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Effect of hydrostatic pressure on modulated structures in thiourea

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The phase diagram of thiourea as a function of temperature and hydrostatic pressure is investigated by means of neutron diffraction. Accurate satellite-position measurements reveal the existence of commensurate phases corresponding to the rational values $\frac{1}{3}$, $\frac{1}{7}$, and $\frac{1}{9}$ for the modulation wave vector. The results are discussed qualitatively in terms of ordinary Landau theory and in the light of Aubry's "devil's-staircase" approach.

I. INTRODUCTION

Thiourea [$SC(NH_2)_2$] is one of the earliest insulators known to undergo commensurate-incommensurate phase transitions.[1]

Above $T_0 = 217.8$ K, its crystalline structure corresponds to the nonpolar orthorhombic space group *Pnma*, with 4 molecules per unit cell.[2] Below $T_c = 191$ K, the structure remains orthorhombic with 4 molecules per cell, but becomes ferroelectric[2] with space group $P2_1ma$. The values of T_0 and T_c quoted above refer to the deuterated compound. Between T_0 and T_c the crystal goes through a number of modulated phases,[3,4,5] as evidenced by the appearance of $(h,k\pm n\delta,l)$ satellite reflections on diffraction patterns ($h,k,l,n=$ integers; δ = modulation wave vector in reduced units).

In a previous investigation,[6,7] the temperature dependence of δ was determined and the existence of a commensurate phase corresponding to $\delta = \frac{1}{9}$ was established. This new phase was found to be stable over a 2-K temperature interval, just above the ferroelectric phase for which $\delta = 0$.

The existence of yet another structure, stable at high pressure, has been reported by several authors.[8–11] In particular, Kabalkina,[10] from x-ray-power diffraction data, showed that the high-pressure phase can be described in terms of an orthorhombic structure with 12 molecules per unit cell. The identification of the high-pressure phase with a commensurately distorted phase corresponding to $\delta = \frac{1}{3}$ was further substantiated by the single-crystal work of Moudden *et al.*[12]

In view of these various results and in the face of continuing theoretical interest, we felt that a systematic neutron-diffraction investigation of the pressure-temperature phase diagram of thiourea would be worthwhile. The results of this study, now completed up to pressures of about 2500 bars, are reported below.

The paper is organized as follows: In Sec. II we describe our experimental conditions. In Sec. III we review results previously obtained at atmospheric pressure. New data on the pressure dependence of δ are presented in Sec. IV. Finally, in Sec. V the resulting (P,T) phase diagram is discussed in the light of ordinary Landau theory and of Aubry's "devil's-staircase" approach.[13]

II. EXPERIMENTAL SETUP

Neutron measurements were performed at the Institute Laue Langevin's IN 2 three-axis spectrometer. The neutron wavelength was 4.08 Å. Higher harmonics were eliminated by means of a cooled beryllium filter. Pyrolitic graphite was used

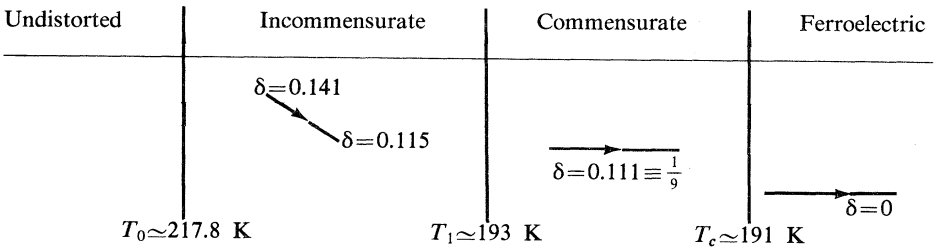
as monochromator and analyzer.

The fully deuterated single-crystal specimen, kindly supplied by Professor J.P. Chapelle, (SDTM, LP 3261, Université Paris-Sud, 91405 Orsay) had an approximate $6\times5\times12$ mm^3 parallelepipedic shape with faces perpendicular to the orthorhombic principal axes. The specimen was placed in an aluminum-wall pressure cell, the cell being itself located inside a variable-temperature cryostat. The temperature definition and stability are estimated to be of the order of ±0.02 K. The pressure transmitted to the specimen (by means of helium gas) is purely hydrostatic and can be varied continuously up to 4500 bars, with an accuracy of ±10 bars.

