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Neutron-diffraction study of thiourea under high electric field

D. Durand and F. Dénoyer
Laboratoire de Physique des Solides, Bâtiment 510, Université Paris Sud,
91405 Orsay, France

R. Currat and C. Vettier
Institut Laue Langevin, BP 156 X, 38042 Grenoble Cedex, France

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The modulation wave vector $\delta\vec{b}^*$ of deuterated thiourea is measured as a function of temperature and for several electric-field values, using neutron diffraction. The only commensurate phase stabilized by the field is found to correspond to $\delta=\frac{1}{8}$. High-order commensurate phases such as $\delta=\frac{2}{15}$, $\frac{4}{29}$, and $\frac{6}{43}$ are not observed, in contrast with a recent high-field x-ray diffraction study. The disagreement between the two techniques is ascribed to radiation damage caused by the x-ray beam itself. Preliminary results on an x-ray irradiated sample are presented.

Thiourea is a molecular ferroelectric compound which exhibits both incommensurate and long-period commensurate (C) phases, characterized by a modulation wave vector of the type $\vec{q}_\delta=\delta\vec{b}^*$. Diffraction experiments, at ambient pressure, have established the existence of a C phase corresponding to $\delta=\frac{1}{9}$ (Ref. 1) stable over a 2-K temperature interval, between the incommensurate $(0.115<\delta<0.141)$ and ferroelectric $(\delta=0)$ phases. Two other C phases with $\delta=\frac{1}{7}$ and $\frac{1}{3}$ have been observed under hydrostatic pressure.[2]

A simple Landau-type argument, taking account of the space-group symmetry $(Pnma)$ of the paraelectric phase and of the transformation properties of the modulated order parameter, confirms that odd ($7b$ and $9b$) superstructures are expected to be more stable than even ($8b$) ones, in good agreement with the diffraction results.[2] The same type of argument also predicts that odd and even C phases should have different spatial symmetries, the latter ones, e.g., $\delta=\frac{1}{8}$, being either ferroelectric $(P2_1ma)$ or ferroelastic $(P2_1/a)$, depending upon the phase of the modulation with respect to the underlying lattice.

The observation of a large zero-field dielectric anomaly[3] at a temperature where the incommensurate modulation wave vector $\delta(T)$ crosses the value $\frac{1}{8}$ suggests that the commensurate $8b$ phase, if stable, would have ferroelectric rather than ferroelastic character.

This conjecture is further confirmed by the more recent finding that a small or moderate dc electric field E, applied along $\vec{a}$ stabilizes the commensurate $8b$ phase over a finite temperature interval $\Delta T_8(E)$.[4-6]

By now, the complete (E,T) phase diagram has been explored and its overall topology is at least qualitatively understood. The stability field of the $8b$ phase, as determined by the position of weak dielectric and birefringence anomalies[7,8] is embedded in the incommensurate region. In particular, $\Delta T_8(E)$ which initially grows as $\sqrt{E}$, saturates for field values of a few hundred V/mm and eventually reduces to zero at ~2000 V/mm. This behavior is well understood in terms of a lock-in potential of the form[7]

$$V^{(8)}\sim\eta^6E \ , \qquad (1)$$

where the modulation amplitude η is itself a decreasing function of E.

A remaining open question concerns the possible stabilization at *large field* values of high-order C phases such as $\frac{2}{15}$, $\frac{3}{22}$, $\frac{4}{29}$, etc., which, as for the $\delta=\frac{1}{8}$ case, may be either ferroelastic or ferroelectric. Within a continuum approximation[9] these high-order C phases are predicted to be much too narrow to be detectable experimentally, except possibly for $\delta=\frac{2}{15}$; furthermore, as mentioned earlier, discreteness effects are not expected to be significant at large field values.

On the experimental side,[7,8] a weak dielectric anomaly is observed at *low fields,* probably corresponding to a narrow $(\Delta T<0.5\text{ K})$ $\delta=\frac{2}{17}$ C phase, whose existence is yet to be confirmed by direct wave-vector measurements.[4,8] In contrast, the only dielectric and birefringence anomalies observed at *high fields* are those corresponding to the $\delta=\frac{1}{8}$ phase, a result which implies that no other C phase exists or, alternately, that the relevant anomalies are too weak to be observable.

