. R_{ci} is the amplitude of the rotational mode. T_{ai} , T_{bi} , and T_{ci} are the amplitudes of the translational modes. ϕ_a , ϕ_b , and ϕ_c are the phases of the translational modes relative to the rotational mode. The molecule-numbering system is the same as in Ref. 5.

Using Eqs. (1) and (2) and Table I, the intensity of the first satellite reflection, of which the scattering vector is \mathbf{Q} , is given as

$$\begin{aligned} I(\mathbf{Q}) = & c_{Rcc}(\mathbf{Q}) R_c^2 + \sum_{m,n} \{ T_m T_n [c_{Tmn}(\mathbf{Q}) \cos(\phi_m - \phi_n) + c'_{Tmn}(\mathbf{Q}) \sin(\phi_m - \phi_n)] \} \\ & + R_c \sum_m \{ T_m [c_{Rm}(\mathbf{Q}) \cos(\phi_m) + c'_{Rm}(\mathbf{Q}) \sin(\phi_m)] \}, \\ & c_{Tmn}(\mathbf{Q}) = c_{Tnm}(\mathbf{Q}), \quad c'_{Tmn}(\mathbf{Q}) = -c'_{Tnm}(\mathbf{Q}), \quad (3) \end{aligned}$$

where m and n represent a , b , and c .

Equation (3) seem to be rather complicated. However, the coefficients c_{Tab} , c_{Tac} , c_{Tbc} , c'_{Ra} , c'_{Rb} , and c_{Rc} are found to be zero for the case of thiourea from the relations of the polarized vectors (Table I). Furthermore, the following relations hold for any pairs of $\mathbf{Q}^+ = \mathbf{Q}(h, k, l + \delta)$ and $\mathbf{Q}^- = \mathbf{Q}(h, k, l - \delta)$ for the same reason:

$$\begin{aligned} c'_{Tac}(\mathbf{Q}^+) & \simeq -c'_{Tac}(\mathbf{Q}^-), \\ c'_{Tbc}(\mathbf{Q}^+) & \simeq -c'_{Tbc}(\mathbf{Q}^-), \\ c'_{Rc}(\mathbf{Q}^+) & \simeq -c'_{Rc}(\mathbf{Q}^-). \end{aligned} \quad (4)$$

Therefore, the phase parameters are partly responsible for generating the asymmetry of the satellite intensities, when not all of the ϕ 's are zero.

In the course of the analysis, the room-temperature atomic coordinates were used for the mean structure. The anisotropic temperature factors were determined by the interpolation of the values in the P phase and the F phase.² Since the hydrogen atom is a weak scatterer in x-ray diffraction, the rigid-molecule model would be better than in the case of neutron diffraction. In the

present analysis, the effect of the hydrogen atoms are neglected.

The phases ϕ_a , ϕ_b , and ϕ_c are important parameters describing the structure of the IC phase; however, the phases and the amplitudes could not be refined simultaneously. So we tried to determine R_c , T_a , T_b , and T_c by least-squares calculations with many sets of the fixed phase parameters.

In the case of $T_c = 0$, as a trial calculation, which neglects the existence of the satellites of $(007\pm\delta)$, the minimum R value 13.5 was obtained for $\phi_a = \phi_b = 0$. When the longitudinal component is taken into account ($T_c \neq 0$), the minimum R factor of 12.7 is obtained for $\phi_a = \phi_b = 0$ and $\phi_c = \pi/2$. All the parameters obtained are given in Table II. The observed and calculated structure factors are given in Table III.

III. DISCUSSION

The values of R_c , T_a , and T_b in Table II are almost the same as those obtained in $\text{SC}(\text{ND}_2)_2$ by McKenzie without considering T_c .³ All the amplitudes of the mode which correspond to the B_{2u} symmetry (T_a, T_b, R_c) have the same order. It suggests that the R_c mode couples to

TABLE II. Parameters at -98°C determined by the least-squares calculation. T_a , T_b , T_c , and R_c are the amplitudes for molecule 1 and ϕ_a , ϕ_b , and ϕ_c are the phases in Eq. (2).

