Thiourea in an electric field: Birefringence measurements and the Landau-Ginzburg theory

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(Received 7 July 1982; revised manuscript received 7 March 1983)

We report birefringence measurements of the field-induced commensurate phase in deuterated thiourea in the whole modulated phase part of the (E,T) plane at atmospheric pressure. A simple Landau-Ginzburg approach is shown to account, in a qualitative and semiquantitative way, for the experimental observation.

I. INTRODUCTION

Deuterated thiourea $[SC(ND_2)_2]$ is well known to exhibit a modulated phase between $T_H = 190$ K and $T_\lambda = 216$ K at ambient pressure and zero electric field. Above T_λ, it is paraelectric and below T_H, which is a first-order transition temperature, it is ferroelectric. With varying pressure and electric field, this interesting system exhibits a variety of modulated phases, some of which are commensurate[1,2] with commensurability order 3,7,8,9. This paper reports birefringence measurements of the phase diagram of deuterated thiourea and especially of the commensurate phase of order 8, under an electric field parallel to the ferroelectric axis, i.e., perpendicular to the anisotropy axis. It should be noticed that it is a somewhat unusual way of determining commensurate phases and commensurate-incommensurate transition lines, since birefringence does not measure a lattice Fourier transform as x-ray or neutron-diffraction measurements do. However, after the prediction of a field-induced commensurate phase of commensurability order 8 determined by thermodynamical measurements[2] was checked[3] by neutron-diffraction measurements, we feel the method is a fully respectable one, and a quite reliable one at that.

This paper also presents a theoretical analysis of the results within the framework of a very simple Landau-Ginzburg approach. It had been noted previously[4] that the overall shape of the modulated phase under field was well accounted for by such an approach. We show here that the peculiar tearshaped commensurate phase of order 8 described in Sec. II is also reasonably well accounted for. Our approach is to take into account the (small) umklapp term of a given order only if it has a physical effect in the field and temperature intervals at hand. The success of this simple theory might be surprising, since $SC(ND_2)_2$ has been claimed to be a good example of a devil's-staircase behavior[1,5,6]: Rigorously speaking, this means that the free energy of thiourea is a nonanalytic function of, say, temperature, the modulation wave vector being a continuous nonanalytic function which is constant in a certain temperature or field interval for each rational number.[7] One might then think that a Landau-Ginzburg approach, based on an analytic expansion in powers of the order parameter, with the underlying assumption that the modulation wave vector is a smoothly varying function of temperature and field, at most a piecewise analytic one, would not be appropriate. What we show, in fact, is that in thiourea one need only consider a few finite steps in the whole staircase, and that high-order commensurate steps have an unphysically small width, and can be neglected.

This paper is organized as follows: Sec. II describes new experimental results on the field-induced commensurate phase of order 8; the complete phase diagram around commensurability order 8 is determined. Section III sets up the Landau-Ginzburg theory of modulated phases under field appropriate to thiourea. Section IV is an application of Sec. III to the case of $SC(ND_2)_2$. Section V discusses the meaning of our results and the limitations of the theory.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experimental method used to measure the birefringence has been explained in Ref. 8 and we shall only mention that we use an acousto-optic modulator to improve the sensitivity of the measurement. The light beam is parallel to the a axis of the cleaved sample and the electric field is applied parallel to this direction so that we measure the birefringence $\Delta n_{bc} = n_b - n_c$, where b is parallel to the modulation wave vector q. Two methods have been used: either at constant dc field by changing the temperature with a constant cooling or heating rate (typically ± 3 mK/sec) or at given temperatures by sweeping the field (stability better than 10 mK during a cycle); as far as the diagram determination is concerned the two methods give the same data.

The field-induced commensurate phase boundaries are determined by plotting the locus of birefringence anomalies. Those match with the locus of susceptibility anomalies at low fields in the region where both methods give observable anomalies. Typical examples of birefringence measurements are shown on Fig. 1 for constant field $E = 750$ V/mm. Figure 2 shows the complete phase diagram of the commensurate phase with $q = b^*/8$ (see also Fig. 3). This phase extends up to a maximum field very close to the isolated critical point[4,8] (E_M, T_M). Figure 4 shows the variation of the amplitude of the birefringence anomaly as a function of field along the commensurate phase boundary.

In the paraelectric phase ($T > 216$ K) deuterated thiourea is orthorhombic and optically biaxial. The birefringence variation with temperature is due to the lattice strain and the electron-phonon coupling, which we write as $(\Delta n_{bc})_0 = n_{b_0} - n_{c_0}$.

