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Neutron diffractometry investigation of the tricritical point of KH_2PO_4

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Résumé. — Le cisaillement spontané et la variation du paramètre de maille C du KH_2PO_4 (K.D.P.) ont été mesurés en fonction de la température et de la pression hydrostatique en utilisant un diffractomètre à neutrons à haute résolution. Les mesures ont été effectuées dans un intervalle de température de $\pm$ 5 K au voisinage de la transition et pour des pressions allant jusqu'à 4 kbars. Tous les résultats sont interprétés de façon cohérente à l'aide d'un développement de Landau de l'énergie libre où les coefficients des termes du second ordre et du quatrième ordre présentent une dépendance linéaire en fonction de la température et de la pression. Ces deux coefficients s'annulent simultanément au point tricritique (P^* = 2,8 $\pm$ 0,3 kbar et T^* = 109 $\pm$ 1 K). Ce comportement de champ-moyen est en accord avec les théories récentes des phénomènes critiques. Des ajustements avec des lois de puissance sont aussi discutés.

Abstract. — The spontaneous shear strain and the variation of the lattice-constant C in KH_2PO_4 (K.D.P.) have been studied as functions of the temperature and hydrostatic pressure using a high-resolution neutron diffractometer. The measurements were performed in a range of $\pm$ 5 K around the transition temperature and for pressure up to 4 kbar. All the data are consistently fitted, using a Landau-type free energy expansion with the quadratic and quartic term coefficients varying linearly with the temperature and pressure. Both these coefficients vanish simultaneously at the tricritical point (P^* = 2.8 $\pm$ 0.3 kbar, T^* = 109 $\pm$ 1 K).
This mean-field behaviour is in agreement with recent theories of critical phenomena. Fits with power-laws are also discussed.

1. **Introduction.** — Griffiths [1] has generated a renewal of interest in the field of critical phenomena, pointing out the special behaviour of systems near a multicritical point, i.e. a point in the thermodynamic parameter space where critical lines meet. For example a tricritical point may be encountered when a system shows a transition which changes its character from first order to second order under the action of a *non-ordering* field P [2].

Labelling E the *ordering* field, conjugate to the order parameter η, the phase diagram in the (P, E, T) space near the tricritical point (T.C.P.) for a system where $+\eta$ and $-\eta$ are equivalent by symmetry, is schematically represented in figure 1 : three lines of critical points meet at the T.C.P. and two *wings*, where the ordered and disordered phases coexist, terminate on the first order transition line.

Tricritical points have been experimentally investigated in several types of system : He_3-He_4 mixtures [3], metamagnets ($FeCl_2$ [4], DyAlG [5], $DyPO_4$ [6]) ammonium halides (NH_4Cl, NH_4Br [7]) and ferroelectrics (T.G.Se [8], SbSI [9], KH_2PO_4 [10, 11]...). In this last class of materials the fields P and E correspond respectively to the hydrostatic pressure and to the electric field. As already pointed out by various authors [10], these ferroelectric materials have the rather unique advantage that the three fields of

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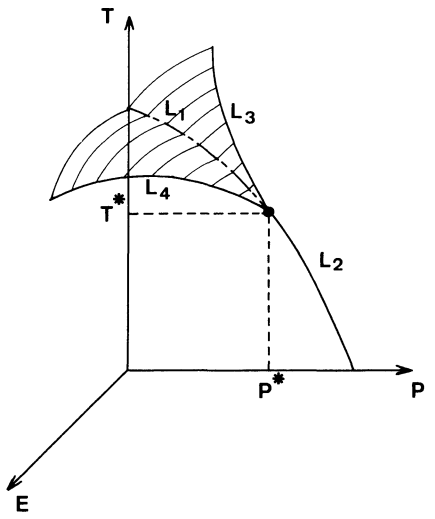

Fig. 1. — Phase diagram near a tricritical point : E is the *ordering field*, P and T are non-ordering fields. L_1 is a line of first order transitions; L_2, L_3 and L_4 are lines of second order transitions which meet at the tricritical point (T^*, P^*, $E = 0$). The *wings* correspond to regions of coexistence of phases.

interest in studying the tricritical behaviour, are all experimentally available, allowing a complete investigation of the *wings*.

From a theoretical point of view, the critical behaviour near a multicritical point is expected to be described by critical exponents generally different from those of the usual critical behaviour [1, 2]. For example, in the case of the 3-dimensional Ising model the exponents are *non-classical* for a critical point and become *classical* (with logarithmic corrections) for a T.C.P. [12] and one expects to observe a *cross-over* between the two types of behaviour.

In the case of uniaxial ferroelectrics, however, the long-range dipolar forces are usually strong and it has been shown that the critical behaviour itself is *classical* (with some logarithmic corrections [13]), so the tricritical behaviour must be *classical* also. Furthermore in ferroelectric-ferroelastic crystals of the K.D.P. type (i.e. in systems where the electric polarization and the elastic deformation are coupled through the piezoelectric effect in the disordered phase) renormalization group theory predicts the *marginal dimensionality* above which the system is fully *classical* to be equal to 2.5 [14], so that one may expect that mean-field theory gives a good description of these systems in the critical and tricritical regions (without logarithmic corrections).

The phase transition in K.D.P. at ambient pressure has been extensively studied for many years [15]. For a long time the transition was considered to be second order, but the more recent results all agree that it is first order but very close to continuous [16, 17, 18] (small latent heat and small thermal hysteresis). Many experiments concerning the static and dynamic properties of the K.D.P.-type crystals were stimulated by the development of a microscopic description of the transition based on a collective tunnelling motion of the protons along hydrogen-bonds [19]. Samara and Peercy [20] have shown that high hydrostatic pressure may be a very important parameter to elucidate the mechanism of the transition, but they did not focus their interest on the problem of the order of the transition. Evidence for the tricritical point in K.D.P. was first demonstrated by V. H. Schmidt *et al.* [10] following a conjecture of its existence in the (P, T) plane by V. H. Schmidt. Using electric polarization measurements these authors estimated the tricritical pressure to be 2.3 $\pm$ 0.3 kbars. The change of the order of the transition between 2 and 3 kbars was confirmed by our preliminary measurements of the variation of the shear angle and dilatation along the C axis under high pressure [11].

In the present paper more extensive and more accurate data concerning the pressure and temperature dependence of these two parameters are presented. In section 2 we describe the general experimental set-up common to both types of measurements. In sections 3 and 4, the principles and the results of the U_{xy} shear angle and the U_{zz} dilatation measurements are given respectively. In section 5, we propose a phenomenological interpretation of our data using a Landau theory adapted to describe the tricritical behaviour. In section 6, our results are compared to other recent experimental and theoretical studies, particularly in the light of the modern theory of critical phenomena.

2. **General experimental set-up.** — The measurements were carried-out at the I.L.L. high flux reactor at Grenoble on the S21 double crystal instrument, installed on one of the thermal neutron guide tubes. The apparatus, described elsewhere [17, 21], is a precision double crystal arrangement with variable scattering angles from 25° to 85°. Angular scans can be run with an angular resolution of 0.5 second of arc. Typical peak intensities were 10^2 counts/second. Accurate temperature control of both the KD_2PO_4 monochromator crystal (d-spacing matched to sample d-spacing) and sample crystals was guaranteed by careful cryogenic design [22] and precision temperature readings, using a 7 digit automatic A.C. bridge (sensitivity $\simeq$ 0.5 mK). The sample cryostat, essentially identical to the monochromator cryostat, was adapted to take the pressure cell. This pressure cell [23] was made of aluminium alloy and could stand pressures up to 5 kbars. Helium gas was used as pressure medium which ensured truly hydrostatic conditions in the experimental temperature range. Pressure was measured with a manganin resistance gauge which had been calibrated against a Bourdon gauge. Pressure stability was carefully maintained especially in the vicinity of the phase transition where it was checked using a special pressure transducer (sensitivity of 0.1 bar).

Data collection (together with the readout of sample and monochromator temperature and the pressure)

was done by a small computer which also did on-line data reduction to yield the angular position of the Bragg peaks together with the relevant scan parameters.

The two samples used were grown from aqueous solution. These crystals had been stored at room temperature for several years and had never been cooled below the transition point before the present experiments. They were carefully out and polished as parallelepipeds of 5 × 5 × 5 mm^3 in size with the edges respectively along the a_1, a_2 and C tetragonal axes. The (001) faces were metallized by evaporating gold electrodes so that the crystal could be short-circuited during the measurements.

