to be published in 'Ferroelectrics' for a special issue: (Feb. 1989)

Proc. 4-th Jpn.-Sov. Symp. Ferroelectricity (Tsukuba, 1988)

25a1

Discommensurations, Modulated Phases and Lock-in Transitions of Thiourea

H. MASHIYAMA, S. JIDA and S. TANISAKI[+]

Department of Physics, Faculty of Science,

Yamaguchi University, Yamaguchi 753, Japan

[+]Yahata University, Kitakyushu 805, Japan

The modulated phases and the successive phase transition of thiourea are reinvestigated by means of dielectric measurements and X-ray scatterings. In the E-T phase diagram, eightfold and ninefold superstructures are designated in h-thiourea. There remain some discommensurations as domain walls in the ferroelectric phase. The structure of discommensurations is discussed based on the structural analysis of the superstructures at -95°C and -103°C.

key words: ferroelectrics, incommensurate-commensurate transition, discommensuration, modulated structure, dielectric susceptibility, X-ray scatterings

1. INTRODUCTION

Thiourea $SC(NH_2)_2$ is a well-known ferroelectric material that exhibits the incommensurate-commensurate phase transition.[1] There are six phases with increasing temperature; ferroelectric phase I, ninefold commensurate phase IIa, incommensurate phase II, eightfold commensurate (ferroelectric) phase III, incommensurate phase IV and

paraelectric phase V. The modulated phases with wavenumber $k_z=\delta c^*$ (δ=0.11~0.14) are bounded by the ferroelectric phase in the electric field (E) vs. temperature (T) phase diagram. These results have been confirmed for d-thiourea and partially for h-thiourea.[2]

Although the dielectric constant shows a large peak or sometimes double ones in phase III,[3] the plateau in the δ(T) curve has only been observed with DC bias field.[4,5] It is still unresolved whether δ is locked-in at $\frac{1}{8}$ without DC field or not. Another interesting phenomenon is the memory effect, which is ascribed to the pinning of the modulation wave by mobile impurities.[6]

The incommensurate structure is generally characterized by a regular array of discommensurations (or domain walls) which separate almost commensurate regions.[7]

In order to demonstrate the formation of discommensurations, we have re-examined $SC(NH_2)_2$ by means of dielectric measurements and X-ray scatterings as well as the crystal structural analysis. Crystal directions and reciprocal coordinates are referred to the unit cell of the room temperature phase V (space group Pbnm) with lattice parameters a<b<c.

2. DIELECTRIC CONSTANT AND X-RAY DIFFRACTION MEASUREMENTS

The temperature dependences of the dielectric constant ε and the modulation wavenumber δ are almost in agreement with previous works.[1,8] We also observed a maximum of ε at -112°C in phase I. In phase IIa, δ is pinned to the commensurate value of $\frac{1}{9}$. The δ(T) curve changes smoothly but has two weak inflections in the temperature range of phase III, which indicates that δ is pinned at $\frac{1}{8}$. The E-T phase diagram determined by X-ray diffraction

measurements is shown in Fig. 1(a).

Figure 1(b) shows a history effect; the sample was heated from -130°C with no bias field after the temperature was decreased from -65°C with bias field of E=2.5kV/mm. In phase I, the maximum of ε almost disappeares and $\varepsilon(T)$ has a plateau. The peak of phase III also disappears as if the bias field is applied. The $\delta(T)$ curve shows plateaus in phases IIa and III. Since the electrodes covered a partial area of the sample, a part of the sample went through the modulated phases on the cooling process. Therefore the sample was no longer a single domain crystal. It is considered that the pinned domain walls work on the memory effect. This effect can be erased by bringing the sample into the room-temperature phase.

Figure 2 shows a temperature change under certain bias field of the intensity distributions along the c^* axis around the (0 2 0) main reflection whose FWHM takes a constant value of $0.004c^*$. At wings of the peak diffuse scatterings are observed if the sample is transformed into phase I from higher temperature phases, while the whole distribution does not change in the temperature range of phases IIa to V. The bias field weakens the wing distributions, which are also observable around other main reflections that accompany satellite reflections in the modulated phases.