$R_c = 5.25 \pm 0.31$ deg	
$T_a = -0.142 \pm 0.005$ Å	$\phi_a = 0$
$T_b = 0.113 \pm 0.007$ Å	$\phi_b = 0$
$T_c = -0.0085 \pm 0.0041$ Å	$\phi_c = \pi/2$

the T_a and the T_b modes at $\mathbf{q} = \delta\mathbf{c}^*$. The softening of the T_a mode in the IC phase (at $\mathbf{q} = 0$) has been found by Chapelle and Benoit⁷ and the possibility of the coupling between the R_c mode and the acoustic T_b mode (at $\mathbf{q} = \delta\mathbf{c}^*$) has been pointed out by Denoyer *et al.*⁶ Their results are consistent with the present work. We added

only the T_c mode which belongs to the irreducible representation B_{3g} . If the other modes of B_{3g} symmetry are added (R_a, R_b as in Table I), the discrepancy factor R would be smaller than 12.7.

McKenzie assumed that the values of ϕ_a and ϕ_b were zero, and if we use the full symmetry analysis in Ref. 8, the values of the ϕ_a , ϕ_b , and ϕ_c are obtained as 0, 0, and $\pi/2$, respectively. However, if the accuracy of the data is not so high, the phase parameters would not be determined definitely.⁹ So we have experimentally confirmed them in order to check the reliability of the present data. The result for the T_c mode seems to be very interesting. Since the R_c mode generates the polarization wave $P_b(z)$,^{2,5} the distance between molecules 1 and 4 (2 and 3) should be largely changed around the nodes of $P_b(z)$ owing to the phase of the T_c . The polarization wave in

TABLE III. Observed and calculated structure factors at -98°C .

h	k	l	$F_o(h\ k\ l + \delta)$	$F_c(h\ k\ l + \delta)$	$F_o(h\ k\ l - \delta)$	$F_c(h\ k\ l - \delta)$
0	0	7	0.59	0.94	0.77	0.89
0	2	0	10.08	9.09	10.06	9.09
0	4	0	9.58	9.29	9.56	9.29
0	6	0	8.28	8.57	8.12	8.57
0	6	1	3.02	3.05	2.80	3.19
0	8	1	3.18	3.30		
0	2	2	8.71	7.86		
0	4	2	9.15	9.19	10.01	9.12
0	6	2	7.52	8.12	7.80	8.07
0	8	2	5.43	6.46	5.29	6.41
0	8	3	3.49	3.22	2.98	3.32
0	2	4	6.95	6.20	6.21	5.76
0	4	4	7.79	8.08	8.86	8.17
0	6	4	6.01	7.06	6.58	7.10
0	8	4	4.83	5.59	4.71	5.40
0	2	6	4.01	4.32	4.83	4.63
0	4	6	6.55	6.11	6.35	6.15
0	6	6	5.63	5.88	5.99	5.64
0	2	8	1.68	3.02	2.98	3.61
0	4	8	4.44	4.50	4.10	4.46
0	6	8	4.39	4.49	3.92	4.13
1	0	0	1.34	2.33	1.35	2.33
5	0	0	8.40	8.09	8.33	8.09
2	0	1	5.37	3.81	4.58	4.03
1	0	2	3.07	3.03	3.06	2.60
5	0	2	3.40	3.66	3.83	4.25
4	0	3	6.92	6.25	6.31	5.21
6	0	3	8.74	6.97	8.28	6.67
3	0	4			7.82	6.81
4	0	5	4.98	4.08	4.40	3.66
3	0	6	2.64	2.30	2.95	3.41
5	0	6	3.78	4.03	3.70	3.41
1	0	4	3.03	2.91	1.69	1.91
1	0	8	1.97	0.81	1.78	0.84
2	0	7	2.58	2.38	1.37	1.90
3	0	2	4.07	5.64	3.90	5.34
3	0	8	1.04	0.98	1.88	1.88
6	0	1	2.00	3.26	1.59	2.85
6	0	5	4.43	4.92	4.39	5.36
7	0	0	4.07	5.35	4.03	5.35
2	0	9	1.29	1.12		

the IC structure makes a sequence of the P structure [around $P_b(z)=0$] and the F structure [around $|P_b(z)|=\max$]. Molecules 1 and 4 (2 and 3) are connected by the hydrogen bonds $S \cdots H-N$ to each other.² It results that the hydrogen bonds would be changed periodically in the IC phase. It is well known that a certain short-range interaction such as the hydrogen bond is necessary for the appearance of the IC and F phases in thiourea.^{10,11,12}

As described below, the T_c mode is supposed to be important in the IC structure of thiourea when the lengths of the hydrogen bonds are taken into account. Since the T_c is maximum near the region where the R_c is almost zero [$P_b(z) \simeq 0$], it is important to observe this region for understanding the meaning of the T_c . The following two cases are expected in this region at any incommensurate q :