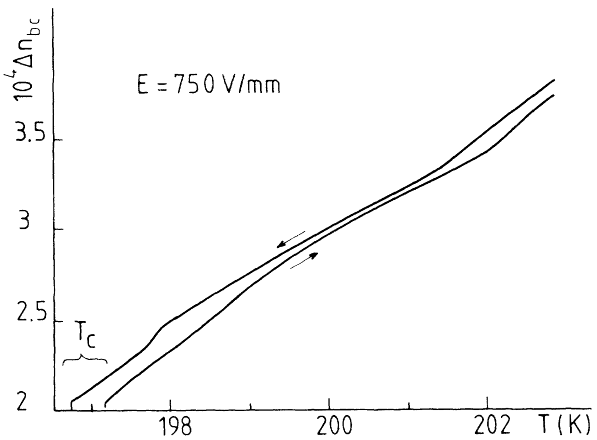

FIG. 1. Birefringence measurement at $E=750$ V/mm for increasing and decreasing temperature around the commensurate phase at $q=b^*/8$. The light propagates along the a ferroelectric axis ($\lambda=6328$ Å).

In the modulated phase we have[9]

$$\Delta n_{bc}=r\langle P_x\rangle+R\langle P_x^2\rangle+(\Delta n_{bc})_0 \quad (1a)$$

$$\simeq rP_0+R(P_0^2+P_q^2)+(\Delta n_{bc})_0 , \quad (1b)$$

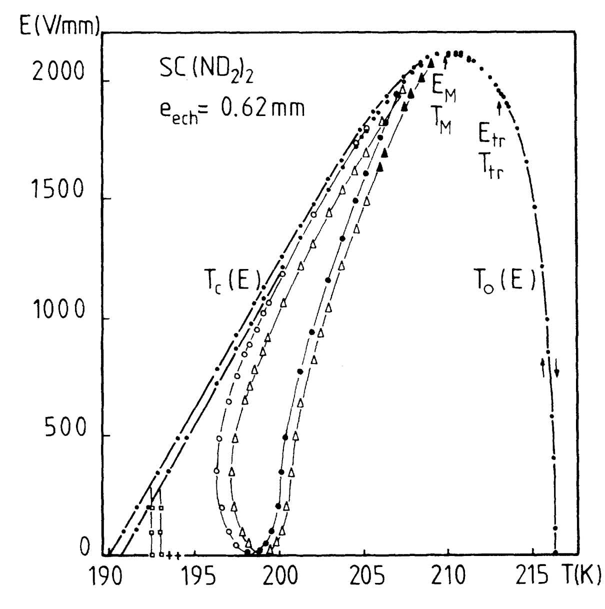

FIG. 2. Phase diagram (E,T) of $SC(ND_2)_2$ for increasing and decreasing temperatures. The solid and open triangles represent the commensurate-incommensurate transitions of the $q=b^*/8$ commensurate phase for increasing temperatures, the solid and open circles for decreasing temperatures. The solid and open squares represent the commensurate-incommensurate transitions for the $q=b^*/9$ commensurate phase, respectively, for increasing and decreasing temperatures; at last the two plus signs on the T axis refer to the positions of the $q=2b^*/17$ susceptibility anomalies for the two temperature variations. All these data have been obtained by susceptibility or birefringence measurements, and the error bars are of the order of the size of the points. The solid lines are aids to the eyes.

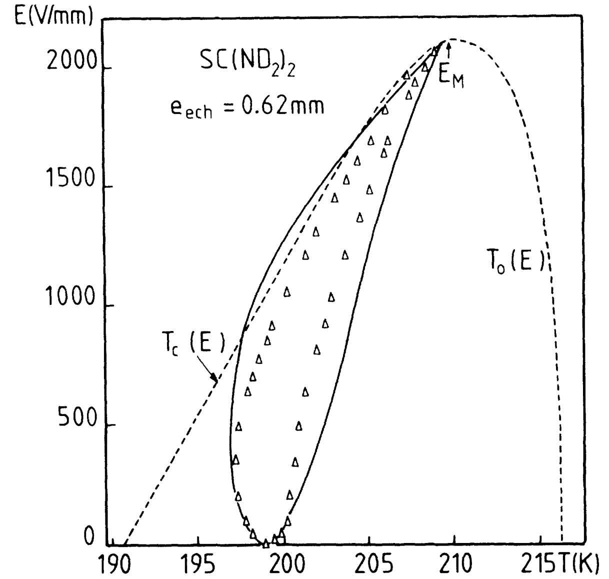

FIG. 3. This features a part of Fig. 2. The solid line represents the theoretical result given by Eq. (14).