All measurements were performed in the $(h,k,0)$ zone. We concentrated mostly on the $(2,\pm n\delta,0)$ satellite reflections ($n=1,2,3,4$). In addition to using long-wavelength neutrons, we tried to maximize the accuracy on the determination of δ by systematic lattice-parameter recalibrations for each pressure and temperature and by choosing higher-order satellites ($n>1$) whenever compatible with intensity requirements. The temperature dependence of the different satellite orders has been discussed by Moudden *et al.*[14], at $P=0$. No attempt has been made here at analyzing their pressure dependence.

II. THIOUREA AT AMBIENT PRESSURE

The succession of phases as a function of temperature is summarized in the diagram below[6]:



We note that the modulation wave vector δ varies continuously from a value somewhat smaller than $\frac{1}{7}$ at T_0 to a value somewhat larger than $\frac{1}{9}$ at T_1. At T_1 the modulation wave vector drops discontinuously to the commensurate value $\frac{1}{9}$. At T_c, i.e., 2 K below, δ jumps again to zero.

Both lock-in transitions are affected by a temperature hysteresis of about 1 K. Hysteresis effects are not confined to the immediate neighborhood of first-order lock-in transitions. Hysteresis on the value of δ is observed in the incommensurate phase, several degrees above T_1.[6,12] This type of behavior, sometimes referred to as "global hysteresis,"[13] is a characteristic feature of many modulated systems.[15,16] The transition at T_0, T_1, and T_c can be correlated to specific heat,[17] dielectric constant,[18] and birefringence[9] anomalies. However, the dielectric measurements suggest the existence of an additional ferroelectric phase stable over 1 or 2 K around 199 K. We speculate (see discussion in Sec. V) that this phase, which is not observed here, corresponds to an electric-field-induced commensurate phase with $\delta=\frac{1}{8}$.

IV. EFFECT OF HYDROSTATIC PRESSURE

The variation of δ with pressure is shown in Fig. 1 for a few selected temperatures. Generally speaking, δ increases with pressure while the modulation amplitude decreases. Above some finite-pressure value $P_0(T)$, the "high-temperature" undistorted phase becomes stable. [For the moment we ignore the $\delta=\frac{1}{3}$ phase (see discussion in Sec. V.)] Within experimental accuracy the transition at P_0 remains continuous.

This type of behavior, illustrated by the 213.6 and 206.4 K isotherms in Fig. 1, is understood qualitatively on the basis of Samara's argument,[20] formulated as follows: (i) the long-period distortion in thiourea is related to the softening of a polar-optic branch near the Brillouin-zone center, as established by optical measurements; (ii) the contribution of long-range Coulomb forces to the square of the ferroelectric soft-mode frequency is negative and relatively pressure insensitive; and (iii) the contribution of all other short-range forces is positive and pressure enhanced. Hence, the soft-

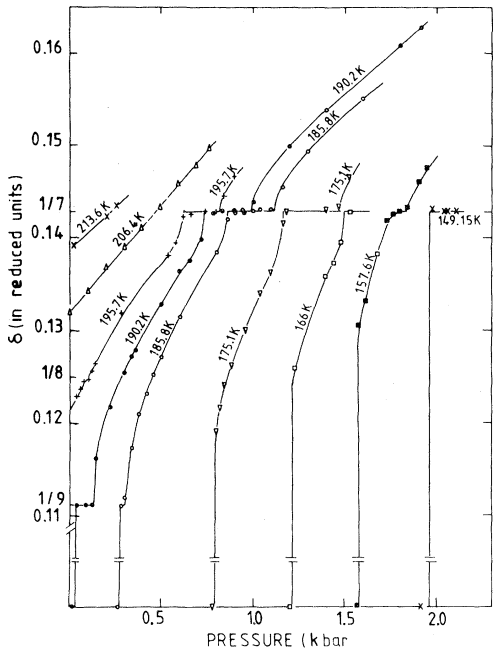


FIG. 1. Isothermal variations of the modulation wave vector $\delta(P,T)$ as a function of applied pressure. All curves have been measured from left to right, i.e., going up in pressure.