3. CRYSTAL STRUCTURE OF MODULATED PHASES

The structures of phases IIa and III are characterized by a rotation of the thiourea molecules along the c axis coupled with a displacement of the center of mass in a plane perpendicular to the axis as shown in Fig. 3. A small longitudinal displacement is also detected. These modes belong to τ_4 representation.[9]

Around the mirror planes ($z=\frac{1}{4}$ and $\frac{3}{4}$) the local structure is isostructural with the ferroelectric phase I. On the other hand the local structure around $z=0$ and $\frac{1}{2}$ is isostructural with the paraelectric phase V. That is, the superstructure is constructed by alternatively polarized layers (almost commensurate regions around the mirror plane), which are sandwiched by domain walls whose width is about twice a basic cell dimension. The primary difference between the eightfold and ninefold superstructure is the period of the modulation. Another important difference is that the eightfold superstructure is a polar one. The polarization of the molecular line 1, 2, ... in Fig. 3 (a) is not cancelled by that of the line 1', 2', ... In other words, the local polarization around $z=\frac{1}{4}$ does not cancel with that around $z=\frac{3}{4}$; i.e. a ferrielectric structure.

4. DISCUSSIONS

The obtained E-T phase diagram is very similar to that of deuterated thiourea[1] and indicates two high-order commensurate phases with $\delta=\frac{1}{8}$ and $\frac{1}{9}$, which have not been shown explicitly in h-thiourea previously. The overall shape of the phase diagram can be constructed theoretically.[10] To account for the phase III without bias field, 4th-order harmonics of the order parameter should not be neglected.

The X-ray scattering indicates remnants of discommensurations in phase I as ferroelectric domain walls. The anomalous part of the dielectric susceptibility can be given by (number density of discommensurations)x(mobility of discommensuration by electric field). Full explanation of the maximum of ε at -112°C is still

left.

If alternatively polarized two eightfold cells are sandwitched by domain walls (let us designate this structure as $\langle 8^2\ \frac{9}{2}\ \bar{8}^2\ \frac{9}{2}\rangle$, where the polar sense of $\bar{8}$ is inverse of 8), then the structure is characterized by the wavenumber $\frac{5}{41} = 0.12195...$. The domain wall $\langle\frac{9}{2}\rangle$ is the half of the ninefold structure and acts as the discommensuration that separates the almost eightfold ferroelectric regions. In such a structure, the phase difference of the modulation wave between the adjacent regions is $\frac{2\pi}{16}$; i.e. the commensurability parameter for phase III is 16.

REFERENCES

1. F. Denoyer and R. Currat, Incommensurate Phases in Dielectrics 2, ed. R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986) pp.129-160, and references therein.
2. J. Hatano, N. Kume, K. Kubota, T. Tsukamoto, H. Futama and K. Gesi, Proc. 6th Int. Conf. Ferroelectricity, Kobe, 1985, Jpn. J. Appl. Phys. 24 (1985) Suppl. 24-2, pp.844-6.
3. K. Gesi, J. Phys. Soc. Jpn. 51, 701 (1982).
4. K. Gesi and M. Iizumi, J. Phys. Soc. Jpn. 51, 1047 (1982).
5. A. H. Moudden, E. C. Svensson and G. Shirane, Phys. Rev. Lett. 49, 557 (1982).
6. P. Lederer, J. P. Jamet and G. Montambaux, Ferroelectrics 66, 25 (1986), and references therein.
7. W. L. McMillan, Phys. Rev. B 14, 1476 (1976).
8. D. R. McKenzie and J. S. Dryden, J. Phys. C 6, 767 (1973).
9. S. Tanisaki, H. Mashiyama and K. Hasebe, Acta Cryst. B 44 (1988) in press.
10. H. Mashiyama, K. Hasebe and S. Tanisaki, J. Phys. Soc. Jpn. 57, 166 (1988).