where $P_x(r)$ is the polarization density along the x axis. As described later (Sec. II), it is sufficient to describe the modulated phase with two nonzero Fourier components of $P_x(r)$, i.e., P_q and $P_0=P_{q=0}$ (single-harmonic approximation); Eq. (1a) holds because the light wavelength is much larger than the modulation wavelength and we measure a mean value of $P_x(r)$ and $P_x^2(r)$—(1b) follows from (1a) in the single-harmonic approximation. In (1a) and (1b),

$$r=\tfrac{1}{2}(n_{c_0}^3r_{31}-n_{b_0}^3r_{21}) ,$$

$$R=\tfrac{1}{2}(n_{c_0}^3R_{31}-n_{b_0}^3R_{21}) ,$$

where r_{ij} and R_{ij} are the elements of the linear and quadratic optical tensors. R, r, and $(\Delta n_{bc})_0$ have slow mono-

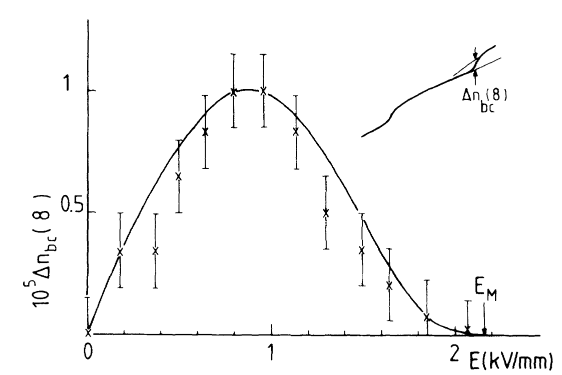

FIG. 4. Birefringence jump at the commensurate-incommensurate transition for $q=b^*/8$ for decreasing temperature as a function of the applied dc field. The large error bars come out from the uncertainty of this determination as can be seen on the inset in the upper right corner. The solid line has been determined from Eq. (16).

tonous variations with T. The linear term is found experimentally to be smaller than the quadratic term by more than 1 order of magnitude. In the next section we discuss a simple Landau-Ginzburg theory of commensurate phases and commensurate-incommensurate transitions under field.

III. LANDAU-GINZBURG THEORY OF MODULATED PHASES UNDER FIELD

We start with the following free energy[4] for a uniaxial system, with the field geometry appropriate to the experiments discussed here:

$$F=F_0+\Delta F\ , \tag{2}$$

$$F_0=\int\left[\frac{1}{2}A_0P_x^2+\frac{1}{4}BP_x^4+\frac{D}{6}P_x^6+\frac{1}{2}\alpha\left[\frac{\partial P_x}{\partial z}\right]^2+\frac{1}{4}\gamma\left[\frac{\partial^2 P_x}{\partial z^2}\right]^2+\frac{\eta}{2}\left[\frac{\partial P_x}{\partial z}\right]^2P_x^2-E_xP_x\right]d^3r\ , \tag{3}$$

and

$$\Delta F=\sum_p\int b_p(r)P_x^p d^3r\ , \tag{4}$$

where $P_x(r)$ is the uniaxial polarization and E is the electric field. $A_0=(T-T_0)/C$, B, D,γ, and η are positive constants and $\alpha(T,E)$ is negative. The sixth-order term $(D/6)P_x^6$ is necessary to describe the modulated part of the phase diagram for fields at and above the tricritical field $E_{\rm tr}$. The term proportional to η has been discussed in Ref. 10 where it is shown to cause field and temperature variation of the modulation wave vector even if α is taken to be constant. It is also shown to lead to a reduced domain of stability of the modulated phase as compared with the theory with $\alpha=$const and $\eta=0$. This term certainly should be included for consistency, even though it was suggested in Ref. 10 not to be very important in thiourea. In order to derive the simplest possible theory for the shape of the commensurate phases under field, we set in the following $D=\eta=0$, so that quantitative agreement should be poor. The limitation of our results due to this simple approximation will be discussed in Sec. III.

In principle, all terms in Eq. (4) with $p\geq 3$ should be included; they give rise to the umklapp terms. However, we are interested in describing a commensurate phase within the modulated region at a definite p value; we shall assume in the rest of the paper that umklapp terms may be treated one at a time and that a pth-order term does not have physical effects on a pth-order commensurate phase. This assumption is not a serious loss of generality.

A crucial step to simplify further the theory is to consider that, in the absence of umklapp terms, the phases of the system are described by a uniform component of the polarization $P_0=P\ (q=0)$ and a polarization P_q of wave vector q.[10–12] As discussed in Refs. 11 and 10 this is not a bad approximation (except maybe in the lowest-temperature part of the modulated phase).

