Acta Cryst. (1988). B**44**, 441–445

Commensurately Modulated Structure of Thiourea at 170 K

By S. Tanisaki* and H. Mashiyama

Department of Physics, Faculty of Science, Yamaguchi University, Yamaguchi 753, *Japan*

and K. Hasebe

Department of Physics, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi 753, *Japan*

(*Received* 13 *July* 1987; *accepted* 6 *April* 1988)

Abstract

The ninefold superstructure of $SC(NH_2)_2$ was determined by single-crystal X-ray diffractometry at 170 K; orthorhombic, *Pbnm*, $a = 5{\cdot}467\ (1)$, $b = 7{\cdot}545\ (1)$, $c = 76{\cdot}867\ (11)$ Å, $V = 3171{\cdot}1$ Å^3, $Z = 36$, $D_x = 1{\cdot}435$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}89$ mm^{-1}, $R = 0{\cdot}048$ for 1510 independent reflections. The commensurate phase is stable between the ferroelectric phase (I) and the incommensurate phase (II), in a temperature range of about 2 K. The structure is characterized by a rotation of the $SC(NH_2)_2$ molecule along the *c* axis coupled with a displacement of the center of mass in a plane perpendicular to the axis. Around mirror planes ($z = \frac{1}{4}$ or $\frac{3}{4}$) the local structure is isostructural with phase I. Therefore the superstructure is constructed of alternately polarized layers which are sandwiched by domain walls (or discommensurations) whose local structure is that of the paraelectric room-temperature phase (V) around $z = 0$ and $\frac{1}{2}$.

Introduction

Since the first report on ferroelectricity in thiourea (Solomon, 1956), the successive phase transitions have been widely investigated (Goldsmith & White, 1959). The crystal structures of the room-temperature phase (phase V: *Pbnm*, $Z = 4$) and the lowest temperature ferroelectric phase (phase I: $Pb2_1m$, $Z = 4$) have been refined successfully (Elcombe & Taylor, 1968).

The incommensurately modulated structures in phases II and IV have also been analyzed (Tanisaki & Nakamura, 1970; Shiozaki, 1971). They observed X-ray scatterings and recognized two extinction rules; *i.e.* $(h_10h_3h_4)$ for $h_1+h_3+h_4 = \text{odd}$ and $(0h_2h_3h_4)$ for $h_2 = \text{odd}$, where h_4 stands for the h_4th-order satellite of main reflection $(h_1h_2h_3)$. Shiozaki assumed a pure transverse sinusoidal displacement of atoms and refined the structure of phase IV. Tanisaki & Nakamura analyzed the structure of phase IV (188 K) by a model in which the molecular directions in successive *c* planes vary sinusoidally along the *c* axis between two directions which correspond to the two oppositely polarized states of the ferroelectric phase I. They also considered a small deviation of the molecular axis from the *c* plane to account for the asymmetry of the satellite intensities.

On the other hand, some weak first-order satellites $(h_10h_3\pm1)$ for $h_1 + h_3 = \text{even}$ were observed in neutron-scattering intensities from deuterated thiourea (McKenzie, 1975). Here, the first extinction rule recognized in earlier work was rejected, and the structure at 205 K refined by a rigid molecular model with the requirement of τ_4 symmetry for the displacements. Yamamoto (1980) re-analyzed the X-ray data of Shiozaki under the four-dimensional space-group consideration. He concluded that the second-order harmonics also condensed in the incommensurate phase.

To the present authors' knowledge, the crystal system of thiourea is orthorhombic and no spontaneous polarization appears either in phases II and IV or in phase V. In addition, the third-order harmonics should become significant in a lower temperature range in the incommensurate phase, whereas second-order harmonics stem only from electric fields or external stress (Ishibashi & Shiva, 1978).

Recently another commensurate phase has been recognized in a narrow temperature region of about 2 K between phase I and phase II (Moudden, Denoyer, Lambert & Fitzgerald, 1979; Tanisaki, Mashiyama & Hasebe, 1984). Since this new phase has a ninefold superstructure and the modulation wavenumber does not differ significantly from the incommensurate one, the structural analysis of this phase would be expected to give much information about the incommensurately modulated structure as well as the incommensurate–commensurate phase transition. If all independent parameters are allowed to move, then we can find all Fourier components of the modulated structure.