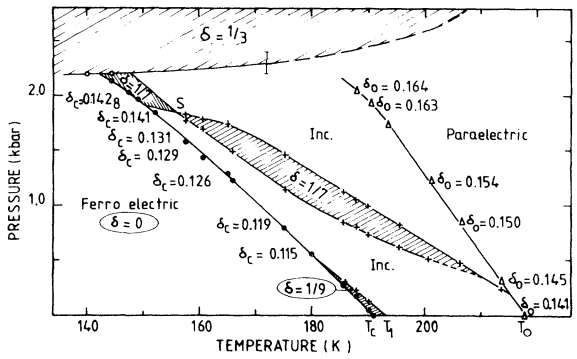


FIG. 2. (P,T) phase diagram. The hatched areas correspond to commensurate phases.

mode frequency increases with pressure or, alternatively, the temperature at which the soft-mode frequency vanishes, $T_0(P)$, decreases with pressure.

Below 207 K, the variation of δ with pressure follows the same qualitative trend as above, but additional features appear due to the existence of commensurate "lock-in" phases. In particular, all isotherms below 207 K display a plateau at $\delta=0.1428\pm2$ (this result represents the first evidence for a pressure-induced lock-in phase of superperiod 7*b*). Note the rapid variation of δ with P, immediately below and above the $\frac{1}{7}$ plateau, a feature which makes it difficult to decide on the nature of the corresponding locking and unlocking transitions (continuous transitions with logarithmic singularities have been predicted theoretically.[13] An exception to the above behavior is observed on the 157.6-K isotherm for which the $\frac{1}{7}$ plateau is almost missing [see (iv) below].

Below 193 K, additional steps at $\delta=\frac{1}{9}$ and $\delta=0$ appear, corresponding to the two zero-pressure commensurate phases. Below 180 K the step at $\frac{1}{9}$ disappears altogether, while at still lower temperatures (cf. 149.15-K isotherm) the system goes directly from the ferroelectric state into the 7*b* phase. The above results are summarized in the (P,T) diagram shown in Fig. 2.

(i) The second-order transition line has been determined up to pressures of about 2.1 kbar. The value of the initial slope $(dT_0/dP)\,|_{P=0}$ $=-13.8\pm0.3$ K/kbar is somewhat lower than that obtained by Gesi[11] (-19.0 K/kbar) and later by Klimowski *et al.*,[18] (-16.8 K/kbar) from dielectric measurements on the hydrogenous compound. The initial value of the modulation wave vector $\delta(P,T_0(P))(\equiv\delta_0)$ varies continuously along the phase-transition line, from a value slightly lower than $\frac{1}{7}$ at ambient pressure to a value of 0.164 at 2060 bars (last point measured on the line).

(ii) The pressure dependence of T_c was determined up to 2150 bars:

$$\left.\frac{dT_c}{dP}\right|_{P=0}=-20.2\pm0.5\ \text{K/kbar}\ ,$$

to be compared with the values -26.0 and -25.5 K/kbar obtained by Gesi and Klimowski (on the hydrogenous compound again).

(iii) As mentioned before, the stability range of the 9 *b* phase becomes progressively narrower with increasing pressure. Eventually the $T_1(P)$ line merges into the $T_c(P)$ line at a triple point of coordinates (550 ± 25 bars, 180 ± 0.5 K). Above the triple point the starting value of δ, $\delta(P,T_c(P))\,(\equiv\delta_c)$ is larger than $\frac{1}{9}$ and reaches $\frac{1}{7}$ at $P\simeq1900$ bar.

(iv) The 7*b* phase has a measurable stability range only below 205 K. Upon cooling, the stability range first increases, then saturates to a maximum value of about 300 bars, decreases to zero at $T\simeq156$ K, and subsequently increases again. Thus, the shape of the phase diagram suggests the

existence of two distinct 7*b* phases, with qualitatively different structures. This interpretation is supported by satellite-intensity measurements in both phases (see Fig. 3).