3. **Shear strain measurements.** — In the paraelectric phase K.D.P. belongs to the piezoelectric tetragonal point group $\bar{4}2$ m, so that a linear coupling between the polarization component P_z and the shear strain U_{xy} is allowed. Therefore when the crystal becomes ferroelectric, a spontaneous shear deformation appears at the same time as the spontaneous electric polarization. At ambient pressure, there is some experimental evidence [18] that the temperature dependences of these two quantities are similar at least in a range of several degrees below T_c. In the absence of an applied d.c. electric field the crystal exhibits a domain structure which corresponds to the two possible orientations of the spontaneous polarization (or of the shear). The domain walls are essentially planar and normal to the **x** and **y** tetragonal axes.

Therefore if one considers a (h, 0, 0) Bragg reflection peak of the paraelectric phase, it splits generally into three peaks when the sample passes to the ferroelectric multidomain state : for domain walls normal to the **y** axis the alternate shear leads to the appearance of two Bragg side-peaks separated by an angle 2 U_{xy} [18] ; for domain walls normal to the **x** axis, the (h, 0, 0) planes are practically unchanged during the transition and they give rise to a single (unsplit) peak.

In fact, the precise orientation of the domain walls may not be exactly those of the axes of the tetragonal phase and may depend on the boundary conditions [24].

However, the measurement of the spontaneous shear relies only upon the relative position of the two side-peaks and not on their positions with respect to the tetragonal frame.

In most of our experiments, only one type of domain wall (normal to **y**) was present in the sample so that the middle peak was absent from the spectrum. This improves the accuracy of the measurements for the following reasons : i) All the diffracted intensity goes into the side-peaks, increasing the signal to noise ratio ; ii) internal stresses due to the contact between **x** and **y** type domain walls are absent ; iii) The side-peaks do not overlap with the central peak when the shear becomes small. As in our previous γ-ray and neutron diffractometry experiments [11], the splitting of the Bragg peaks was measured by rotating the sample around its **z** axis, the incoming neutron beam remaining fixed (ω-scan). Most of the scans were carried out using 25 s of arc step width and they took a time of about 10 min. Typical scans of the (4, 0, 0) Bragg reflection are shown in figure 2. The determination of the shear was made by subtracting the background and taking the angular separation between the first moments of the two side-peaks.

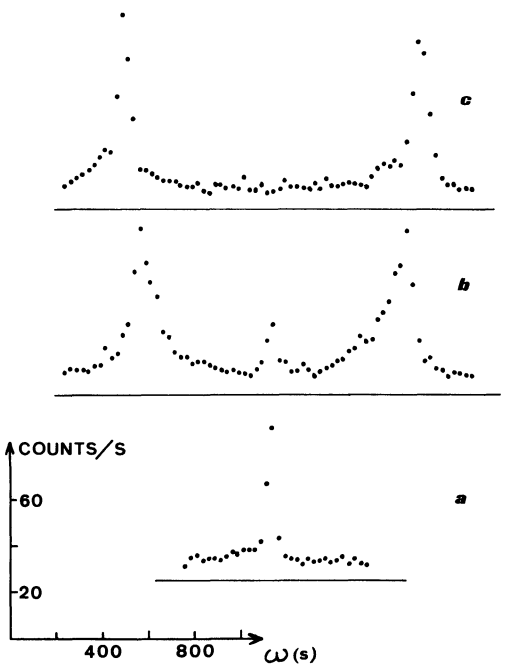

Fig. 2. — Typical rocking curves for shear measurements at 1 bar. *a*) $T > T_c$ (the low integrated intensity is due to extinction phenomena). *b*) $T \simeq T_c$: coexistence of the ferroelectric phase (side-peaks) and of the paraelectric phase (middle-peak). *c*) $T < T_c$.

The width of the peaks is the result of different factors : i) resolution broadening due to imperfect matching of the monochromator and sample lattice parameters (especially at high pressure) ; ii) mosaic spread ; iii) inhomogeneity of the shear due to internal stresses and temperature gradients [25]. These last contributions become most important near the transition point where they produced a systematic broadening of the peaks (F.W.H.M. $\simeq$ 2 min.).

In addition a spectrum with three peaks was observed very close to T_c. For the lowest pressures (< 1.5 kbar) the three peaks were well separated and correspond clearly to the coexistence of two well defined phases near a first order phase transition [21]. For higher pressures a weak middle peak systematically appeared over the temperature range

$$T_c - T \lesssim 0.02 \text{ K} .$$

The fact that this feature was practically independent of the pressure suggests that it may rather be due to inhomogeneous shifts of the transition temperature by local stresses (a hydrostatic pressure of 2 bars pro-

duces a change in T_c of $\sim$ 0.01 K) and to a small temperature gradient across the sample. A similar observation has also been made near the second order phase transition of RbDP [18]. One might also guess that the three peak spectrum is due to the appearance of orthogonal domains (random strains, that produce the static central peak in light scattering, may cause such a rearrangement of the domain structure). However this seems unlikely during heating since the domain texture is already established; optical observations at atmospheric pressure give no evidence of any modification of this type.

Some of our constant pressure measurements of the temperature dependence of the spontaneous shear angle are shown on figures 3 and 4, for temperature

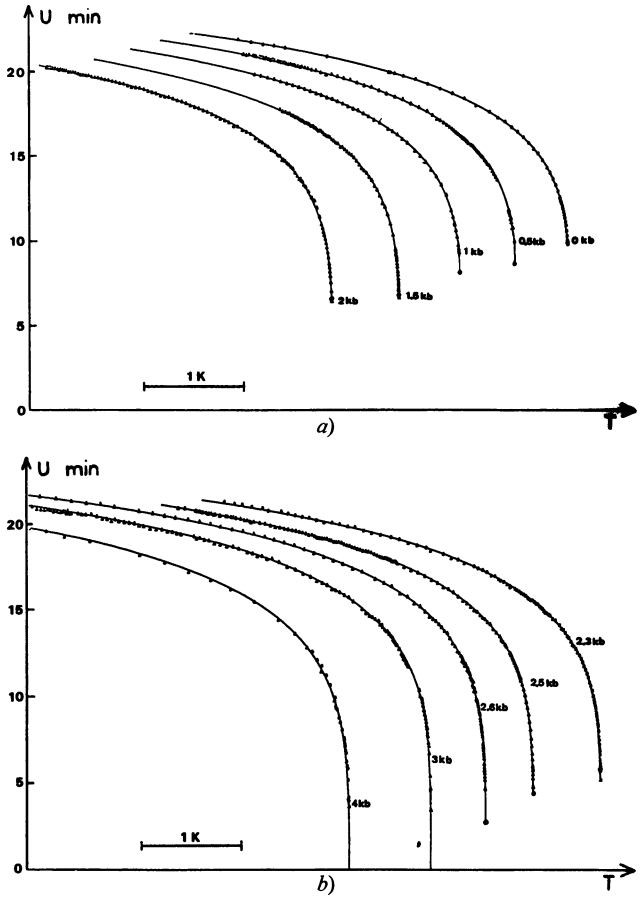

Fig. 3. — Temperature dependence of the spontaneous shear U_{xy} for various hydrostatic pressures P. *a*) P = 0 to 2 kbars; *b*) P = 2.3 to 4 kbars. (The origin on the temperature scale is different for each curve.) The full line corresponds to the Landau theory (Eq. (7)) using the parameters of column (2) in table I.

ranges of 5 K and 1 K respectively and for pressures up to 4 kbars. These curves were obtained by heating the sample at a rate decreasing from 5 mK/minute far from the transition, to 0.1 mK/minute close to T_c. A range of about 0.2 K around the transition was also investigated upon cooling and a small thermal hysteresis was observed for pressures lower than 1 kbar. The time required to record a complete temperature run was about 20 hours.