Experimental and structure refinements at 170 K

Single crystals were grown from an ethanol solution by slow evaporation at room temperature. A spherical

---

* Present address: Faculty of Law and Economics, Yahata University, Kitakyushu 805, Japan.

0108-7681/88/040441-05$03.00

specimen of radius 0·167 mm was prepared from a transparent part of the grown crystal, and mounted on an automatic four-circle single-crystal diffractometer (Rigaku AFC-5). The temperature of the sample was held at 170±0·5 K by controlled nitrogen gas flow. Monochromatic (bent graphite) Cu $K\alpha$ radiation generated from a rotating anode generator operating at 50 kV and 150 mA was used for measuring the intensities by the θ–2θ scan method for reflections with $2\theta_{\max} = 130°$ ($0 \le h \le 6$, $0 \le k \le 8$, $0 \le l \le 90$). The scan speed was 10° min^{-1} in θ and the scan width in θ was $(0{\cdot}7+0{\cdot}2\tan\theta)°$. The background was counted at both ends of each scan. Every 100 observations, four standard reflections including a satellite one were monitored; no significant variation was detected. Standard deviations of the structure factors were calculated from counting statistics and the reflections with $F \ge 3\sigma(F)$ were used for the analysis. Absorption and Lorentz–polarization corrections were made (transmission factors 0·50–0·57). Lattice parameters were determined from 20 reflections with $\theta = 29$–$63°$.

The extinction rules recognized in phase IV (Tanisaki & Nakamura, 1970; Shiozaki, 1971) correspond to ($h0l$) for $h+l=$ odd and ($0kl$) for $k=$ odd for the ninefold cell dimensions along the c axis in the new phase. Among 1593 significant reflections with $F \ge 3\sigma(F)$, 81 reflections did not satisfy the rules. In order to check the rules we investigated another sample. This showed that 72 of the reflections were weak enough to be discounted. The remaining nine reflections were suspected of either being caused by multiple reflection effects or being part of a nearby main reflection, and were ignored in further analysis. The strong reflections have pronounced tails along the c^* direction, which may be another reason why some weak forbidden reflections were 'detected'.

The space group *Pbnm* was assigned in this way (see also Mashiyama, Hasebe & Tanisaki, 1988). It belongs to the orthorhombic crystal system and is nonpolar. From group theoretical considerations, the ninefold superstructure which stems from the prototype *Pbnm* phase by a condensation of τ_4 mode is conjectured to have either a *Pbnm*, $Pbn2_1$, $Pb2_1m$ or $P2_1/b11$ space group. Here the notation of irreducible representation is referred to Kovalev's Table (Kovalev, 1965). The nonpolar orthorhombic phase should be *Pbnm*. Another nonpolar orthorhombic space group is $P2_12_12_1$, which can be induced by the freezing of τ_2 or τ_3 modes. By assuming both cases and applying least-squares calculations, space group *Pbnm* was found to give superior results to $P2_12_12_1$.

There are two independent models which satisfy the symmetry relation of *Pbnm*. In the case of model 1, one of the thiourea molecules at site 1 defined by Elcombe & Taylor (1968) satisfies the mirror symmetry by itself at $z = \frac{1}{4}$, and in model 2 the molecule at $z = \frac{3}{4}$. The difference between these two models is the shift of molecules by $\Delta z = \frac{1}{18}$ along the c axis. The models are not related by an antiphase domain.

Table 1. *R factors in the two models*

The R factor for the nth-order satellite reflections is denoted by R_n. The R factor including two reflections omitted in the final refinement because of secondary extinction is shown by R^*. The number of reflections N and the mean structure factors $|\bar{F}_o|$ are also given.