(v) Above 2.2 kbar a new phase corresponding to a 3*b* superperiod is known to exist from x-ray work.[9,12] The phase transition being violently first order, its exploration by means of single-crystal diffraction is uneasy, and in fact only a few points of the phase boundary were determined here. Not much is known about the 3*b* phase. Its x-ray diffraction patterns look similar to those obtained in the other condensed phases and, on this basis, it would seem to qualify as just another lock-in phase. This conjecture is, *a priori,* difficult to reconcile with the fact that the 3*b* phase persists all the way up to room temperature (and above), i.e., much above the $T_0(P)$ line. A tentative explanation of this apparent inconsistency is presented in the next section.

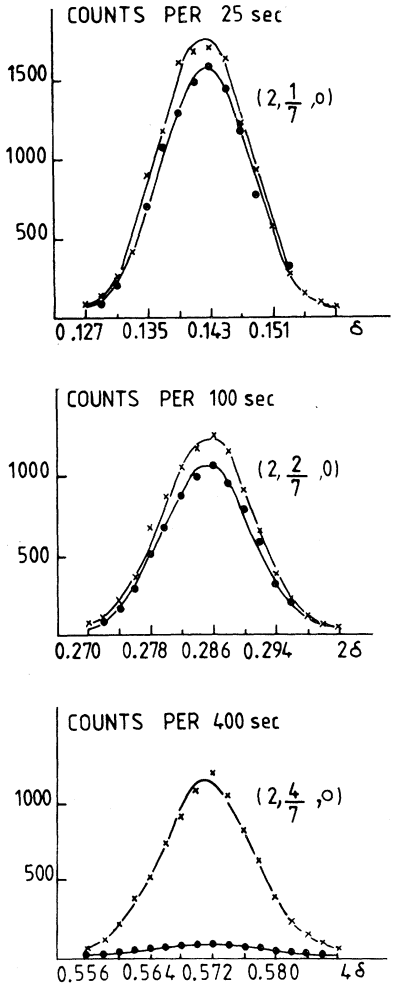


FIG. 3. Comparison of various superlattice reflections in the two 7*b* phases at ●(160.1 K-1750 bars) and ×(153.1 K-1860 bars), respectively. Note the difference between the two $(2,\frac{4}{7},0)$ reflections.

V. DISCUSSION

The stability of modulated structures is usually discussed in terms of a Landau free-energy expansion in which the modulation amplitude is taken as the primary order parameter. This approach, formulated in such a way as to take advantage of the parent-structure spatial symmetry, has proved to be valuable in the discussion of modulated phases in such systems as $TaSe_2$,[21] K_2SeO_4, and isomorphs,[22,15] $(NH_4)_2BeF_4$,[23] etc.

An attempt to discuss the above diagram along those same lines meets with two serious difficulties: (i) the free-energy expansion must be carried up to fairly high orders (ninth order at least, to account for the 9*b* superstructure) and (ii) the strength of some of the higher-order satellite reflections suggest that, at low temperatures, the modulation is far from being sinusoidal. A realistic free energy should therefore include some of the distortion harmonics as secondary order parameters.

Clearly, the task of quantitatively setting up and discussing such a complex free-energy function is beyond the scope of this work. Instead we shall concentrate on trying to account for three qualitative features of the above phase diagram. One question which can be readily answered is why odd superstructures such as 9*b*, 7*b*, 3*b* are preferred to even ones, to say 8*b*. For this purpose, let us consider the corresponding lock-in terms in the free-energy expansion. They are of the form

$$V^{(n)}(\vec{q}_\delta,\Sigma_4)Q^n(\vec{q}_\delta,\Sigma_4)\ , \tag{1}$$

where $Q(\vec{q}_\delta,\Sigma_4)$ is a soft-mode normal coordinate with wave vector

$$\vec{q}_\delta=\delta\vec{b}^*$$

and point-group symmetry Σ_4 (τ_4 in Kovalev's notation[24]), while $V^n(q_\delta,\Sigma_4)$ is an appropriate nth-order anharmonic coefficient. The latter vanishes identically unless

$$n\vec{q}_\delta=\vec{G}\ , \tag{2}$$

where $\vec{G}$ is a reciprocal-lattice vector of the undis-

torted structure. Taking

$$\vec{G}=m\vec{b}^{*} ,$$

condition (2) becomes

$$\delta=\frac{m}{n} \quad (m,n=\text{integers}) .$$

In addition the $V^{(n)}$'s must satisfy point-group selection rules, which in the present case restrict m and n to be of the same parity (see Ref. 22, Sec. VII). Hence a $9b$ superstructure corresponds to a lock-in term of order 9, while an $8b$ superstructure would involve a lock-in term of order 16.