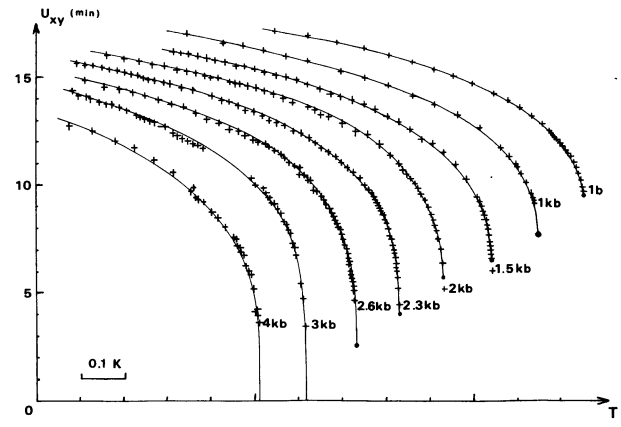

Fig. 4. — Temperature dependence of the spontaneous shear $U_{xy}(T)$ for various pressures over a small range of temperature around the transition. (The curves have been arbitrarily displaced along the temperature axis.) The full line corresponds to equation (7).

The small drifts of pressure ($\Delta P < 1$ bar) which strongly affect the measurements close to T_c were corrected for by shifting the corresponding measured temperature by an amount $\Delta T = \frac{\partial T_c}{\partial P} \Delta P$. This procedure is justified by the fact that for such small pressure fluctuations the curve $U_{xy}(T)$ is simply translated along the T axis to within a very good approximation.

The resulting curves appear to vary very smoothly with T, the random fluctuations of the (corrected) temperature being less than $\pm$ 2 mK.

A constant temperature (T = 110.86 K) $U_{xy}(P)$ curve was also recorded by slowly decreasing the pressure (see Fig. 5). The small temperature variations ($\leqslant$ 0.01 K) were also corrected by readjusting the pressure readings.

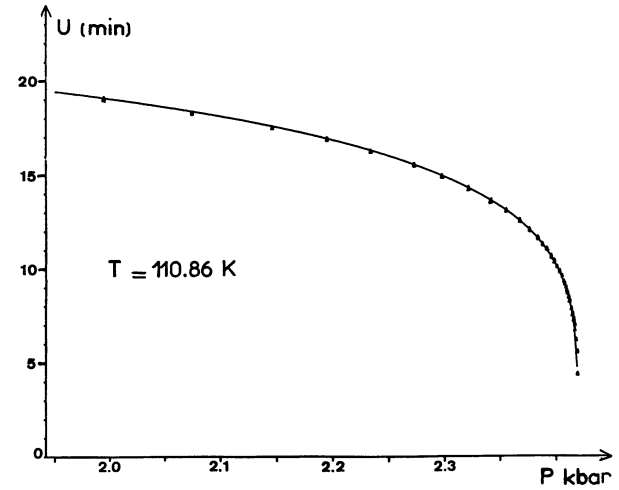

Fig. 5. — Pressure dependence of the spontaneous shear $U_{xy}(P)$ for T = 110.86 K. The full line corresponds to equation (7) with the parameters of column (3) of table I (last row).

4. **Temperature and pressure variations of the lattice parameter C.** — The thermal expansion of the K.D.P. crystal along its C axis (denoted as U_{zz}) is affected by

the ferroelectric transition through the electrostriction effect, so that it may be separated into a *normal* part uncoupled to the polarization P_z — the normal thermal expansion which increases with temperature— and an *anomalous* part which appears in the ferroelectric phase and which decreases with temperature. By symmetry, this latter part can be coupled only to even powers of P_z, and consequently is not affected by the domain structure (except possibly inside domain walls). The experimental determination of the variation of U_{zz} was performed by studying the shifts $\Delta\theta_B$ of the angular position θ_B of an (004) Bragg peak. This $\Delta\theta_B$ was itself obtained through an ω-scan. As is clear from the Bragg formula :

$$U_{zz} = \frac{\Delta C}{C} = -(\text{cotan}\,\theta_B)\,\Delta\theta_B\,,$$

the sensitivity in the U_{zz} measurement increases when θ_B approaches 90°. However, since it was not possible to keep the sample and monochromator C-lattice parameters exactly equal, the *instrumental* width of the Bragg peak increases rapidly when θ_B approaches 90°. Therefore a value $\theta_B \simeq 80°$ was adopted. The calibration of the $U_{zz}(T, P)$ curves was achieved by measuring the change $\Delta\theta_B/\Delta T$ near $T = 130$ K at ambient pressure and using the known value of the thermal expansion in this case [11]. $U_{zz}(T, P)$ is arbitrarily taken to be zero for this temperature and pressure in the following and all its variations are referred to this origin.

In contrast with the shear angle, the thermal expansion requires the measurement of an angular shift relative to a fixed external frame. Therefore particular care was taken, when building the pressure cell holder which is located inside the cryostat, to avoid any rotation of this cell relative to the moving arm which drives the rotation of the cryostat, especially during cooling. Typical rocking curves are shown in figure 6. The width of the peaks increases with pressure, due to the increasing mismatch between the sample and monochromator C-lattice parameter. Figure 6*b* shows a double peak spectrum recorded close to the transition for a pressure of 0.5 kbar. Such a spectrum (only observed for pressures $\lesssim 1$ kbar) was interpreted as evidence of coexistence between the paraelectric and ferroelectric phases [21] : for low pressures the jump of the C-lattice parameter was sufficiently large to allow the observations of a well resolved double peak. For high pressures only a broadening of the peak near T_c could be observed (Fig. 6*c*, *d*).

Figure 7 shows some of our results for the temperature dependence of $U_{zz}(T)$ at constant pressure ranging between 1 bar and 3.95 kbar. Figure 8 is an enlarged view showing thermal hysteresis effects for

$$P < 1 \text{ kbar}\,.$$

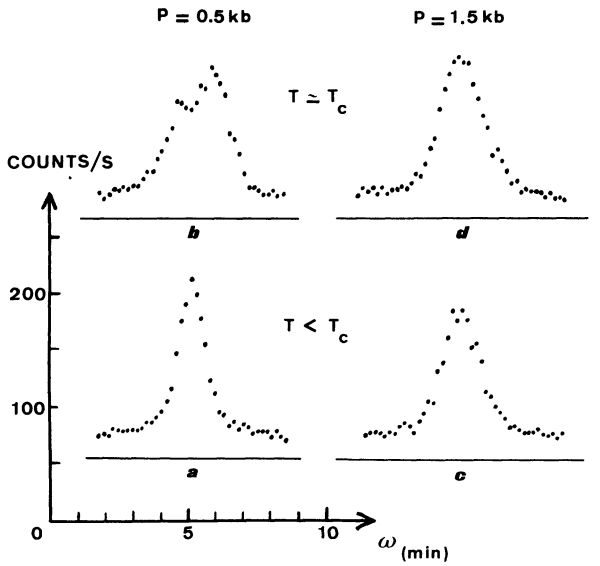

Fig. 6. — Rocking curves for C-lattice parameter variation measurements. *a*) $P = 0.5$ kbar, $T < T_c$; *b*) $P = 0.5$ kbar, $T \simeq T_c$ (coexistence of phases) ; *c*) $P = 1.5$ kbar, $T < T_c$; *d*) $P = 1.5$ kbar, $T \simeq T_c$.

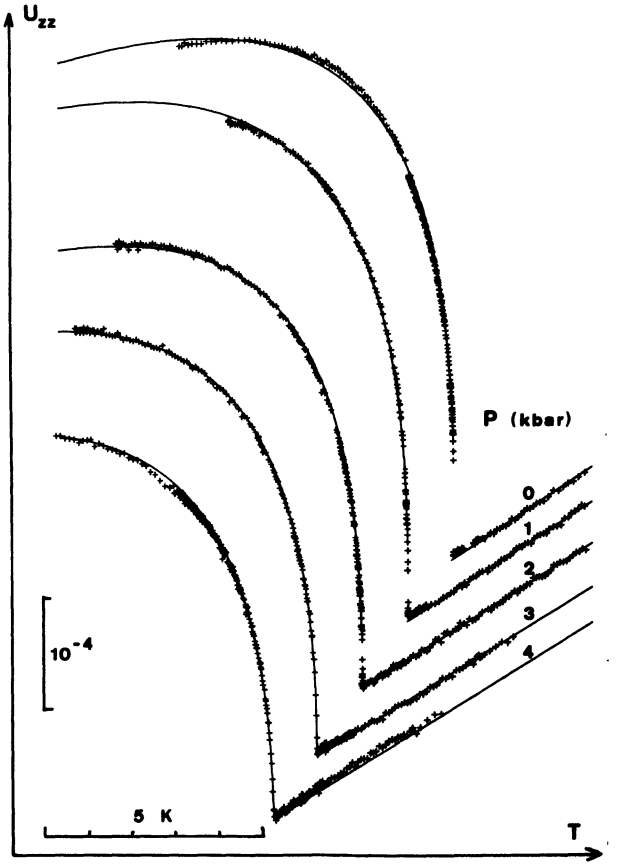

Fig. 7. — Temperature dependence of the C-lattice parameter $U_{zz}(T)$ for various pressures P. The curves have been arbitrarily translated along the U_{zz} and T axes. The full line corresponds to the Landau theory (Eq. (14)) with the parameters of column (2) in table III.