	Model 1	Model 2	N	$\bar{F}_o$
R	0·0478	0·0480	1510	32·25
R_o	0·0368	0·0371	314	84·60
R_1	0·0420	0·0420	546	31·27
R_2	0·1059	0·1056	358	9·92
R_3	0·1608	0·1610	219	5·61
R_4	0·2104	0·2147	73	3·88
R^*	0·0500	0·0501	1512	32·82

Table 2. *Positional parameters and equivalent isotropic thermal parameters of thiourea at* 170 K *with e.s.d.'s in parentheses*

The parameters of the H atoms have been deposited. Here B_{eq} is given by $\frac{4}{3}\sum B_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
Model 1				
S1	0·1016 (4)	0·0253 (3)	0·25 (fixed)	2·33 (5)
S2	0·1028 (3)	0·0217 (2)	0·36103 (2)	2·11 (3)
S3	0·1139 (3)	−0·0004 (2)	0·47224 (2)	2·17 (3)
S4	0·1228 (3)	−0·0280 (2)	0·58329 (2)	2·28 (3)
S5	0·1253 (2)	−0·0426 (2)	0·69433 (3)	2·02 (3)
C1	−0·1940 (15)	0·1024 (10)	0·25 (fixed)	1·94 (18)
C2	−0·1921 (11)	0·0985 (7)	0·36110 (8)	2·05 (13)
C3	0·1742 (12)	0·0939 (7)	0·47256 (8)	2·24 (14)
C4	−0·1520 (11)	0·0828 (7)	0·58356 (8)	2·12 (13)
C5	−0·1436 (9)	0·0761 (6)	0·69457 (11)	1·97 (10)
N1	−0·3121 (10)	0·1305 (7)	0·26476 (7)	2·83 (12)
N2	−0·3099 (10)	0·1295 (8)	0·34657 (7)	3·17 (14)
N3	−0·3087 (10)	0·1273 (8)	0·37616 (7)	3·08 (13)
N4	−0·2912 (10)	0·1302 (8)	0·45790 (7)	3·04 (13)
N5	−0·2841 (11)	0·1306 (8)	0·48745 (7)	3·19 (13)
N6	−0·2578 (12)	0·1293 (7)	0·56883 (7)	3·13 (13)
N7	−0·2555 (11)	0·1274 (7)	0·59838 (7)	2·86 (12)
N8	−0·2508 (11)	0·1225 (7)	0·67966 (7)	2·60 (12)
N9	−0·2455 (11)	0·1236 (7)	0·70931 (7)	2·81 (12)
Model 2				
S1	0·1018 (2)	0·0239 (2)	0·30555 (3)	2·12 (3)
S2	0·1069 (3)	0·0142 (2)	0·41663 (2)	2·41 (3)
S3	0·1196 (3)	−0·0141 (2)	0·52774 (2)	2·05 (3)
S4	0·1243 (3)	−0·0370 (2)	0·63883 (2)	2·19 (3)
S5	0·1257 (4)	−0·0456 (3)	0·75 (fixed)	1·95 (4)
C1	−0·1944 (9)	0·1011 (6)	0·30563 (11)	2·01 (11)
C2	−0·1853 (11)	0·0961 (7)	0·41685 (8)	2·03 (13)
C3	−0·1605 (12)	0·0891 (7)	0·52809 (8)	2·38 (14)
C4	−0·1478 (11)	0·0783 (7)	0·63902 (8)	1·90 (12)
C5	−0·1415 (16)	0·0754 (10)	0·75 (fixed)	2·05 (18)
N1	−0·3115 (10)	0·1311 (8)	0·29077 (7)	2·92 (13)
N2	−0·3125 (10)	0·1286 (8)	0·32032 (7)	3·00 (13)
N3	−0·3030 (10)	0·1285 (8)	0·40228 (7)	3·11 (14)
N4	−0·2993 (10)	0·1283 (8)	0·43191 (7)	3·10 (14)
N5	−0·2739 (11)	0·1315 (8)	0·51345 (7)	3·17 (13)
N6	−0·2672 (11)	0·1302 (7)	0·54287 (7)	3·10 (13)
N7	−0·2534 (11)	0·1245 (7)	0·62427 (7)	2·87 (12)
N8	−0·2493 (12)	0·1249 (7)	0·65390 (7)	2·80 (12)
N9	−0·2460 (11)	0·1228 (7)	0·73515 (7)	2·66 (12)

The scattering factors for neutral atoms and the dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The structure analysis was started from the parameters determined at 188 K (Tanisaki & Nakamura, 1970) by a block-diagonal least-squares program which was rewritten from the diagonal least-squares program in *UNICS* (Sakurai, 1967). Here the value of wR^2