Case I. Molecule 4 is located near U in Fig. 2, and the neighboring molecule 1 is near V . In this case, $z_{G4} < z_{G1}$ and

$$R_{c1} \sin(q\xi) > 0, \quad T_{c1} \sin(q\xi + \phi_c) < 0,$$

$$R_{c4} \sin(q\xi) > 0, \quad T_{c4} \sin(q\xi + \phi_c) > 0.$$

Case II. Molecule 1 is near U in Fig. 2 and the neighboring molecule 4 is near V ; namely, $z_{G1} < z_{G4}$, and

$$R_{c1} \sin(q\xi) < 0, \quad T_{c1} \sin(q\xi + \phi_c) < 0,$$

$$R_{c4} \sin(q\xi) < 0, \quad T_{c4} \sin(q\xi + \phi_c) > 0.$$

Figure 3 shows schematically the situation of case I. The distances of N-S are elongated by the R_c mode, while the T_c mode shortens the N-S lengths. It is understood that the obtained parameters of the T_c mode make plausible compensation. If any other set of the parameters of the T_c mode are adopted, this compensation would not be expected and the strength of the hydrogen bond in this region would be altered more drastically from the mean structure. Consequently, the direct origin of the T_c mode must be in the short-range interaction. For case II, the same interpretation is derived in the same manner.

It should be noted that the existence of the T_c mode and its phase difference to the soft mode R_c are in accordance with the theory given by Levanyuk and Sannikov¹³ and Heine and McConnell.¹⁴ Therefore, it is possible that our T_c is the subsidiary mode in their theory. We think that this is the next problem to be solved by further experiments and simulations based on their model for thiourea.

Recently, Kucharczyk and Paciorek studied the IC structure of NaNO_2 .¹⁵ They found the existence of the displacive wave in addition to the polarization wave, and revealed that there is no phase shift between them. The displacive wave in NaNO_2 corresponds to the T_b mode in thiourea.

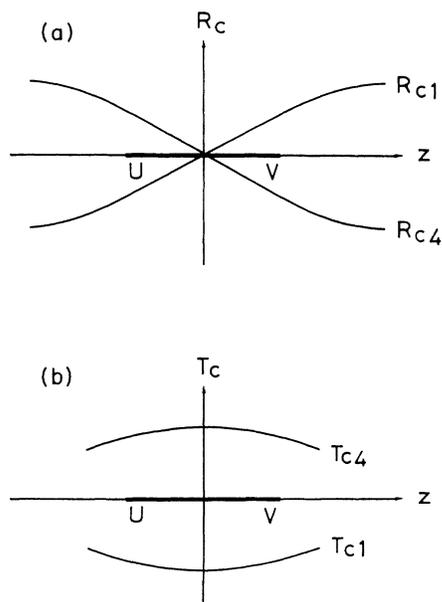


FIG. 2. Schematic representations of (a) R_c and (b) T_c around $P_b(z)=0$ for the case of $\phi_c = \pi/2$. Here, R_{ci} and T_{ci} mean $R_{ci} \sin(qz)$ and $T_{ci} \sin(qz + \phi_c)$, respectively ($i=1,4$). The node of R_c exists between molecule 4 and 1 (case I) or between molecule 1 and 4 (case II) in the linear chain $\cdots 1 \cdots 4 \cdots 1 \cdots 4 \cdots 1 \cdots$ at incommensurate q .

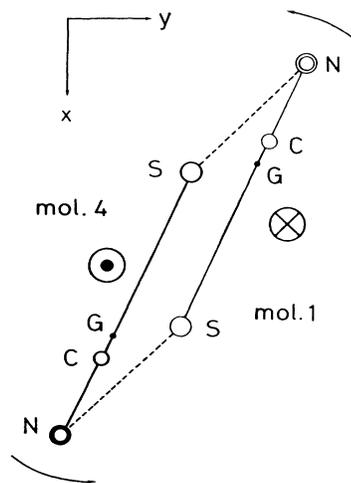


FIG. 3. Schematic illustration of molecules 1 and 4 for case I. The value of z_G of molecule 1 is larger than that of molecule 4 ($z_{G4} < z_{G1}$). The arrows represent the direction of R_c and point G represents the center of mass. The symbol \otimes near molecule 1 represents that the displacement along the z axis owing to the T_c is negative; $T_{c1} \sin(q\xi + \phi_c) < 0$. The symbol \odot near molecule 4 shows that the displacement is positive; $T_{c4} \sin(q\xi + \phi_c) > 0$. Hydrogen atoms are ignored.

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