Figure Captions

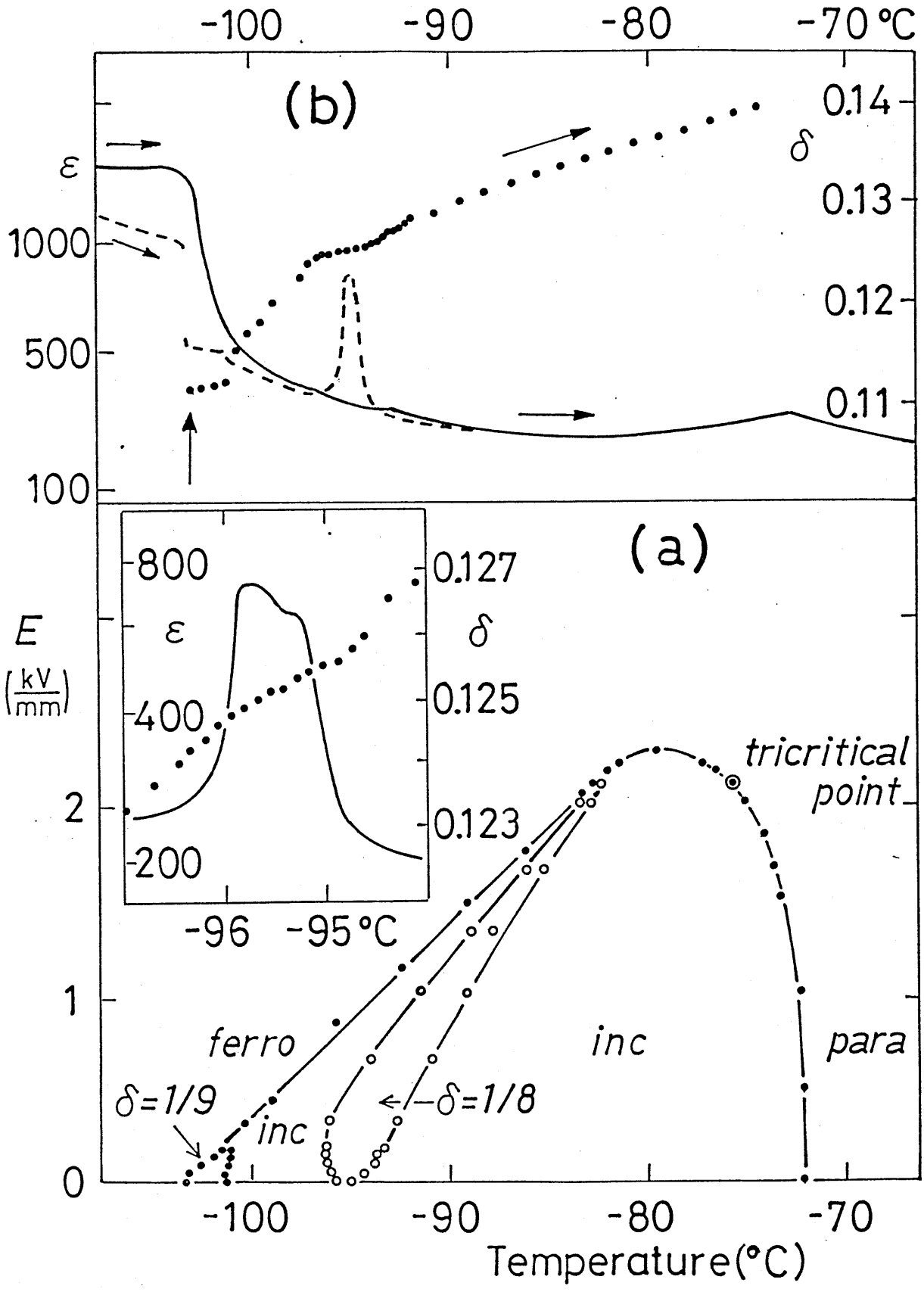
Fig. 1. The E-T phase diagram and the temperature dependences of the dielectric constant ε and the modulation wavenumber δ of $SC(NH_2)_2$. The insert shows ε(solid curve) and δ(dots) on a cooling run with no DC bias field. Maxima in ε at -112°C and -95°C disappeared if the sample was heated after removing the bias field applied from -60 to -130°C. The wavenumber was measured simultaneously with ε shown by solid curves. The broken curve gives ε free from DC field.