$= \sum(|F_o| - |F_c|)^2/\sum|F_o|^2$ was minimized. The difference Fourier maps gave all the H-atom positions. At the final stage of the calculations, two reflections (0,0,18) and (120) were omitted because they seemed to be affected by secondary extinction. All the parameters were refined with anisotropic thermal parameters for S, C and N and isotropic ones for H; the final R factors were 0·048 for both models 1 and 2, where R is defined by $R = \sum||F_o| - |F_c||/\sum|F_o|$. In the final cycle, $wR = 0{\cdot}044$, $S = 2{\cdot}83$ and $(\Delta/\sigma)_{\max} = 0{\cdot}36$. The difference Fourier synthesis revealed no peaks larger than $\Delta\rho = 0{\cdot}35$ e Å^{-3}.*

The final R values for satellite reflections are listed in Table 1. The fourth-order satellite intensities were not reliable since they were too weak. Positional and thermal parameters are given in Table 2. Mean bond lengths and angles are shown in Fig. 1.†

Experimental at 153 K

In the same way as mentioned above, a structural refinement was also performed at 153 K; orthorhombic, $Pb2_1m$, $a = 5{\cdot}476$ (2), $b = 7{\cdot}531$ (4), $c = 8{\cdot}541$ (3) Å, $V = 352{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}435$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}639$ mm^{-1}. The least-squares calculation converged at $R = 0{\cdot}051$, $wR = 0{\cdot}046$ with $S = 0{\cdot}39$, $(\Delta/\sigma)_{\max} = 0{\cdot}40$ and $\Delta\rho = 0{\cdot}44$ e Å^{-3} for 1455 independent reflections with $0 \le h \le 11$, $0 \le k \le 15$ and $0 \le l \le 17$ ($2\theta_{\max} = 92°$). The positional and thermal parameters are given in Table 3.

Table 3. *Positional parameters and equivalent isotropic thermal parameters of thiourea at* 153 K

The H-atom parameters have been deposited.

	x	y	z	B_{eq}(Å^2)
S1	0·0998 (1)	0·0265 (fixed)	0·25 (fixed)	1·77 (1)
S2	−0·1255 (1)	0·0457 (2)	0·75 (fixed)	1·69 (1)
C1	−0·1959 (5)	0·1014 (5)	0·25 (fixed)	1·63 (4)
C2	0·1403 (6)	−0·0731 (4)	0·75 (fixed)	1·60 (4)
N1	−0·3158 (4)	0·1295 (4)	0·3829 (2)	2·46 (4)
N2	0·2471 (5)	−0·1219 (4)	0·6164 (2)	2·36 (4)

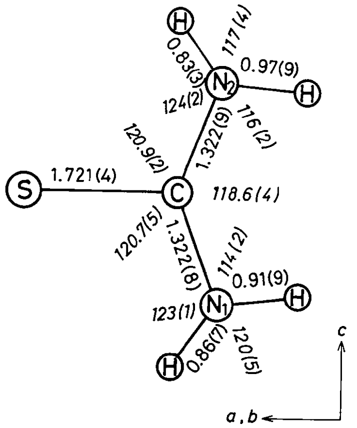

Fig. 1. Thiourea molecule showing the mean bond lengths (Å) and bond angles (°) for model 1 at 170 K. The values for model 2 are almost the same.

Discussion

The molecules are very flat at 170 K as in phases I and IV except for H atoms, whose positional parameters are not so reliable as those obtained by neutron diffraction. The H—N bond length is rather short compared with the previous value of about 1 Å (Elcombe & Taylor, 1968).

It is hard to decide which model is more appropriate, because the difference in R factors (Table 1) is small. In the following we discuss model 1, noting that the molecules are shifted by $\Delta z = \frac{1}{18}$ along the c axis in model 2.