The main term of the free energy (with $D=\eta=0$) reduces to

$$F_0=\tfrac{1}{2}A_0P_0^2+A(q)\,|P(q)|^2+\frac{B}{4}P_0^4$$

$$+3BP_0^2\,|P_q|^2+\tfrac{3}{2}BP_q^4-EP_0\ , \tag{5}$$

where $A_q=A_0-\alpha^2/2\gamma$ with $q_0=(-\alpha/\gamma)^{1/2}$. P_0 and P_q are determined from $\partial F_0/\partial P_0=0$ and $\partial F_0/\partial P_q=0$ so that

$$|P_q|^2=\frac{T_0-T+q^4\tilde{\gamma}/2}{3T_0}-P_0^2 \tag{6}$$

and P_0 is the appropriate solution of the following equation:

$$P_0(A_0-2A_q)-5T_0P_q^3=CE \tag{7}$$

in (6) and (7), $\tilde{\gamma}=C\gamma$ and the coefficients are chosen so that $P_0(T=0,E=0)=1$. In the remainder of this paper, polarizations are expressed in units of $P_0(T=0,E=0)$.

In the vicinity of the equilibrium modulation wave vector $q_0(T,E)$, F_0 can be expanded as

$$F_0=F_{0\,\rm min}+4\gamma q_0^2[q-q_0(T,E)]^2\,|P_q|^2\ . \tag{8}$$

In metallic modulated structure with fixed chemical potential, $q_0(T,E)$ is independent of temperature (of order $2k_F$). In that case, there exists a critical value $(P_q)_c$ such that if $|P_q|>|P_q|_c$ the commensurate phase is more stable.[13,14] The situation is different when $q_0(T,E)$ has a noticeable variation in temperature, and goes smoothly through a commensurate value, say $q_p=2\pi/pb$, at a temperature T_p (b is the lattice constant). Let us linearize q around q_p and write

$$q=q_p+(T-T_p)\frac{dq}{dT}\Big|_{q=q_p}+\cdots\ .$$

Then the umklapp term of order p in (4) stabilizes a commensurate phase of order p within a temperature interval ΔT on either side of T_p. Provided $b_pP_x^p \ll BP_x^4$, ΔT is given by

$$b_p\,|P_q|^p=\frac{\pi^2}{2}\gamma q^2(\Delta T)^2\zeta^2\,|P_q|^2 \tag{9}$$

so that

$$\Delta T=\frac{\sqrt{2}}{\pi}b_p^{1/2}\gamma^{-1/2}(\zeta q)^{-1}\,|P_q|^{(p-2)/2}$$

with

$$\zeta=\frac{dq}{dT}\Big|_{q=q_p}$$

(ζ will be assumed independent of field).

The curve $q(T,E)=q_p$ in the (E,T) plane thus determines the contours of the commensurate phase through (9). To a first approximation, they are symmetrical in T with respect to the equal $-q$ curve. [Corrections due to the fact that $\partial P_q(T)/\partial T\neq 0$ are unsymmetrical.] There is a small change in $|P_q|^2$ at the commensurate-incommensurate transition, which for high commensurability order p, is given by (also in the limit that $b_p P_x^p \ll B P_x^4$)

$$\delta(|P_q|^2)=\frac{p b_p}{6T_0}|P_q|^{p-2} . \quad (10)$$

The width of a discommensuration wall[13,14] associated with a commensurate-incommensurate transition of order p is[15]

$$l_p=\frac{1}{p}\left[\frac{2q^2\gamma}{b_p|P_q|^{p-2}}\right]^{1/2} = \frac{2\pi}{p^2}\left[\frac{2\gamma}{b_p}\right]^{1/2}|P_q|^{(2-p)/2} , \quad (11)$$

where l_p is finite at the commensurate-incommensurate transition and varies with T and E.

Indeed, combining (11) and (9), we have

$$l_p=\frac{4}{\pi}(p\zeta\Delta T)^{-1} . \quad (12)$$

(This simple relation, derived within the molecular-field picture, may be more general.)

Depending on the symmetry properties of the crystal, it may happen that certain umklapp terms vanish when $P_0=0$. For example, in thiourea,[1] $b_8=b_8'P_0$ when the electric field is applied along the direction of the ferroelectric polarization. Take $b_p=b_p'P_0$. Then the umklapp term is equivalent to an applied field $E_{\text{eff}}=b_p'|P_q|^p$, so that a nonzero polarization $P_{0,p}$ exists in zero external field:

$$P_{0,p}=\chi E_{\text{eff}}=\chi b_p'|P_q|^p , \quad (13)$$

where χ is the polarizability in the absence of the umklapp term. For high commensurability order, $P_{o,p}$ is small; Eqs. (10) and (12) hold provided b_p is replaced by $b_p'\chi(E+E_{\text{eff}})$. Neglecting E_{eff} [which can be typically of order 1V/mm for $p=8$ and for $(T-T_\lambda)/3T_0\sim\frac{1}{30}$, where T_λ is the disordered modulated transition temperature] we have, in this special symmetry case,