It is noteworthy that a uniform electric field applied along a, couples linearly to a lattice distortion of the type Q $(0,\Sigma_4)$, and hence can induce the $8b$ superstructure via a symmetry-allowed (and more plausible) lock-in term of the type

$$\propto Q^{8}(\vec{q}_{\delta},\Sigma_4)Q(0,\Sigma_4) .$$

The coefficients $V^{(n)}$ are temperature and pressure dependent. [For instance, $V^{(2)}(\vec{q}_{\delta},\Sigma_4)$ vanishes identically along the second-order $T_0(P)$ line]. Similarly the existence of two distinct $7b$ phases can be accounted for if we postulate that the corresponding lock-in coefficient $V^{(7)}(\vec{q}_{\delta},\Sigma_4)$ vanishes along some line passing through point S in Fig. 2. The two lock-in phases would thus differ by a $\pi/7$ phase shift of the distortion wave with respect to the parent lattice. Such a phase shift is presumably responsible for the observed change in satellite intensitites as seen in Fig. 3.

If we think of the $3b$ phase, at least tentatively, as just another lock-in phase, the relevant lock-in term is given by expression (1) with $n=3$. Clearly, the presence of such a cubic term in the free energy will give rise to a strongly first-order lock-in transition. In fact, if the minimum in the soft-mode dispersion did occur at a wave vector δ_0 close to $\frac{1}{3}$, the incommensurate phase would be suppressed altogether and the system would go directly from the undistorted phase into the $3b$ phase. In the present case we see from Fig. 2 that although δ_0 increases with pressure along the $T_0(P)$ line, the incommensurate phase becomes unstable with respect to the $3b$ phase when $\delta_0(P)$ is still a long way from $\frac{1}{3}$. This fact would seem to suggest that either the cubic lock-in term is indeed quite large, or a totally different mechanism must be envisioned. Obviously a more quantitiative analysis based on more extensive data is required in order to proceed further.

More elaborate descriptions of modulated structures, going beyond ordinary Landau theory, have been proposed.[25,25] Close to lock in, these theories lead to the concept of phase solitons. Aubry[13] has pointed out that pinning of the solitons by the underlying atomic lattice can lead to important effects. In particular the effect of pinning will influence the way in which the modulation wave vector changes as a function of an external field.

Aubry's approach is based on the epitaxial chain model (i.e., a string of interacting atoms subjected to a periodic substrate potential). His discussion is relevant to that of three dimensional modulated structures such as thiourea, since, to some extent, the two problems can be mapped onto each other. Depending upon the strength of the substrate potential (here, the amplitude of the modulation), Aubry distinguishes two regimes: (i) the modulation wave vector proceeds by steps and the resulting phase diagram is made up of an infinity of pinned commensurate phases (complete devil's staircase, corresponding to large potential values), and (ii) between steps the wave vector may vary continuously as the phase diagram is a mixture of commensurate and truly incommensurate phases (incomplete devil's staircase).

Similar results have been obtained by Bruce[27] and Bak,[28] based on the analysis of various discrete anisotropic models.

From an experimental standpoint, case (i) is expected to give rise to global wave-vector hysteresis while case (ii) implies the existence of a gapless phason branch.

In an attempt of assess which of the two regimes describes best the incommensurate phases of thiourea, we may note that along the $T_0(P)$ line (where the modulation amplitude vanishes) the continuous model should be applicable, and near $T_c(0)$ global hysteresis has been clearly seen,[6] implying that the pinned-soliton description is more appropriate.

On the other hand, our inelastic neutron measurements (to be reported elsewhere) remain so far inconclusive as to the existence of a phason branch. Another negative result is the absence of experimental evidence for statellite broadening[28] throughout the (P,T) phase diagram, despite the rather favorable experimental conditions. Efforts to clarify these two negative results are currently underway.