These curves were obtained using continuous heating at the same rates as in the shear angle measurements. The sample was heated from $(T_c - 5$ K) to $(T_c + 0.1$ K), then cooled to $(T_c - 0.1$ K) to test the

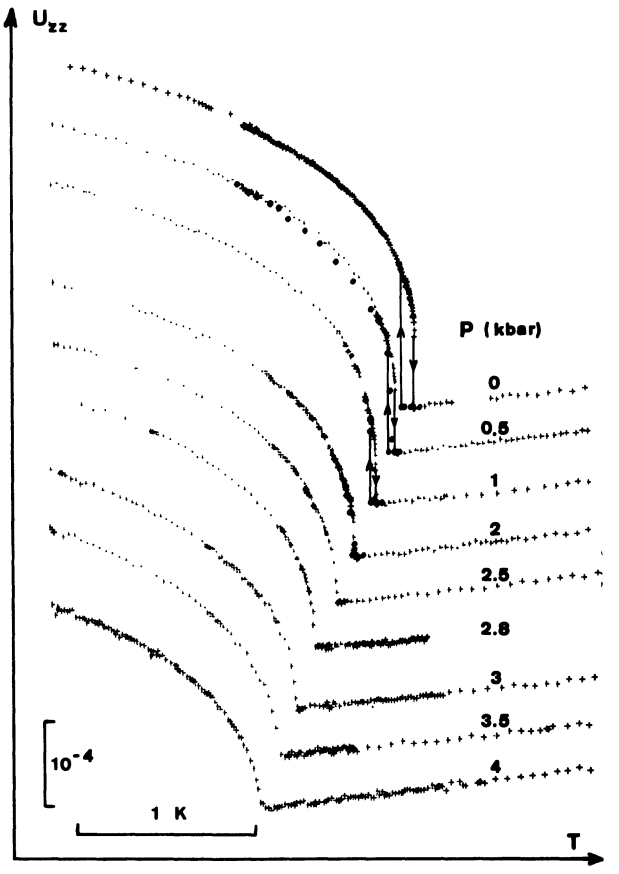

Fig. 8. — Temperature dependence of $U_{zz}(T)$ for various pressures in a restricted range of temperature around the transition. The crosses (+) correspond to heating. Some of the points obtained on cooling are also represented (full points ●) in order to show the thermal hysteresis. The curves have been arbitrarily translated along the T and U_{zz} axes.

hysteresis and heated again up to (T_c + 5 K). The time required for such a run was approximately 30 to 40 hours. Small pressure variations have more important effects on U_{zz} than on U_{xy} measurements since the *normal* part of U_{zz} is directly coupled to the pressure through the compressibility coefficient. In addition the *anomalous* part is affected in essentially the same way as U_{xy} through changes in T_c.

The global effect of a small pressure change is a translation of the $U_{zz}(T)$ curve along both the U_{zz} and T axes. Short time variations of the pressure (of a few tenths of a bar) were found to have an effect negligible compared to the uncertainty in the determination of U_{zz} due to the peak width and neutron counting statistics ($\simeq \pm 0.5 \times 10^{-5}$). However long term drifts of the calibration of the pressure measuring apparatus ($\lesssim \pm 2$ bars over a temperature run) cannot be excluded, which may affect the $U_{zz}(T)$ curves to a much larger extent than the $U_{xy}(T)$ ones.

Just as for the U_{xy} measurements, the U_{zz} values were determined from the rocking curves by subtracting the background intensity and by calculating the angular position of the first moment of the peak.

The shape of the preceding shear and thermal expansion curves show that the transition is clearly first order at low pressures and changes continuously to second order at high pressure, but the accuracy of our measurements does not allow a direct determination of the exact location of the tricritical point. An analysis of the shape of the curves with a theoretical model appears necessary to give a more accurate answer to this question.

5. **Phenomenological interpretation of experimental data.** — 5.1 LANDAU THEORY NEAR A TRICRITICAL POINT. — The phenomenological theory of phase transitions (Landau-Devonshire theory) has successfully described the static properties of a large number of structural phase transitions, particularly in ferroelectric and ferroelastic crystals [15]. According to this theory the Gibbs thermodynamic potential φ can be expanded in even powers of the order parameter η and, for a uniaxial ferroelectric like K.D.P., one can write :

$$\varphi = \varphi_0 + \tfrac{1}{2} a\eta^2 + \tfrac{1}{4} b\eta^4 + \tfrac{1}{6} c\eta^6 + \cdots . \quad (1)$$

A priori, the coefficients a, b, c, ... depend on the external intensive parameters, such as the temperature and pressure [27], which are not linearly coupled to the order parameter. In order to describe the phase transition it is sometimes sufficient to take into account the temperature and pressure dependence of a in the form $a = a_T(T - T_0(P))$, neglecting the variations of b and c. If b is positive, there is a line of second order phase transitions $T = T_0(P)$ in the (P, T) plane; if b is negative there is a line of first order transitions. It is clear that this approximation cannot be valid when a change of the order of the transition occurs in the phase diagram, since b must vanish at this point and its relative variations become very large. The simplest way to extend the Landau theory is to take into account the pressure and temperature dependence of a and b and to neglect that of c. There is *a priori* no reason to impose a different role to T and P (assuming for example that b depends only on P). Since $a(P, T)$ and $b(P, T)$ must vanish at a point (P^*, T^*) (the tricritical point), and if one assumes that they are regular functions in the vicinity of this point, then they may be expanded in the form [28] :

$$\left.\begin{aligned} a(P, T) &= a_T(T - T^*) + a_P(P - P^*) + \cdots \\ b(P, T) &= b_T(T - T^*) + b_P(P - P^*) + \cdots \end{aligned}\right\} . \quad (2)$$

Within the linear approximation, these relations mean that the equations $a(P, T) = 0$ and $b(P, T) = 0$ are two straight lines, generally not parallel to the P and T axes, which cross at the tricritical point. The equations of these lines can be written :

$$\left.\begin{aligned} T_0(P) &= T^* - \frac{a_P}{a_T}(P - P^*) \\ T_1(P) &= T^* - \frac{b_P}{b_T}(P - P^*) \end{aligned}\right\} \quad (3)$$

$T_0(P)$ corresponds to the usual Curie temperature. Using (3) the Gibbs energy expansion (1) becomes :

$$\varphi = \varphi_0 + \frac{1}{2}\, a_T(T - T_0(P))\, \eta^2 + \\ + \frac{1}{4} b_T(T - T_1(P))\, \eta^4 + \frac{c}{6}\, \eta^6 + \cdots \quad (4)$$

(a similar expansion may obviously be obtained by reversing the roles of T and P).