Surprisingly, Moudden, Moncton, and Axe,[10] in a recent high-field x-ray diffraction study, report several lock-in phases at $\delta=\frac{2}{15}$ and $\frac{4}{29}$ $(E=1200\text{ V/mm})$ and $\delta=\frac{6}{43}$ $(E=1800\text{ V/mm})$, stable over temperature intervals of 6–15 K. In addition, the reported width of the $\delta=\frac{6}{43}$ plateau appears to be much larger than the overall stability range of the modulated region, as obtained from dielectric and birefringence measurements at the same field value. In view of the irreproducible character of the results obtained by Ronzaud and Durand[11] in a similar x-ray study, we were led to speculate that the disagreement between the macroscopic and diffraction data, could arise from radiation damage caused by the x-ray beam. It is known from previous irradiation experiments that even moderate doses can affect significantly the dielectric properties of ferroelectric molecular crystals such as triglycine sulfate (TGS), Rochelle salt,[12] and thiourea itself.[13] We thus felt it necessary to obtain independent diffraction data using thermal neutrons rather than x rays in order to avoid radiation damage.

Neutron-diffraction measurements were performed on the IN2 three-axis spectrometer at the Laue-Langevin Institute, using a PG-filtered incident neutron wavelength of 2.36 Å; collimations were adjusted to 60′-10′-10′-60′ in order to obtain a transverse momentum resolution of 0.003 Å^{-1} full-width at half maximum (FWHM). A single-crystal plate of deuterated thiourea ($1.5 \times 6 \times 9$ mm^3) was cleaved from a large sample grown by Professor J. P. Chapelle (SDTM, LP 3261, Université Paris-Sud, 91405 Orsay). The large faces, perpendicular to the ferroelectric axis, were gold plated using the vacuum deposition technique. Thin gold leads fixed with platinum laquer were used as electrodes. The specimen was mounted in a cryostat with a temperature stability better than 0.05 K. Electric-field inhomogeneities were minimized by purposely reducing the neutron beam cross section in such a way as to mask off the periphery of the specimen.

The aim of the experiment is to monitor the intensity and the position of the strong $(2, \pm\delta, 0)$ satellite reflections, as a function of temperature and electric field, independently.

The observed variation of δ with temperature is shown in Fig. 1 for three values of the electric field $E = 1800$, 1200, and 500 V/mm. The latter curve was obtained in a previous measurement performed on another sample under slightly different experimental conditions. It is included here for the sake of completeness. The three curves exhibit a similar behavior.

(i) δ decreases smoothly between $\delta(T_i)$ and $\delta = \frac{1}{8}$; in particular, no steps are found at possible commensurate values such as $\frac{2}{15}$, $\frac{3}{22}$, and $\frac{4}{29}$ at 1200 V/mm and $\frac{2}{15}$ at 1800 V/mm.

(ii) Along the $T_i(E)$ transition line, δ decreases regularly with increasing field from $\delta(T_i = 216.5\text{ K}) = 0.140$ at 500 V/mm to $\delta(T_i = 214.5\text{ K}) = 0.1355$ at 1800 V/mm.

(iii) A plateau at $\delta = \frac{1}{8}$ is observed on all three curves. Its width $\Delta T_8(E)$ is of the order of 3 K at 500 and 1200 V/mm and decreases to less than 0.5 K at 1800 V/mm.

(iv) The width of the lower incommensurate region (between the $8b$ and the ferroelectric phases) decreases with field and vanishes between 1200 and 1800 V/mm.