$$\Delta T\simeq b_p^{1/2}E^{1/2}|P_q|^{(p-2)/2}(\zeta q)^{-1} . \quad (14)$$

Note that this formula breaks down for $E\lesssim E_{\text{eff}}$. In zero external field, $\Delta T(E=0)$ is not zero, even though it may be small. Thus

$$\Delta T(E=0)=\frac{\sqrt{2}}{\pi}(b_p'\chi E_{\text{eff}})^{1/2}\gamma^{-1/2}(\zeta q_p)^{-1}|P_q|^{(p-2)/2} = \frac{\sqrt{2}}{\pi}b_p'\chi^{1/2}\gamma^{-1/2}(\zeta q_p)^{-1}|P_q|^{p-1} . \quad (14')$$

IV. APPLICATION TO THIOUREA

The Landau-Ginzburg approach outlined above can be used to interpret the data provided one remembers that the symmetry of thiourea imposes[1] $b_8=b_8'P_0$. To account for the overall shape of the $b^*/8$ commensurate phase, one needs the hypothesis that the equal $-q$ line in the E,T plane at $q=b^*/8$ in the absence of the umklapp term is

$$T_8^*+\epsilon E^2\simeq T_8[1+(E/E_0)^2] \quad (15)$$

with $\epsilon=2.5\times10^{-6}$ K V^{-2} mm^2, or $E_0\simeq0.9\times10^4$ V/mm. One may think of this field dependence as due to the field dependence of the coefficient α. In fact, it is naturally accounted for by the η term,[10] which we have neglected here.

We now use $|P_q(T_8^*,E)|^2$ and $P_0(T_8^*,E)$ calculated from (5)–(7) with $T_\lambda=216$ K and $T_0=199$ K. This determines $\tilde{\gamma}q^4/2=17$, $E_{\text{tr}}=1200$ V/mm, $T_{\text{tr}}=212$ K, $E_M=1400$ V/mm, and $T_M=208$ K to be compared with the experimental values: $E_{\text{tr}}=2050$ V/mm, $T_{\text{tr}}=212$ K, $E_M=2285\pm10$ V/mm, and $T_M=210\pm0.2$ K.

As expected, taking $\alpha=cst$ yields poor agreement with the low-temperature part of the modulated phase: One has $T_H=124$ K instead of the experimental value 190 K, a discrepancy which is accounted for by the η term. The result for the shape of the $\frac{1}{8}$ commensurate phase is shown in Fig. 3, with one parameter adjusted to the low-field part ($E\simeq100$ V/mm) of the curve to fix the parameter b_8; the theoretical curve has been rescaled so as to let the experimental and theoretical points (E_M,T_M) coincide. As can be seen, the theory accounts for the overall shape of the commensurate phase, as well as for the order of magnitude of ΔT although the experimental result gives a reduced domain of stability compared with the theoretical curve. A number of reasons can account for that discrepancy. Probably the most important one is the neglect of the η term, but one should also note that we have neglected the higher-order harmonics of the modulated phase, which start having a noticeable amplitude below 203 K; critical fluctuations, which occur probably in the whole modulated part of the phase diagram have been shown to reduce somewhat the stability of the commensurate region.[16] Finally, walls near the commensurate-incommensurate transition have thermal fluctuations which lower their free energy and lower the stability of the commensurate phase, in a way which should depend on the wall width. Figure 5 exhibits the wall width variation with field along the $\frac{1}{8}$ commensurate phase boundary. The continuum approximation is valid all along the

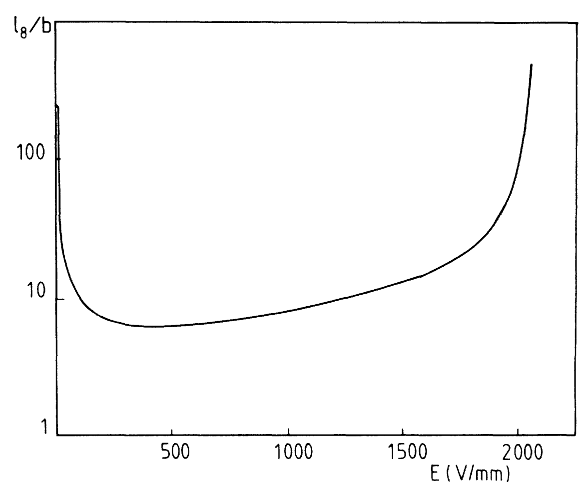

FIG. 5. Variation of the width l_8 of discommensuration walls at the $\frac{1}{8}$ commensurate-incommensurate transition as a function of field. The value at zero field corresponds to $\Delta T\sim0.1$ K in zero field.

phase boundary, since the wall width is always significantly larger than the interatomic distance. Therefore, wall fluctuations are insensitive to the lattice potential. We cannot evaluate at present the relative contributions of the various terms we have just discussed to the corrections to our simple theory.