The formula (4) is identical to the usual Landau expansion except for the temperature dependence of the quartic term coefficient. It was found convenient to define the following new quantities :

$$\eta_0 = \left(\frac{a_T}{|\, b_T\,|}\right)^{1/2}, \qquad T_2 = \frac{c a_T}{b_T^2}, \quad s = \text{sign of } b_T\,. \quad (5)$$

The expansion (4) truncated at the sixth order term is then written :

$$\varphi - \varphi_0 = a_T\, \eta_0^2 \left\{ \frac{1}{2}(T - T_0)\left(\frac{\eta}{\eta_0}\right)^2 + \right. \\ \left. + \frac{1}{4} s(T - T_1)\left(\frac{\eta}{\eta_0}\right)^4 + \frac{1}{6} T_2 \left(\frac{\eta}{\eta_0}\right)^6 \right\}. \quad (6)$$

From this Gibbs energy, all the thermodynamic properties can be readily calculated by minimization : for example the spontaneous order parameter η_s is :

$$\eta_s(P, T) = \pm\, \eta_0 \left\{ \left[\left(\frac{T - T_1(P)}{2\, T_2}\right)^2 - \right. \right. \\ \left. \left. - \left(\frac{T - T_0(P)}{T_2}\right) \right]^{1/2} - s\left(\frac{T - T_1(P)}{2\, T_2}\right) \right\}^{1/2}. \quad (7)$$

The entropy S and the volume change V (per unit volume) are given by :

$$S = -\left(\frac{\partial \varphi}{\partial T}\right)_P = S_0(P, T) - \\ - \left(\frac{a_T}{2}\, \eta_s^2(P, T) + \frac{b_T}{4}\, \eta_s^4(P, T)\right) \quad (8)$$

$$V = +\left(\frac{\partial \varphi}{\partial P}\right)_T = V_0(P, T) + \\ + \left(\frac{a_P}{2}\, \eta_s^2(P, T) + \frac{b_P}{4}\, \eta_s^4(P, T)\right).$$

Depending on the relative values of the coefficients a_T, a_P, b_T, b_P, different phase diagrams can be obtained. In the present paper we do not discuss all the possibilities, but we examine only the case of interest for K.D.P. : since $(a_T > 0)$ one sees that the experimental observation $\mathrm{d}T_0/\mathrm{d}P < 0$ indicates that a_P is positive. To get a first order transition at zero pressure one must have $b(P = 0,\ T_0) = b_T(T_0(0) - T_1(0)) < 0$. Thus either $b_T > 0$ and $(T_0(0) - T_1(0)) < 0$ or $b_T < 0$ and $(T_0(0) - T_1(0)) > 0$. In the latter case, which happens to hold for K.D.P. as shown below, one must have $\dfrac{\partial(T_0 - T_1)}{\partial P} = \left(\dfrac{a_P}{a_T} - \dfrac{b_P}{b_T}\right) < 0$, in order to get a tricritical point for a positive pressure.

For low pressures the transition is first order, and one may calculate the pressure dependence of the critical temperature $T_c(P)$ (defined by

$$\varphi(\eta_s, T_c, P) = 0)$$

and the upper and lower bounds of the possible thermal hysteresis region ($T_u(P)$ and $T_L(P)$) predicted by the present theory :

$$\left.\begin{aligned} T_c(P) &= \left(T_1(P) + \frac{8\, T_2}{3}\right) - \left(\frac{64}{9}\, T_2^2 - \frac{16}{3}\, T_2(T_0(P) - T_1(P))\right)^{1/2} \\ &\simeq T_0(P) + \frac{3}{16}\, \frac{[T_0(P) - T_1(P)]^2}{T_2} \quad \text{for} \quad P \to P^* \\ T_u(P) &= (T_1(P) + 2\, T_2) - 2(T_2(T_2 + T_1(P) - T_0(P)))^{1/2} \\ &\simeq T_0(P) + \frac{1}{4}\, \frac{[T_0(P) - T_1(P)]^2}{T_2} \quad \text{for} \quad P \to P^* \\ T_L(P) &= T_0(P)\,. \end{aligned}\right\} \quad (9)$$

The jumps in η_s, S and V at $T_c(P)$ are respectively given by :

$$\left.\begin{aligned} \Delta\eta_s(P) &= \left[-\frac{3\, b_T}{4\, c}(T_c(P) - T_1(P)) \right]^{1/2} \simeq \left[-\frac{3\, b_T}{4\, c}(T_0(P) - T_1(P)) \right]^{1/2} \cdots \\ \Delta S(P) &= -\left(\frac{a_T}{2}\Delta\eta_s^2 + \frac{b_T}{4}\Delta\eta_s^4\right) \simeq \left[\frac{3\, a_T\, b_T}{8\, c}(T_0(P) - T_1(P))\right] + \cdots \\ \Delta V(P) &= \left(\frac{a_P}{2}\Delta\eta_s^2 + \frac{b_P}{4}\Delta\eta_s^4\right) \simeq -\left[\frac{3\, a_P\, b_T}{8\, c}(T_0(P) - T_1(P))\right] + \cdots \end{aligned}\right\} \quad (10)$$

where the last expression on the right is the first term of an expansion near the tricritical point.

5.2 INTERPRETATION OF THE SPONTANEOUS SHEAR DATA BY THE LANDAU THEORY. — The nature of the order parameter η in K.D.P. type crystals has been a matter of discussion : the ordering of the protons on the H_ bonds is now generally considered to be the leading mechanism of the transition. Therefore the *true* order parameter is the average value of the *pseudo-spin* component $\langle S_z \rangle$ describing this proton order in the de Gennes formalism [19]. This parameter is linearly coupled to the polarization P_z and to the shear strain U_{xy} : this leads to the so-called *improper* ferroelectric ferroelastic transition [29, 30]. In the following, however, we make the assumption that in the range of temperature and pressure studied, the improper character of the transition is not important and that the variations of P_z and U_{xy} are proportional to η.

We tried to interpret our $U_{xy}(T, P)$ data using a formula similar to equation (7) (where η_0 is then renamed U_0). Each constant pressure curve was first fitted using a four parameter least squares procedure. It was found that s, the sign of b_T, must be the minus sign; the whole set of experimental data could be fitted very well with four parameters. All deviations were smaller than the experimental errors. The parameters (U_0, T_0, T_1, T_2) and the mean square deviation σ are listed in table I. One may note that both U_0 and T_2 exhibit rather small variations with pressure in agreement with the above assumptions (eqs. (2) and (5)). Furthermore their variations are obviously correlated : therefore we tried to fix the coefficients T_2 and U_0 at their average value

$$T_2 = 7.116\ \text{K}, \quad U_0 = 29.24'$$

and to fit the constant pressure curves again with only 2 adjustable parameters T_0 and T_1. The quality of the fit is only weakly affected by this procedure, except for the two lowest and the two highest pressures; the resulting $T_0(P)$ and $T_1(P)$ curves are very close to straight lines in agreement again with our linear approximation of section 5.1, eq. (3) (see table I and Fig. 9). These lines indeed cross, defining the tricritical point coordinates. When U_0 is allowed to vary with T_2 still fixed at the same value as above, a very good fit is again recovered over the whole range of pressure (see Figs. 3 and 4) and U_0 shows a weak linear variation $\left(\frac{1}{U_0}\frac{dU_0}{dP} \simeq 1\ \%/\text{kbar}\right)$. Neglecting this small temperature dependence of U_0, we can conclude that the whole set of constant pressure curves $U_{xy}(T, P)$ are consistently fitted using our Landau expansion (Eq. (6)) with only 6 independent parameters :

$$\left.\begin{array}{ll} T^* = 108.98 \pm 0.14\ \text{K} & U_0 = 29.2 \pm 0.2' \\ P^* = 2.830 \pm 0.030\ \text{kbar} & T_2 = 7.12 \pm 0.03\ \text{K} \\ & dT_0/dP = -4.57 \pm 0.02\ \text{K/kbar} \\ & dT_1/dP = -4.15 \pm 0.02\ \text{K/kbar}. \end{array}\right\} \quad (11)$$

Table I. — *Parameters obtained from fitting* 13 *constant pressure* $U_{xy}(T)$ *curves and one constant-temperature* $U_{xy}(P)$ *curve, using the Landau theory* (Eq. (7)). *The pressures* (P, P_0, P_1, P_2) *are in kilobars; the temperatures* (T, T_0, T_1, T_2) *are in Kelvin and the shear angles* (U_0, U_0', σ) *are in minutes of arc. Column* 1 *corresponds to a* 4*-parameter-fit. In columns* 2 *and* 3, T_2 *has been fixed at* 7.116 K; *in column* 3, U_0 *has been fixed at* 29.24 *minutes* (*or* P_2 *at* 1.888 kbars *and* $U_0' = 30.68$ *minutes for the constant temperature curve*).
σ is the root mean square deviation between the calculated and experimental shear angles.