The molecular plane is parallel to the c axis, and the molecular axis (the direction from S to C) is in the ab plane. The modulated structure is mainly characterized by a translation of the center of mass perpendicular to the c axis and by a rotation of the molecule about an axis parallel to the c axis. Fig. 2 shows the projection of the molecules on the ab and ac planes. The center of mass

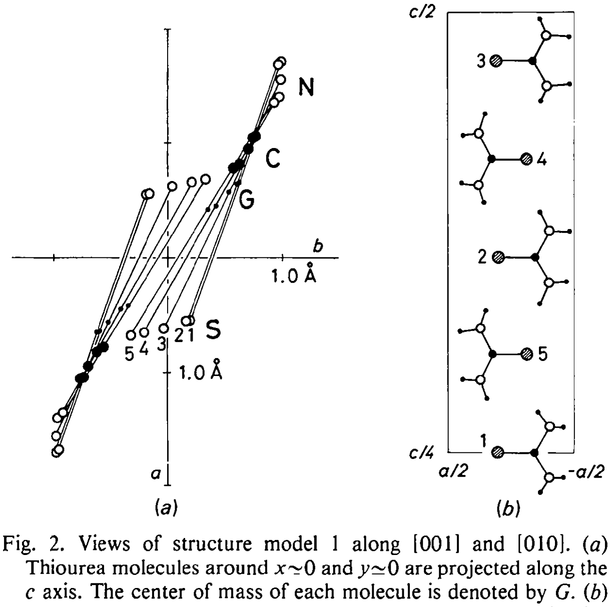

Fig. 2. Views of structure model 1 along [001] and [010]. (*a*) Thiourea molecules around $x \simeq 0$ and $y \simeq 0$ are projected along the c axis. The center of mass of each molecule is denoted by G. (*b*) Thiourea molecules in one-eighth of the unit cell ($-\frac{a}{2}$ to $\frac{a}{2}$, $-\frac{b}{4}$ to $\frac{b}{4}$, $\frac{c}{4}$ to $\frac{c}{2}$) projected along the b axis. Molecules 4 and 5 are transposed by inversion symmetry from those in Table 1.

---

* If a full-matrix least-squares program was used further, then the positional parameters changed slightly, within e.s.d.'s at the same level of $R = 0{\cdot}048$. Therefore, the results of the block-diagonal least-squares calculations are presented in this report.

† Lists of structure factors, bond lengths and angles, and anisotropic thermal parameters at 170 K and 153 K have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44896 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is denoted by G. The mean position of the molecules almost coincides with that of phase V at room temperature: $\Delta x = 0{\cdot}0017$, $\Delta y = -0{\cdot}0010$ and $\Delta\varphi = 0{\cdot}48°$, where the azimuth angle φ is the angle between the molecular axis and the a axis.

The molecule containing S3 is around $z = \frac{1}{2}$ and the local structure is nearly that of paraelectric phase V. On the other hand the molecules containing the S1 and S5 atoms are around $z = \frac{1}{4}$ and $\frac{3}{4}$, where the local structures are those of the phase I with negative and positive polarizations, respectively. The azimuth angle around $z = \frac{1}{4}$ is either $-19{\cdot}8°$ for the S1 molecule or $-31{\cdot}4°$ for S5, which is in good agreement with the $-19{\cdot}1$ or $-31{\cdot}6°$ in our refined results at 153 K. According to the reported structure at 110 K, these angles are $-16{\cdot}9$ and $-32{\cdot}8°$ (Elcombe & Taylor, 1968). Therefore, the molecules are more tilted about the c axis at 110 K than at 153 K so as to produce greater polarization.

As shown in Fig. 3, the displacement of the center of molecular mass is almost along a line making an angle of about 45° with the b axis. The rotation angles of the molecular direction (polar and azimuth angles) are also plotted in the figure. These quantities can be fitted to a relation

$$X = \bar{X} + \sum_{n=1}^{4} [A_n\cos(2\pi n\zeta) + B_n\sin(2\pi n\zeta)], \qquad (1)$$

where $\bar{X}$ is the mean value and ζ is the nominal height parameter (*e.g.* $\zeta = \frac{1}{4} + \frac{2}{9}$ for S3). The Fourier coefficients A_n and B_n are listed in Table 4. The displacement of an atom on the molecular axis is represented by

$$X = \bar{X} + B_1\sin(2\pi\zeta) + A_2\cos(4\pi\zeta)$$
$$+B_3\sin(6\pi\zeta) + A_4\cos(8\pi\zeta),$$