The Landau-Ginzburg estimate for $\delta\Delta n_{bc}$ is

$$\frac{\delta\Delta n}{R}=\delta(|P_q|^2)=\frac{4b'_8}{3T_0}P_0(T_8^*,E)|P_q^*(T_8,E)|^6 \quad (16)$$

where it is easy to see that

$$\delta(P_0^2)=(|P_q|^2/2)\delta|P_q| \ll \delta(|P_q|^2) .$$

Combining (16) and (11) we find

$$\frac{\delta\Delta n}{R}=\frac{\pi^2}{6T_0}\gamma q^2\zeta^2(\Delta T)^2 . \quad (16')$$

The result of (16) is plotted in Fig. 4, again with one adjustable parameter. Note that the phase amplitude decoupling approximation is quite a good one for the discommensuration walls (or solitons) in the vicinity of the $b^*/8$ commensurate phase,[15] as

$$\delta(|P_q|^2)/|P_q|^2=\frac{4b'_8}{3T_0}P_0|P_q|^4 \ll 1$$

[experimentally $\delta(|P_q|^2)/|P_q|^2 \sim 10^{-2}$ near $b^*/8$]. Notice also that for an odd-order umklapp term in deuterated thiourea, e.g., $p=9$,

$$\left[\frac{\delta\Delta n}{R}\right]_9=\frac{3b_9}{2T_0}|P_q(T_9)|^7 ,$$

does not vanish at low field. We find, if $b_9 \simeq b'_8$, that $(\delta\Delta n)_9$ at $E=0$ is about $2.5(\delta\Delta n)_8$ at $E=1000$ V/mm as observed. The width l_8 of the $\frac{1}{8}$ discommensuration walls is estimated from (12): l_8 has a local maximum of order $250b$ at zero field [if $\Delta T(E=0) \lesssim 0.1$ K], then decreases to a minimum of about $10b$ around 1000 V/mm, and then increases again and diverges as P_q^{-3} at high field[17] (see Fig. 3).

We show in Fig. 6 the variation of the wall thickness l_9 associated to the commensurate phase at $q=b^*/9$ as a function of temperature in zero field. Walls are well defined, of course, only when their distance is larger than their width. Notice that in the vicinity of the $\frac{1}{9}$ commensurate phase in zero field, the wall width is of the order of the unit-cell length, so that one might think that discreteness effects may play some role in that part of the phase diagram. See our comments on this in Sec. V.

Our interpretation depends crucially on the validity of Eq. (15). We have experimentally checked that it was correct by measuring the equal $-q$ curve in the (E,T) plane for $q \simeq 2\pi/7.5b$, due to a new memory effect which has been reported elsewhere.[18] We find $\epsilon=(2.5\pm0.1)\times10^{-6}$ K V^{-2} mm^2, in excellent agreement with (15).

Formally, Eq. (9) leads to nonzero ΔT for all rational values of q.[13] However, it is easy to show that the analyticity breaking terms (the umklapp terms) become already vanishingly small for such relatively simple rational values as $q=3b^*/23$, or $q=3b^*/25$. Indeed, if one assumes that all Landau-Ginzburg coefficients b_p in (4) have the same order of magnitude, one may estimate $\Delta T \simeq 10^{-6}$ K for the above-mentioned commensurate values. In zero field, the umklapp terms corresponding to $q=2b^*/13$ or $q=2b^*/15$ are of order 26 and 30, for symmetry reasons.[1] It is therefore quite reasonable to neglect them altogether. One should keep in mind also, that crystal inhomogeneities will destroy commensurability at sufficiently high order, and lead to hysteresis of the modulation wave vector.

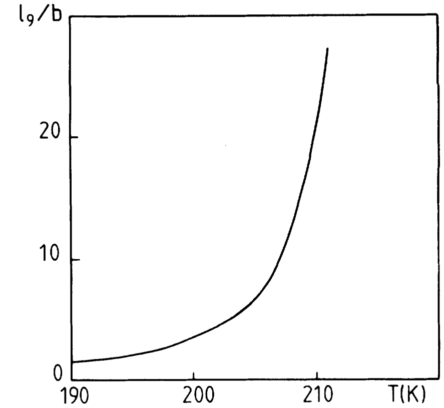

FIG. 6. Variation of the width l_9 of discommensuration walls at the $\frac{1}{9}$ commensurate-incommensurate transition as a function of temperature, in zero field. Walls are well defined only when their distance is larger than their thickness. We estimate this occurs for $T \lesssim 205$ K.