	1					2				3		
P	T_0	T_1	T_2	U_0	σ	T_0	T_1	U_0	σ	T_0	T_1	σ
0	121.768	120.658	7.718	30.10	0.024	121.772	120.749	29.72	0.026	121.754	120.577	0.108
0.5	119.558	118.791	7.084	29.74	0.036	119.558	118.786	29.76	0.036	119.529	118.527	0.104
1.02	117.217	116.480	7.558	29.78	0.028	117.221	116.551	29.54	0.043	117.208	116.418	0.063
1.5	115.043	114.510	7.962	30.11	0.043	115.044	114.562	29.47	0.043	115.041	114.507	0.066
1.79	113.746	113.276	7.703	29.70	0.054	113.744	113.280	29.22	0.069	113.745	113.285	0.069
2.0	112.755	112.452	6.269	28.72	0.053	112.752	112.367	29.28	0.051	112.751	112.352	0.053
2.09	112.356	112.126	6.411	28.82	0.06	112.356	112.093	29.36	0.064	112.356	112.080	0.078
2.2	111.822	111.524	7.639	29.62	0.073	111.823	111.553	29.28	0.074	111.823	111.545	0.075
2.31	111.325	111.094	7.466	29.54	0.048	111.325	111.109	29.29	0.049	111.325	111.100	0.052
2.52	110.380	110.196	6.995	29.09	0.046	110.380	110.188	29.18	0.046	110.380	110.207	0.049
2.63	109.900	109.873	6.327	28.69	0.070	109.900	109.822	29.17	0.081	109.900	109.838	0.084
3.03	108.054	108.050	6.913	28.87	0.076	108.054	108.041	29.01	0.076	108.055	108.109	0.114
4.04	103.309	103.717	6.46	28.35	0.148	103.308	103.688	28.71	0.151	103.312	103.863	0.246
T	P_0	P_1	P_2	U_0'	σ					P_0	P_1	σ
110.86	2.420	2.361	1.957	30.76	0.036					2.420	2.367	0.048

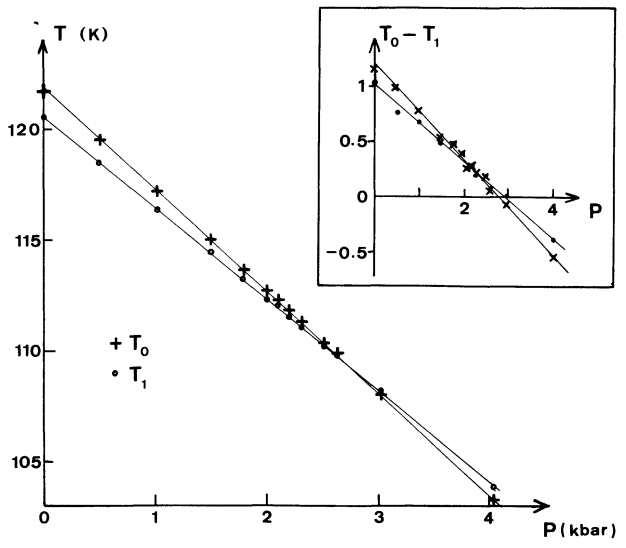

Fig. 9. — Pressure dependence of $T_0(P)$ and $T_1(P)$ defined respectively as the temperatures where the quadratic and the quartic term of the Landau energy expansion vanishes. These curves cross at the tricritical point. The difference $T_0 - T_1$ is also plotted using an enlarged temperature scale (inset). Full points (●) and crosses (×) correspond respectively to the values given in columns (2) and (3) of table I.

The uncertainties quoted above correspond to the range of values allowed to fit our data within the framework of the present theory. It is remarkable that the transition is always close to tricritical [44] in the range of pressure studied $\left(\text{because } \frac{dT_0}{dP} \simeq \frac{dT_1}{dP}\right)$ and a different interpretation of our data may lead to values of the tricritical point coordinates well outside the range of uncertainties given in (11); we estimate that our data may be consistent with the values $T^* = 109 \pm 1$ K and $P^* = 2.8 \pm 0.3$ kbars. The values previously reported for P^* are lower [10, 11], but the difference arises mainly from the method used to determine the T.C.P.

The constant temperature curve $U_{xy}(P)$ can also be fitted to a formula similar to equation (7) (with U_0' instead of η_0 and P_0, P_1, P_2 instead of T_0, T_1, T_2 respectively). It is easily seen that, within the approximations of section 5.1, one has :

$$U_0' = U_0\left(-\frac{\partial T_0}{\partial P}\right)^{1/2}\left(-\frac{\partial T_1}{\partial P}\right)^{1/2} = 30.68 \text{ min.}$$
$$P_2 = T_2\left(-\frac{\partial T_0}{\partial P}\right)\left(-\frac{\partial T_1}{\partial P}\right)^{-2} = 1.888 \text{ kbars.} \quad (12)$$

The fit obtained by imposing these values and allowing P_0 and P_1 as free parameters is again very good (see Fig. 5). The P_0 and P_1 values fall close to the $T_0(P)$ and $T_1(P)$ lines in the phase diagram (see Fig. 9).

It is noteworthy that the Gibbs energy (4) contains in fact 7 parameters (a_T, a_P, b_T, b_P, c, T^*, and P^*) so that one of them cannot be determined by order parameter measurements alone. One way to get approximate values for all these 7 parameters, is to use the known values of the ratio [11, 18]

$$b_{36} \simeq \frac{U_{xy}}{P_z} = 4.8 \times 10^{-7} \text{ esu}$$

and the Curie constant $C = 3\,250$ K [10]. The coefficient a_T of the expansion (4) in powers of U_{xy} is then readily shown to be given by :

$$a_T = \frac{4\pi}{C}\frac{1}{b_{36}^2} \simeq 1.67 \times 10^{10} \text{ esu.} \quad (13)$$

The other coefficients of this expansion can then be deduced from the set of values (11); they are listed in table II, as well as the corresponding coefficients of the Gibbs energy expansion in powers of the spontaneous polarization P_z. It is quite remarkable that if a negative value is chosen for b_T ($s = -1$), equation (7) predicts a rapid saturation of (η_s) at the value η_0 with decreasing T. Such rapid saturation is observed experimentally and is predicted by certain microscopic theories [42, 43]. It is predicted by the usual Landau theory only if terms having high powers of

Table II. — *Coefficients of the Landau expansion* :

$$\varphi - \varphi_0 = \frac{1}{2}[a_T(T - T^*) + a_P(P - P^*)]\,\eta^2 + \frac{1}{4}[b_T(T - T^*) + b_P(P - P^*)]\,\eta^4 + \frac{c}{6}\eta^6$$

deduced from our shear angle measurements.
The first row corresponds to $\eta = U_{xy}$, *the second row to* $\eta = P_z$ *assuming* $U_{xy} = b_{36} P_z$, *with*

$$b_{36} = 4.8 \times 10^{-7} \text{ esu.}$$

The value $a_T = 3.9 \times 10^{-3}$ (P_z *expansion*) *has been taken from dielectric measurements* (Ref. [20]). *All the values are in* esu.

	a_T	a_P	b_T	b_P	c
U_{xy} expansion	1.67×10^{10}	0.76×10^{2}	-2.3×10^{14}	-9.6×10^{5}	2.2×10^{19}
P_z expansion	3.9×10^{-3}	1.78×10^{-11}	-1.25×10^{-11}	-5.2×10^{-20}	2.9×10^{-19}

the order parameter [31] are included, whereas equation (5) results from a free energy troncated at the η^6 term.

In fact one of our $U_{xy}(T)$ curves (for $P = 2.63$ kbar) has been fitted using equation (7) on a large range of temperature ($T_0 - T \simeq 15$ K) without any systematic deviations. On the other hand the value of P_z calculated using the parameters of table II, with $P = 1$ bar and $T = 76$ K, is $P_z = 5.6$ μC/cm^2. This value differs from that found by Samara [32] ($P_z = 4.95$ μC/cm^2). The difference may be due to a small decrease of b_{36} with temperature (or to a non-linear relation between U_{xy} and P_z).