or

$$X = \bar{X} + B_1\sin(2\pi\zeta) + B_3\sin(6\pi\zeta)$$
$$+ A_4\sin(10\pi\zeta) + A_2\sin(14\pi\zeta), \qquad (2)$$

because of the mirror symmetry. Although the displacements for the N1 and N2 atoms (see Fig. 1) have other components, N atoms as a whole satisfy the mirror symmetry and displacement should also be represented only by odd-order harmonics as in (2). Thus the displacive mode is generated by a condensation of a normal mode with $\mathbf{k} = \frac{1}{9}\mathbf{c}_0^*$ where $\mathbf{c}_0^*$ is the reciprocal cell vector in the prototype phase V. This mode belongs to the τ_4 representation. The higher harmonics stem from the fourth-order coupling term. The third-order harmonics, and not the second-order ones, are important in describing the modulated structure. The fifth and seventh harmonics (A_4 and A_2 terms) are outside the first Brillouin zone and therefore belong to the τ_1 representation.

Since the dominant displacement with the primary wavenumber is represented by a translational mode in the ab plane and the rotational mode about the c axis, the primary order parameter has the character of the Γ_6 representation, to which the polarization along the b axis belongs. However, a small longitudinal displacement can be detected, which has been noted previously (Tanisaki & Nakamura, 1970). Since the τ_4 mode is connected both to Γ_6 and Γ_7 modes by the compatibility relation, it is natural that the τ_4 mode also permits this displacement. The amplitude of the longitudinal displacement of the center of mass of the molecule can be estimated from the atomic positions obtained and is about 0·019 Å – very small compared with the transverse mode. Therefore we can say that the primary order parameter of the incommensurately modulated phase of thiourea is the spatially varying polarization (Ishibashi & Shiba, 1978).

Yamamoto (1980) re-analyzed the phase IV structure by taking the first and the second harmonics into account. However, the diffraction pattern used scarcely contained second-order satellites and neither third- nor fourth-order ones. In our analysis, all orders of satellites were used and it has been shown that the frozen mode is the τ_4 symmetry and can be represented only by odd-order harmonics.

Here we note the modulation of model 2. Although the atomic positions are shifted by $\Delta z = \frac{1}{18}$ along the c direction, the Fourier coefficients are almost the same as those of model 1, *i.e.* the two models show effectively

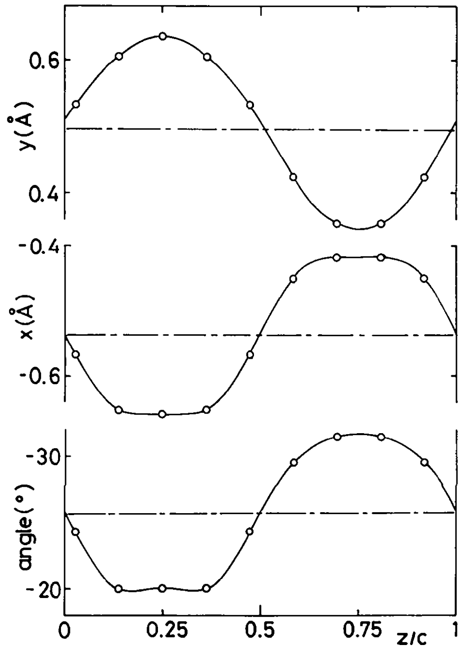

Fig. 3. The translational waves of the center of mass of thiourea along the a and b axes. The rotational wave along the c axis is also shown. Open circles represent observed positions, and solid lines are the relation fitted to (1), whose coefficients are listed in Table 4.

Table 4. *Fourier coefficients for the positional parameters* ($\times 10^4$) *defined by* (1)

The center of mass is denoted by G, and θ and φ are the polar and azimuth angles (°) of the molecular direction.