In conclusion, the present investigation has revealed a number of novel features in the (P,T) phase diagrams of thiourea, such as the existence of two new commensurate phases with a $7b$ modu-

lation period. Additional experimental and theoretical effort[29] will be required in order to fully characterize the nature of the various modulated structures encountered. Meanwhile, we hope that the work presented here has shown that such an effort is indeed warranted and that thiourea is a very appropriate substance for the study of discrete lattice effects in modulated systems.

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[1]A. L. Solomon, Phys. Rev. 104, 1191 (1956).
[2]M. M. Elcombe and J. C. Taylor, Acta Crystallogr. Sec. A 24, 410 (1968).
[3]H. Futama and A. Chiba, unpublished.
[4]T. Mitsiu, E. Nakamura, Y. Shiozaki, H. Motigi, T. Sekido, M. Ichikawa, T. Takama, M. Hosoya, K. Shibukawa, N. Wakaki, and J. Furuichi, Proceedings of the International Meeting on Ferroelectrics, Prague, Vol. 1, 222 (1966).
[5]H. Futama, Y. Shiozaki, A. Chiba, E. Tanaka, T. Mitsui, and J. Furuichi, Phys. Lett. 25A, 8 (1967).
[6]A. H. Moudden, F. Denoyer, M. Lambert, and W. Fitzgerald, Solid State Commun. 32, 933 (1979).
[7]F. Denoyer, A. H. Moudden, M. Lambert, Ferroelectrics 24, 43 (1980).
[8]P. W. Bridgman, Proc. Am. Acad. Art. Sci. 72, 227 (1937); 76, 71 (1948).
[9]S. S. Kabalkina, Zh. Fiz. Khim. 35, 276 (1961).
[10]P. Figuiere and M. Ghelfenstein, J. Chem. Phys. Lett. 33, 199 (1975).
[11]K. Gesi, J. Phys. Soc. Jpn. 26, 107 (1969).
[12]A. H. Moudden, L. Gatebois, F. Denoyer, and M. Lambert, Rev. Sci. Instrum. 51, 836 (1981); A. H. Moudden, thesis, Université Paris-Sud, Orsay, 1980, (unpublished).
[13]S. Aubry, in *Solitons and Condensed-Matter Physics,* edited by A. R. Bishop and T. Schneider (Springer, New York, 1978); S. Aubry, in *Seminar on the Rieman Problem, Spectral Theory and Complete Integrability,* in *Lecture Notes in Mathematics,* edited by D. G. Chudnovsky (Springer, Berlin, 1980); S. Aubry, *Les Houches,* edited by R. Balian and M. Kleman (1980).
[14]A. H. Moudden and J. Als-Nielsen (unpublished).
[15]C. J. De Pater, J. D. Axe, and R. Currat, Phys. Rev. B 19, 4684 (1979).
[16]R. Comes, G. Shirane, S. M. Shapiro, A. F. Garito, and A. J. Heeger, Phys. Rev. B 14, 2376 (1976).
[17]S. S. Chang and E. F. Westrum, Phys. Chem. Org. Solid State 1, 126 (1963).
[18]J. Klimowski and W. Wanarski, and D. Ozgo, Phys. Status Solidi A 34, 697 (1977).
[19]J. P. Jamet, A. M. Quittet, and A. H. Moudden, EPS Conference Anvers, Belgium, 1980, *Recent Developments in Condensed Matter Physics* (Plenum, New York), Vol. 9, p. 61.
[20]G. A. Samara, Comments Solid State Phys. 8, 13 (1977).
[21]D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. 34, 734 (1975).
[22]M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B 15, 4392 (1977).
[23]H. Shiba and Y. Ishibashi, J. Phys. Soc. Jpn. 44, 1592 (1978).
[24]O. V. Kovalev, *Irreducible Representation of the Space Groups* (Gordon and Breach, New York, 1965).
[25]W. L. McMillan, Phys. Rev. B 14, 1496 (1976).
[26]P. Bak and V. J. Emery, Phys. Rev. Lett. 36, 978 (1976).
[27]D. A. Bruce, J. Phys. C 13, 4615 (1980).
[28]P. Bak, Phys. Rev. Lett. 46, 791 (1981), and references therein.
[29]A. Yamamoto, Phys. Rev. B 22, 373 (1980).