5.3 INTERPRETATION OF THE C-LATTICE PARAMETER MEASUREMENTS. — The dilatation $U_{zz}(T, P)$ may be expanded as a function of the order parameter in the same way as the volume change V (Eq. (8)) (since $V = U_{zz} + 2\,U_{xx}$). With the assumption that U_{xy} is proportional to η, one has :

$$U_{zz}(T, P) = U^0_{zz}(T, P) + (QU^2_{xy}(T, P) + RU^4_{xy}(T, P)) \quad (14)$$

where $U^0_{zz}(T, P)$ describes the *normal* thermal expansion and compressibility along the C axis in the paraelectric phase, and the last two terms correspond to the *anomalous* part related to the order parameter. The last term has not been taken into account in our previous paper [11], but its introduction in the present analysis appears necessary *a priori* to be consistent with the introduction of a pressure dependence in the coefficient b of the Gibbs energy expansion (Eq. (1)). We first analyse the data taken in the paraelectric phase; $U_{zz}(T, P)$ is approximately linear except for a possible rounding near T_0; this last effect, however, is too small compared to the experimental uncertainties to be fitted reliably. Thus each curve $U^0_{zz}(T, P)$ for the various pressures was fitted independently over the range ($T_0 + 1$ K) to ($T_0 + 5$ K) using the linear form :

$$U^0_{zz}(T, P) = U^0_{zz}(T_0, P) + \alpha(P)\,(T - T_0(P)). \quad (15)$$

The value $T_0(P)$ was taken from the phase diagram (Fig. 9). The thermal expansion $\alpha(P)$ is approximately equal to $(2.5 \pm 0.1).10^{-5}$ (K)$^{-1}$ and shows a weak systematic decrease with pressure

$$\left(\frac{1}{\alpha}\frac{d\alpha}{dP} \simeq -\,2.5\,\%\,(\text{kbar})^{-1}\right).$$

$U^0_{zz}(T_0(P))$ is also found to vary linearly with pressure at a rate

$$\frac{dU^0_{zz}(T_0, P)}{dP} = -\,1.13 \times 10^{-3}\,(\text{kbar})^{-1}$$

(see Fig. 10).

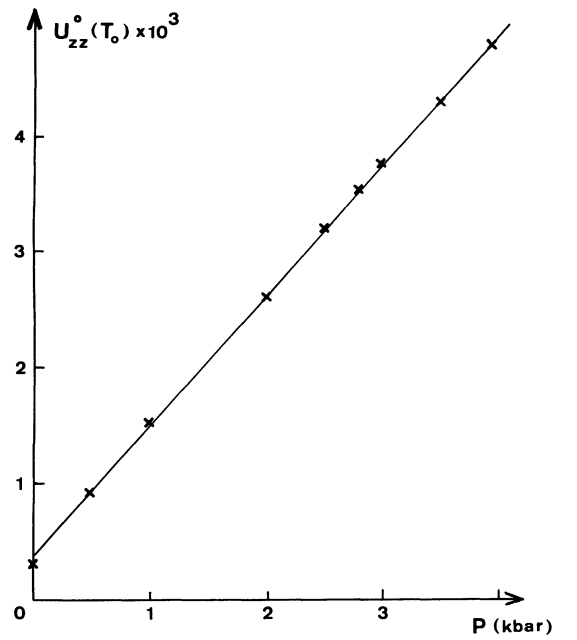

Fig. 10. — Pressure variations of $U^0_{zz}(T_0, P)$, the C-lattice parameter changes measured at the temperature $T_0(P)$.

Writing :

$$\frac{dU^0_{zz}(T_0, P)}{dP} = \left(\frac{\partial U^0_{zz}}{\partial T}\right)_P \left(\frac{dT_0}{dP}\right) + \left(\frac{\partial U^0_{zz}}{\partial P}\right)_T \quad (16)$$

and using the values $(\partial U^0_{zz}/\partial T)_P = \alpha(P)$ and dT_0/dP quoted above, one can deduce the isothermal compressibility coefficient :

$$K_3 = -\left(\frac{\partial U^0_{zz}}{\partial P}\right)_T = 1.02 \times 10^{-3}\,(\text{kbar})^{-1}. \quad (17)$$

This result is in excellent agreement with published data [33]. In order to fit our data taken in the ferroelectric phase we assumed that the *normal* part $U^0_{zz}(T, P)$ can be extrapolated linearly from the paraelectric phase (this procedure is supported by the fact that $U_{zz}(T, P)$ shows approximately the same slope far below T_0 and just above T_0) [26].

The difference $U_{zz}(T, P) - U^0_{zz}(T, P)$ was then fitted using equation (14) and equation (7), for each different pressure. T_2 and $T_1(P)$ were fixed to the values found in section 5.2, while adjustment of $T_0(P)$ was allowed because the fit is quite sensitive to small changes in this parameter. The two other adjustable parameters were (QU^2_0) and (RU^4_0); if they were both free the fit was generally good for each curve $U_{zz}(T)$ — except for the 1 bar curve, where a small deviation occurred for $T_0 - T \geqslant 2$ K. The results are shown in table III and figures 7 and 8. The parameter Q was found to be nearly constant; R fluctuates strongly from one curve to other but its contribution to U_{zz} is always small so that a small relative variation $\Delta Q/Q$ is correlated to a large $\Delta R/R$. To get a better determination of R, we attempted to

Table III. — *Fitting parameters of the $U_{zz}(T)$ curves for various pressures P, using the formula :*

$$U_{zz}(T, P) = U^0_{zz}(T, P) + QU^2_{xy}(T, P) + RU^4_{xy}(T, P) ,$$

$U^0_{zz}(T)$ was approximated by a straight line. $U_{xy}(T, P)$ was calculated using (Eq. (7)) *and parameters deduced from column* (2) *of table I.*
In column (1), *the parameters Q and R were free.*
In column (2), *the value $Q = 13.4$ was imposed.*
σ is the root mean square deviation between calculated and experimental values of $U_{zz}(T, P)$.

	1				2		
P	T_0	Q	$R \times 10^{-4}$	$\sigma \times 10^5$	T_0	$R \times 10^{-4}$	$\sigma \times 10^5$
—	—	—	—	—	—	—	—
0	121.780	12.2	+ 2.4	0.21	121.762	− 1.3	0.47
0.5	119.508	13.1	− 1.7	0.35	119.505	− 1.3	0.38
1	117.272	14.1	− 2.1	0.28	117.277	− 0.2	0.41
2	112.922	12.8	− 0.8	0.34	112.919	− 2.5	0.49
2.5	110.542	13.5	− 3.4	0.20	110.543	− 3.1	0.21
2.8	109.171	13.7	− 2.9	0.18	109.177	− 2.2	0.21
3	108.266	12.9	− 0.7	0.20	108.256	− 2.0	0.25
3.5	105.943	13.9	− 4.0	0.22	105.951	− 1.6	0.29
3.95	103.838	13.6	− 4.3	0.21	103.835	− 2.8	0.34

keep Q constant ($Q = 13.4$) : the fit was again fairly good (see Table III) and the fluctuations in R were partially removed. This coefficient was found to be negative : $R \simeq -2 \times 10^4$. In view of the approximations made concerning the extrapolation of U^0_{zz} in the ferroelectric phase, this value must not be taken too seriously. Using the value of the ratio $U_{xy}/P_z = b_{36}$ given above, one can calculate the electrostrictive coefficient :

$$\left.\begin{aligned} Q_{33} &= Q(b_{36})^2 = (3.10 \pm 0.3).10^{-12} \text{ esu} \\ R_{33} &= R(b_{36})^4 = (-1.0 \pm 0.3).10^{-21} \text{ esu} \end{aligned}\right\} . \quad (18)$$

The former is in good agreement with published data [34]. The *anomalous* change of the volume in the ferroelectric phase as a function of the polarization P_z can be written :

$$V(T, P) - V^0(T, P) = (Q_{33} + 2Q_{13})P_z^2 + (R_{33} + 2R_{13})P_z^4 = \tfrac{1}{2}a_P P_z^2 + \tfrac{1}{4}b_P P_z^4 \quad (19)$$

where a_P and b_P are the coefficients of the Landau expansion (1) in powers of P_z. Using the results of table II and (11) one may deduce the other electrostrictive coefficients :

$$\left.\begin{aligned} Q_{13} &= (2.9 \pm 0.4).10^{-12} \text{ esu} \\ R_{13} &= (-6.0 \pm 0.5).10^{-21} \text{ esu} \end{aligned}\right\} . \quad (20)$$

The value of Q_{13} is in agreement with that found by Kobayashi *et al.* [34], but is lower than that given by Von Arx and Bantle [35] ($Q_{13} = 3.84 \times 10^{-12}$ esu). These last authors found that U_{xx} is not exactly proportional to P_z^2 ; their data can be fitted by adding a term in $R_{13}P_z^4$ but with positive R_{13}. On the other hand Uesu *et al.* [30] found unusual behaviour of U_{xx} under a d.c. field which cannot be explained by the present theory. Accurate measurements of $U_{xx}(T, P)$ are required to clarify this question. One must note that the values of the coefficients R_{33} and R_{13} (Eqs. (18-20)) relie strongly on the assumption of an exact proportionality between U_{xy} and P_z (through a temperature independent b_{36}).