		Mean	A_1	B_1	A_2	B_2	A_3	B_3	A_4	B_4
G	x	−983	0	−248	4	0	0	−33	1	0
G	y	658	0	194	12	0	0	3	5	0
G	z	0·0	−1·8	0	0	−0·3	−0·7	0	0	−0·3
	θ	90·0	0·77	0	0	−0·24	0·01	0	0	0·21
	φ	−25·43	0	6·55	−0·02	0	0	0·57	−0·38	0
S	x	1146	0	−132	17	0	0	−12	8	0
S	y	−81	0	370	8	0	0	21	−6	0
C	x	−1687	0	−282	3	0	0	−27	5	0
C	y	894	0	133	13	0	0	1	11	0
N1	x	−2795	26	−362	6	−4	1	−44	−2	17
N1	y	1279	−5	29	22	−2	3	−12	7	9
N2	x	−2795	−26	−362	6	4	−1	−44	−2	−17
N2	y	1279	5	29	22	2	−3	−12	7	−9

the same modulation. If the modulation wavenumber is not just $\frac{1}{9}\mathbf{c}_0^*$, then the modulation is incommensurate and the displacement pattern changes from that of model 1 to model 2 along the c axis with a long period.

If we regard this ninefold superstructure as an 'incommensurate' one, then the local structure around $z=\frac{1}{4}$ and $\frac{3}{4}$ corresponds to 'almost commensurate' regions (microdomains of ferroelectric phase I, the polar sense changing alternately along the b axis), which are separated by 'discommensurations' (or domain walls) around $z=0$ and $\frac{1}{2}$. It should be noted that the discommensuration width is about two basic cell dimensions in thiourea.

The authors wish to thank Mr S. Takagi and Mr Y. Yoshida for their help in computer calculations. This work was partly supported by a Grand-in-aid for Scientific Research from the Ministry of Education, Science and Culture.

References

ELCOMBE, M. M. & TAYLOR, J. C. (1968). *Acta Cryst.* A**24**, 410–420.

GOLDSMITH, G. J. & WHITE, J. G. (1959). *J. Chem. Phys.* **31**, 1175–1187.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

ISHIBASHI, Y. & SHIBA, H. (1978). *J. Phys. Soc. Jpn*, **45**, 409–413.

KOVALEV, O. A. (1965). *Irreducible Representations of the Space Groups*. New York: Gordon & Breach.

MCKENZIE, D. R. (1975). *J. Phys. C*, **8**, 1605–1619.

MASHIYAMA, H., HASEBE, K. & TANISAKI, S. (1988). *J. Phys. Soc. Jpn*, **57**, 166–175.

MOUDDEN, A. H., DENOYER, F., LAMBERT, M. & FITZGERALD, W. (1979). *Solid State Commun.* **32**, 933–936.

SAKURAI, T. (1967). Editor. *Universal Crystallographic Computation Program System*. The Crystallographic Society of Japan, Tokyo, Japan.

SHIOZAKI, Y. (1971). *Ferroelectrics*, **2**, 245–260.

SOLOMON, A. L. (1956). *Phys. Rev.* **104**, 1191.

TANISAKI, S., MASHIYAMA, H. & HASEBE, K. (1984). 39th Annu. Meet. Phys. Soc. Jpn, Fukuoka, Advanced Abstracts Vol. 2, p. 101.

TANISAKI, S. & NAKAMURA, N. (1970). *J. Phys. Soc. Jpn*, **28**, Suppl. 293–294.

YAMAMOTO, A. (1980). *Phys. Rev. B*, **22**, 373–379.

Acta Cryst. (1988). B**44**, 445–448

Can Statistical Analysis of Structural Parameters from Different Crystal Environments Lead to Quantitative Energy Relationships?

BY HANS BEAT BÜRGI

Laboratory for Chemical and Mineralogical Crystallography, University of Berne, CH-3012 Berne, Switzerland

AND JACK D. DUNITZ

Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland

(*Received* 13 *October* 1987; *accepted* 5 *April* 1988)

Abstract

Two recent attempts to derive quantitative energy relationships from statistical analysis of structural parameters observed in different crystal environments are examined. Both are based on the assumption of a Boltzmann-like distribution for the probability of a structure being observed in a deformed state. This assumption is shown to be untenable. An alternative model taking explicit account of the perturbing *forces* responsible for structural deformation is then considered. Although low-energy regions of molecular potential energy surfaces can certainly be recognized and mapped from distributions of observed structures,

0108-7681/88/040445-04$03.00