V. CONCLUSION

As evidenced above, a standard Landau-Ginzburg continuum approach provides us with a qualitative and semiquantitative understanding of the phase diagram of thiourea.[19] In our view, this sheds some light on an interesting problem, that of the piecewise analyticity of thermodynamic functions in thiourea. The latter has been quoted in the literature as a good example of "devil's-staircase" behavior.[1,5,6] This behavior can be demonstrated to occur in a variety of one-dimensional models at zero temperature, for example, the Frank–Van der Merwe model when the discreteness of the atomic chain is taken into account.[5] When the ratio U/λ of the substrate potential U to the elastic energy λ exceeds a critical value $(U/\lambda)_c$ the model exhibits analyticity breaking[5]; the energy is not an analytic function of the chemical potential anymore.

This behavior is related to the discreteness of the atomic chain. The critical value $(U/\lambda)_c$ corresponds to a discommensuration width of order $\frac{1}{10}$ of an interatomic distance: Walls experience a strong pinning potential to the substrate. When $U/\lambda \ll (U/\lambda)_c$, variations of atomic displacements from one atom to its nearest neighbor are small compared with the interatomic distance, and the continuum approximation is valid; walls are thick, and the wall pinning potential to the lattice (Peierls's potential) can be neglected: The energy is a piecewise analytic function of the chemical potential.

At finite temperatures, fluctuations mask the commensurate-incommensurate transition in one-dimensional systems. In two-dimensional anisotropic systems, the wall fluctuations result in qualitative changes of the commensurate-incommensurate transition.[20–22] In anisotropic three-dimensional systems (such as deuterated thiourea), the situation should differ when walls are thick, or when walls are thin. Thin walls interact strongly with the periodic lattice, and at low enough temperature, their thermal fluctuations are strongly suppressed: The walls are well below their roughening transition temperature[22]; one expects the devil's-staircase picture to hold. On the contrary, thick walls interact weakly with the periodic lattice, the continuum approximation inherent to the Landau-Ginzburg picture is valid; walls are rough[22] in the sense that their thermal fluctuations are practically insensitive to the discreteness of the lattice[23] even at temperatures well below T_R. The average distance between walls may vary in a continuous fashion, and the thermodynamic functions are piecewise analytic; the role of thermal fluctuations is to reduce the stability of the commensurate phase.

One may argue that lattice discreteness is essential in giving rise to umklapp terms; however this "soft discreteness" (where walls are thick) gives rise to a periodic potential but does not result in the qualitative change of behavior of thermodynamic functions described by the devil's-staircase concept. Taking into account higher and higher-order umklapp terms becomes rapidly unphysical, as the stair width decreases exponentially with $(p-2)/2$, where p is the order of commensurability.[13]

We believe that we have shown that thiourea can be described in a satisfactory fashion in the continuum approximation, and that symmetry-breaking umklapp terms are small compared to the free-energy terms which describe the incommensurate modulation and its variation with temperature. In fact, relatively wide stairs of orders 7, 8, and 9 may be observed in thiourea because the natural (i.e., in the absence of the umklapp term) wave-vector variation in temperature is unusually slow: The coefficient

$$(\zeta q)^{-1} = \left[\frac{dq}{dT} q \right]^{-1} \Big|_{q=b^*/8}$$

is of order 160 in thiourea, whereas the same coefficient for $q=b^*/9$ is of order 13 in $NaNO_2$.[24] As noted above a consistent theory of the wave-vector variation with temperature and electric field requires a nonzero η term.

Our simple Landau-Ginzburg approach is complementary to other approaches, such as numerical molecular-field calculations on the anisotropic next-nearest-neighbor Ising (ANNNI) model[25] or microscopic one-dimensional models which attempt to take into account the long-range dipolar interaction in $SC(ND_2)_2$.[26] Both these models fail to account for the observed peculiar tear-shaped commensurate phase at $\frac{1}{8}$ because they do not incorporate the field dependence of T_8^* [Eq. (15)] and the specific structure of the eighth-order umklapp term. Otherwise, they are similar to the present approach, and should be corrected by incorporating wall thermal fluctuations.

In conclusion, we have reported birefringence measurements on thiourea under an electric field and at atmospheric pressure. The observed commensurate phase diagram, which we analyze as the $\frac{1}{8}$ commensurate phase, is semiquantitatively accounted for in a Landau-Ginzburg approach which considers the umklapp term of order 8 as a weak perturbation. Corrections to the present theory should include a nonzero η term, wall thermal fluctuations, order-parameter critical fluctuations, higher-order harmonics in the description of the modulated phase order parameter, and impurity effects. Work along these lines is in progress at the moment.