Figure 2 shows the temperature variation of the integrated first-order satellite $(2\ \pm\delta\,0)$ intensity for two values of electric field: 1200 and 1800 V/mm. The modulation amplitude varies monotonically as a function of temperature and decreases slowly with increasing field, at fixed temperature. Also shown in Fig. 2 are the positions and widths of the $\delta = \frac{1}{8}$ plateau. As mentioned earlier, the modulation amplitude near lock-in decreases with field. In fact, with the help of expression (1), we can predict an *increase* of about 30% in the discommensuration width $l(E) = (V^{(8)})^{-1/2}$ between 1200 and 1800 V/mm.

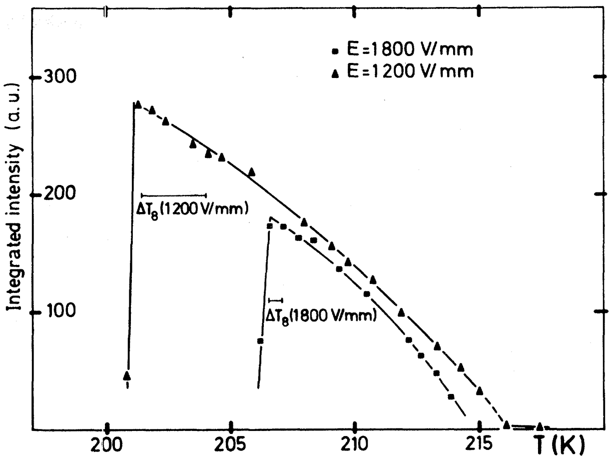

FIG. 2. Integrated intensity of the $(2\ \pm\delta\,0)$ satellite reflections as a function of temperature for $E = 1200$ and 1800 V/mm.

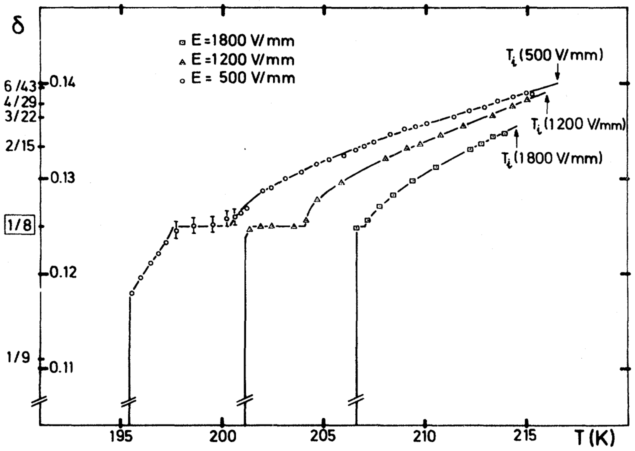

FIG. 1. Temperature variation of the modulation wave vector $\delta(E,T)$ for several electric-field values. All curves have been measured from right to left, i.e., going down in temperature from the paraelectric state. Between two successive values of the field the specimen is annealed above T_i.

Finally, Fig. 3 shows a typical scan along the $[0\zeta 0]$ direction across the (200) main Bragg reflection and its two $(2\ \pm\delta\,0)$ satellites for $T = 210.7$ K and $E = 1200$ V/mm. No evidence is found, even at high field, for satellite broadening.

The essential conclusions of this work are as follows.

(i) The neutron-determined (E,T) phase diagram is in good agreement with the birefringence and dielectric results of Refs. 7 and 8.

(ii) The only C phase observed corresponds to $\delta = \frac{1}{8}$. Higher-order C phases, such as $\frac{2}{15}$, $\frac{3}{22}$, $\frac{4}{29}$, . . . , if they exist, must be stable over temperature intervals lower than