6. **Discussion.** — As shown in the preceding section, a simple phenomenological theory allows a consistent description, with a minimum of assumptions, of the pressure and temperature dependence of the strains U_{xy} and U_{zz} of KH_2PO_4 near its tricritical point. The Landau theory was also recently used by Western *et al.* [10] to interpret their dielectric measurements near this T.C.P. ; they did not take into account any temperature dependence of the coefficient b of the quartic term, but their measurements were made over a small temperature interval of $\simeq 0.5$ K around T_c, so that the relative variation of b may be small, except very close to the tricritical pressure. Their results are in fair agreement with ours although they found a somewhat lower value for the tricritical pressure (2.3 ± 0.3 kbar). As discussed above, this is due to the difficulty in getting a direct experimental determination of this point.

Recent Brillouin scattering experiments in K.D.P. under pressure and in d.c. electric field [36] also confirm that the transition can be described well by the phenomenological theory. In RbDP, where the transition is second order at atmospheric pressure but close to the T.C.P., γ-ray and birefringence measurements [37] are well fitted using an expression similar to equation (7).

Such a *classical* critical behaviour of the K.D.P.-type crystals is in agreement with modern theories of critical phenomena which make use of the scaling laws and renormalization group techniques. It has

been shown [14] that for systems which exhibit a ferroelastic transition, the critical behaviour must be classical in three dimensions. In K.D.P. the transition is at the same time ferroelectric and ferroelastic, due to the piezoelectric coupling in the high temperature phase, and one expects that the marginal dimension is 2.5 [14] (far away from the tricritical region). In particular, one may think that the long range forces of dipolar and elastic origin prevent the divergence of the specific heat which exists in 3-d Ising systems with short range interactions only. When the transition becomes tricritical, the system exhibits a *cross-over* to a generally different *universality class*, and the critical exponents change. However, it has been shown in the Ising model that the marginal dimensionality is then lowered [12]. In the case of K.D.P., we conclude that the transition becomes *even more* classical near the T.C.P. One expects that the critical exponents α and β change from 0 and 0.5 respectively in the critical regime to 0.5 and 0.25 at the T.C.P.

In our experiments, the *anomalous* thermal expansion $(\partial U_{zz}/\partial T)_P$ must vary as the specific heat (Pippard's Relations). It is experimentally clear that in the ferroelectric phase this quantity becomes divergent near the T.C.P., but in the paraelectric phase, the divergence — if it exists — is very difficult to observe since the small *rounding* of $U^0_{zz}(T, P)$ does not emerge very much above the random fluctuations. This is again probably connected to the fact that local order fluctuations are prohibited by the long range interactions so that a mean-field behaviour is observed almost everywhere. A direct determination of the critical exponent β may be attempted by fitting our shear strain data with an expression of the form :

$$U_{xy} = U_0\left(\frac{T_c - T}{T_c}\right)^{\beta}. \qquad (21)$$

However this procedure should be used with caution when a cross-over between two different regimes occurs [38]. The true β predicted by the theory concerns the asymptotic behaviour when T goes to T_c and the range of temperature where this is actually observable may be very small. For example, the *effective* β [39] obtained by fitting our 4 kbar curve with expression (21) changes continuously from 0.28 to 0.43 when the temperature range $T_c - T$ goes from 3 K to 0.1 K. On the 2.63 kbar curve it changes from 0.22 to 0.25 in the same circumstances. For pressure between 2 and 2.3 kbars, the effective exponent becomes approximately independent of the temperature range and equal to about 0.20; but even in this case, the β value obtained has to be taken with caution because the transition may be slightly first order. Furthermore, we have tried to fit our 2.3 kbars curve using the expression :

$$U_{xy} = U_0\left(\frac{T_c - T}{T_c}\right)^{0.25}\left|\mathrm{Log}\left(\frac{T_c - T}{\Delta}\right)\right|^{0.25} \qquad (22)$$

which is the form expected for the tricritical behaviour of an Ising model with short range interactions [12, 10, 41]. We found that this fit too was surprisingly good over a large range of temperature (see Fig. 11).

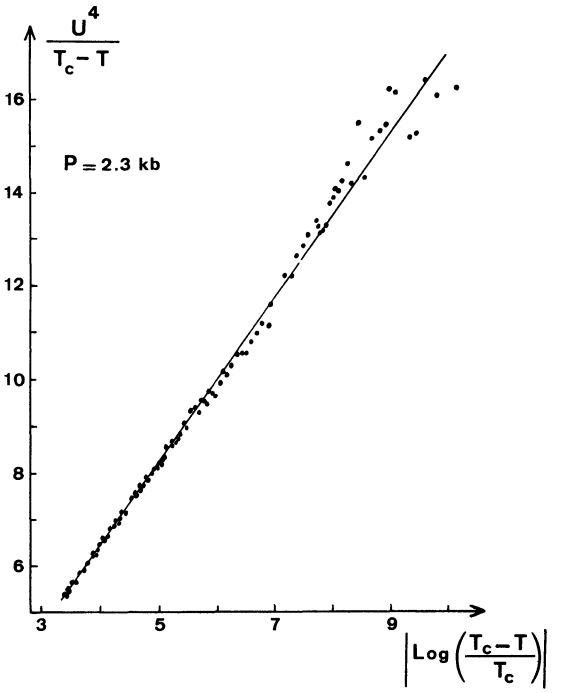

Fig. 11. — Plot of $\frac{U^4_{xy}(T)}{T_c - T}$ as a function of $\left|\mathrm{Log}\left|\frac{T_c - T}{T_c}\right|\right|$ for a pressure P = 2.3 kbar. A straight line is expected from the theory of Riedel and Wegner (Ref. [12]) for the tricritical behaviour of the 3-d Ising model with short range interactions.

The introduction of a logarithmic correction is equivalent to a small reduction of the effective exponent β (from 0.25 to $\simeq$ 0.22). This illustrates the difficulty of determining unambiguously the critical exponents when *cross-over* effects are present and shows the flexibility of a formula including logarithmic corrections to fit the data. In the present case, we consider that the main advantage of the phenomenological theory is to give a description of the whole set of data with a unique formula and to include in that the change of the critical exponents as one approaches the T.C.P. A rather similar conclusion was drawn from an analysis of the order parameter measurements near the T.C.P. in NH_4Cl [7, 28].

Another interesting aspect of the phenomenological Landau theory is its connections with microscopic models of the transition. Recently Torstveit [42] discussed the ability of the Blinc-Svetina theory [43] to describe the pressure dependence of the static properties of K.D.P. This Gibbs free energy expansion is of the same form as that of section 5.1 (Eq. (4)) and it includes in particular a temperature and pressure dependence of the b coefficient. We disagree however with his assumption that $b_P = (\partial b/\partial P)_T > 0$. This estimate is based on two different published data of $U_{xx}(T)$ [30, 35], but as discussed in section 5.3,

these data are not in very good agreement, so that their interpretation may be ambiguous. Our present results suggest that $b_P < 0$. The sign of this coefficient is important since it was that point which lead Torstveit to conclude that the long range dipolar interaction parameter of the Blinc theory was negative ; a complete discussion of our data using the Blinc and Svetina theory will be given in a future paper.

To conclude, our present measurements of the spontaneous shear U_{xy} and C-lattice parameter U_{zz} in the (T, P) plane show that the ferroelectric transition of K.D.P. becomes tricritical for $T \simeq 109.0 \pm 1$ K and $P \simeq 2.8 \pm 0.3$ kbar and our data are fitted by a phenomenological Landau type free energy expansion. To complete the present measurements it would be interesting to explore the critical behaviour in the full space (T, P, E). Unfortunately the technique used to measure the shear strain required the presence of a domain structure and thus cannot be used when an electric field is applied. However birefringence measurements are an adequate method to investigate the order parameter variations in a single domain sample ; such experiments are in progress now.

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