ACKNOWLEDGMENTS

Stimulating discussions with Professor J. Friedel, A. P. Levanyuk, and G. Montambaux are gratefully acknowledged. We also thank F. Denoyer, D. Durand, and A. H. Moudden for numerous discussions and for showing us their results prior to publication. Friendly interaction with J. Ferré is acknowledged with pleasure. One of us (M.N.B.) thanks the Conselho Nacional de Desenvolvimento Científico e Technologico (CNPq) for a research fellowship and the Laboratoire de Physique des Solides, Orsay, for their hospitality.

[1] F. Denoyer, A. H. Moudden, R. Currat, C. Vettier, A. Bellamy, and M. Lambert Phys. Rev. B 25, 1697 (1982).

[2] J. P. Jamet, P. Lederer, and A. H. Moudden, Phys. Rev. Lett. 48, 442 (1982).

[3] A. H. Moudden, E. R. Svensson, and G. Shirane, Phys. Rev. Lett. 49, 557 (1982).

[4] P. Lederer and C. M. Chaves, J. Phys. (Paris) Lett. 42, L127 (1981); A. P. Levanyuk, and D. G. Sannikov, Fiz. Tverd. Tela. (Leningrad) 18, 1927 (1976) [Sov. Phys.—Solid State 18, 1122 (1976)].

[5] S. Aubry, in *Seminar on the Riemann Problem, Spectral Theory and Complete Integrality,* Vol. 225 of *Lecture Notes in Mathematics,* edited by D. G. Chudnosvsky (Springer, Berlin, 1978); Ferroelectrics 24, 53 (1980).

[6] S. Aubry, J. Phys. (Paris) 44, 147 (1983).

[7] S. Aubry, in *Solitons and Condensed Matter Physics,* edited by A. R. Bishop and T. Schneider (Springer, Berlin, 1978), p. 264.

[8] J. P. Jamet, J. Phys. (Paris) Lett. 42, L123 (1981).

[9] I. S. Zheludev and O. G. Vlokh, Kristallografiya 3, 639 (1958) [Sov. Phys.—Crystallogr. 3, 647 (1958)].

[10] Y. Ishibashi and H. Shiba, J. Phys. Soc. Jpn. 45, 409 (1978); D. Durand, F. Denoyer, D. Lefur, R. Currat, and L. Bernard, J. Phys. (Paris) Lett. 44, L207 (1983).

[11] A. Michelson, Phys. Rev. B. 16, 577 (1977).

[12] M. D. Coutinho-Filho and M. A. de Moura, J. Magn. Mater. 15-18, 433 (1980).

[13] I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. 47, 992 (1964) [Sov. Phys.—JETP 20, 665 (1965)]; 46, 1420 (1964);[19, 960 (1964)]; *Nobel Symposium Collective Properties of Physical Systems* (Academic, New York, 1974), p. 143.

[14] W. L. McMillan, Phys. Rev. B 12, 2042 (1975); 14, 1496 (1976).

[15]P. Lederer, J. T. N. Medeiros, and G. Theodorou, Solid State Commun. 32, 1247 (1979). One should not use Eq. (11) without a word of warning. Strictly speaking it is valid only if the phase of the modulation near commensurability obeys a sine-Gordon equation, which is not the case with the functional in Eq. (3). The differential equation for the phase involves fourth-order derivatives of the phase (see, e.g., Ref. 10). However, we argue that near commensurability 8, a sine-Gordon equation for the phase is valid, as suggested by Eq. (8). We are currently checking if the complete solution confirms this point of view.

[16]A. Aharony and P. Bak, Phys. Rev. B 23, 4770 (1981).

[17]In Ref. 2, the estimate for l_8 did not take into account E_{eff} at zero external field.

[18]J. P. Jamet and P. Lederer, J. Phys. (Paris) Lett. 44, L257 (1983).

[19]There is little doubt in our mind that the same approach explains the phase diagram under pressure, provided the umklapp terms of order 7 and 3 are taken into account. See. Ref. 1.

[20]V. L. Pokrovsky and A. L. Talapov, Phys. Rev. Lett. 42, 65 (1979).

[21]H. J. Schulz, Phys. Rev. B 22, 5274 (1980).

[22]M. E. Fisher and D. S. Fisher, Phys. Rev. B 25, 3192 (1982); S. T. Chui and J. D. Weeks, *ibid.* 14, 4978 (1976).

[23]P. Lederer and G. Montambaux (unpublished).

[24]D. Durand, Thèse de Troisième Cycle, Université de Paris—Sud, Orsay (unpublished).

[25]C. S. O. Yokoi, M. D. Coutinho Filho, and S. R. Salinas, Phys. Rev. B 24, 4047 (1981).

[26]K. Michel and K. Parlinski (unpublished).