Fig. 2. The X-ray scattering distribution scanned along c^* direction around (0 2 0). The logarithm of the intensity is plotted with shifting one digit for each figure; (a) -60°C, (b) -110°C with bias field E=2.5kV/mm applied on a cooling from -65°C, (c) -110°C after removing the field, and (d) -110°C with no bias field on a cooling from -65°C. The side peak around ζ=0.008 comes from the ill-oriented part of the sample.

Fig. 3. Superstructure of thiourea. The projection on y-z plane is shown with arbitrary scales for (a) eightfold structure $Pb2_1m$ at -95°C, and (b) ninefold structure Pbnm at -103°C. No hydrogen atom bonding to nitrogen (small circles) is shown.

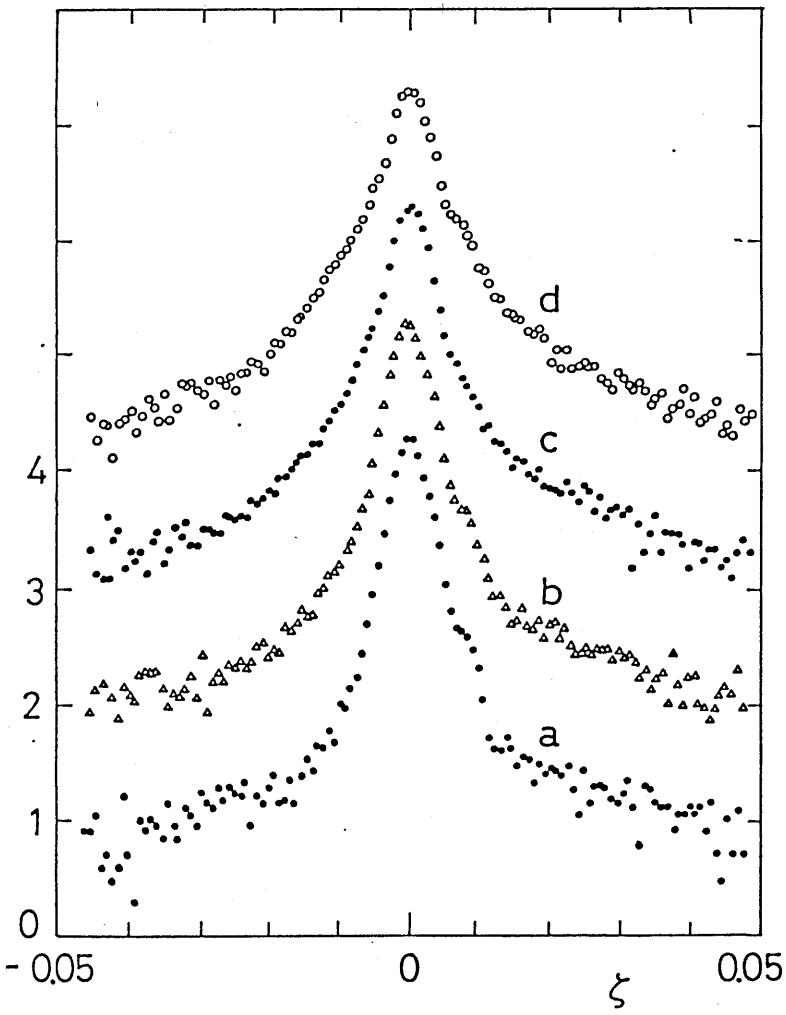
Mashiyama et al

Fig. 1.



Mashiyama et al

Fig. 2.



Mashiyama et al

Fig. 3.