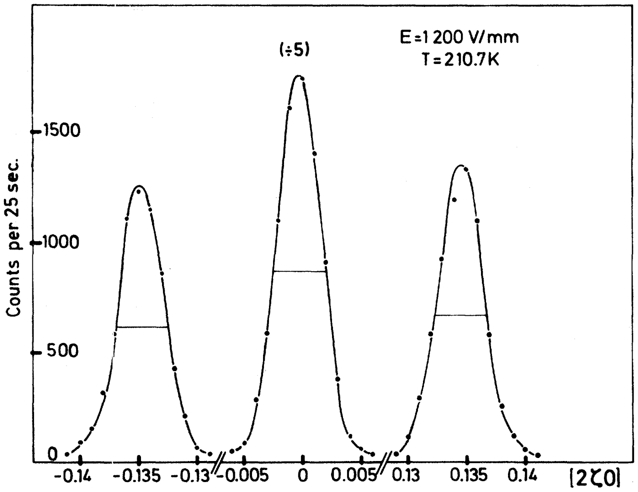

FIG. 3. Typical scan along the $[0\zeta 0]$ direction across the $(2\ \pm\delta\,0)$ satellite reflections and the $(2\,0\,0)$ main Bragg. The observed FWHM is 0.003 Å^{-1} for all three peaks.

0.5 K, in contradiction with the high-field x-ray diffraction results of Moudden *et al.*[10]

The most plausible interpretation for the disagreement between the neutron and x-ray results is to assume that the latter are strongly affected by radiation damage. In an attempt to test this hypothesis we have performed wave-vector measurements, under the same neutron-diffraction conditions as above, using a specimen irradiated by x rays at room temperature, with a radiation dose estimated at a few hundred Mrad. The resulting $\delta(T,E=0)$ curve is shown in Fig. 4 and compared to the corresponding data from a virgin crystal.[10] The obvious result is an overall shift of about 2 K between the two sets of data. In addition, a substantial broadening of the satellite reflections is observed. However, we wish to stress that the data shown in Fig. 4 have been obtained under poorly controlled irradiation conditions: in particular, the coloration of the crystal after irradiation indicates an inhomogeneous distribution of defects across the specimen volume, an effect which may account for a large part of the observed satellite broadening as well as blur out possible small steps in the $\delta(T)$ curve. Nevertheless, these results are illustrative of the extent to which radiation damage, even at moderate levels, affects the characteristics of modulated systems. In particular, they suggest that great care should be exercised in interpreting diffraction results obtained from high-power x-ray sources, where comparable doses can be easily accumulated.

The mechanism through which such defects may give rise to a C or quasi-C plateau in the $\delta(T,E)$ curve, remains to be elucidated. One particularly difficult aspect of the problem lies in the fact that in an x-ray experiment the radiation dose increases *as the measurement proceeds.* Also since the irradiation defects are at least partially mobile, they give rise to enhanced memory effects,[8,14] and unless a systematic annealing procedure is followed, the observed value of the modulation wave vector is expected to depend on the complete thermal and irradiation history of the specimen.

In the same context it may be noted that dilute chemical defects obtained by substituting K impurities for Rb ions in Rb_2ZnCl_4 (Ref. 15) lead to somewhat similar pinning effects on the modulation wave vector.

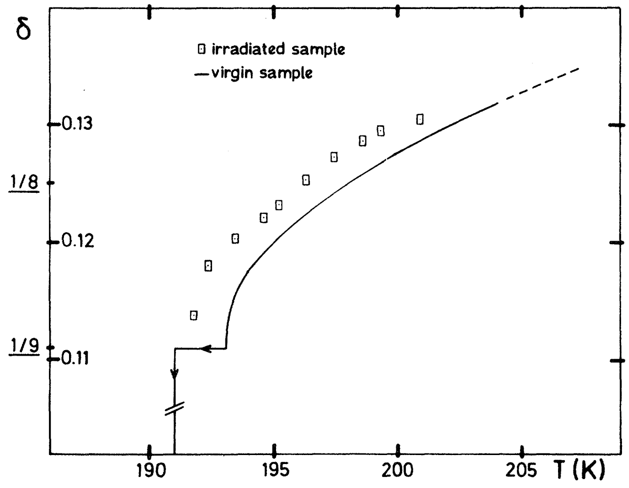

FIG. 4. Modulation wave vector $\delta(T,E=0)$ for an x-ray irradiated sample (□) compared to the results obtained (Ref. 10) on a virgin crystal (full line).

Further work is in progress, using neutron-diffraction and dielectric susceptibility measurements, in order to investigate the coupling mechanisms between the irradiation defects and the modulation wave.

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