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Simultaneous measurements of the second harmonic generation and of the birefringence of KH_2PO_4 near its ferroelectric transition point

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We report some measurements of the variation of the nonlinear optical-susceptibility coefficient $\chi_{31}^{2\omega}$ with temperature and dc electric fields in the vicinity of the 122°K ferroelectric-transition point of KH_2PO_4 (KDP). Simultaneous measurements of the birefringence $\Delta n = n_1' - n_2'$ were also made and this quantity was found to be proportionnal to $\chi_{31}^{2\omega}$; they are both closely related to the order parameter of the transition. A comparison of our results with some measurements of the spontaneous polarization P_3 and of the spontaneous shear x_6 is made. Our data indicate that the transition is first order and may well be interpreted in the framework of the Landau theory if terms of sixth and eighth order are taken into account in the free-energy expansion. An attempt is also made to fit our results to the statistical theory of Silsbee, Uelhing, and Schmidt.

I. INTRODUCTION

The ferroelectric phase transition in potassium dihydrogen phosphate (KDP) has been extensively studied [1] since its discovery in 1935. Nevertheless, many features of this phase change remain unclear and in particular the order of the transition is still under discussion: While some recent experiments [2–6] indicate a first-order transition, some authors[7–9] report no evidence of discontinuous jump of the polarization P_3 or of the elastic constant C_{66}^E. If the transition is interpreted as being second order, the usual dependence of the spontaneous polarization $P \sim (T_0 - T)^{1/2}$, according to the phenomenological Landau-Devonshire theory, is not observed, but a smaller value of the exponent is generally found ($\sim \frac{1}{6}-\frac{1}{8}$), which indicates a very sharp decrease of P near T_0. So, one has been led to question the applicability of the phenomenological theory, at least in its usual form, for one KDP transition.

On the other hand, Slater proposed[10] in 1941 a statistical model, based on the "ice rule," which predicts a discontinuous transition, the spontaneous polarization going directly from zero to its maximum value at T_0. Some modifications of this theory by Takagi[11] and by Senko, [12] developed by Silsbee, Uehling, and Schmidt[13] (SUS) have given rise to a statistical theory where the transition may be either first or second order according to the values of the parameters introduced. Although it may be successful in giving a microscopic insight of the transition in fair agreement with equilibrium experimental values, the dynamical aspects of the transition are not taken into account; in the light of recent data, [14,15] proton tunneling and soft optic and acoustic modes must be introduced to give a full description of the phenomena.

From an experimental point of view, various techniques have been used to investigate the temperature dependence of the order parameter (hysteresis loops, [8] static measurement of polarization, [5,6] electrocaloric effect, [2,4] x-ray shear measurements[3]...), but the optical techniques have been less used since the initial birefringence measurements by Zwicker and Scherrer[16] in 1944. The nonlinear optical susceptibility, which has been extensively studied at room temperature, was investigated in the ferroelectric phase by Van der Ziel and Bloembergen, [17] but these authors have not studied the vicinity of the transition point. Optical susceptibilities are affected by the transition because the electronic properties of the crystal are modified when the equilibrium positions of the ions are displaced; in particular, changes of symmetry induce the presence of new susceptibility coefficients (in the lower phase) which are obviously closely related to the order parameter.

In the ferroelectric phase, if no dc electric field (or uniaxial stress) is applied, a domain structure spontaneously appears[18] and the optical properties are no longer homogeneous inside the crystal; so diffraction effects may take place: Linear diffraction by KDP domains was first reported by Hill and Ichiki[19]; nonlinear diffraction[20] has been also studied by the present author and will be published elsewhere. [21] An accurate measurement of the temperature dependence of the optical susceptibilities requires a single-domain crystal, and this may be achieved by applying dc electric fields.

Before giving our experimental results we shall review in more detail the linear and nonlinear optical properties of KDP in the paraelectric and ferroelectric phases and particularly their relation to the order parameter (Sec. II).

In Sec. III, we shall describe the experimental setup used to make simultaneous measurements of the second-harmonic generation (SHG) and of the birefringence and we shall present the experimental results.

In Sec. IV these results will be interpreted in the framework of the Landau theory and compared to the predictions of the SUS theory. A comparison with other order-parameter data will also be made.

II. LINEAR AND NONLINEAR OPTICAL PROPERTIES OF KDP

A. Linear optical susceptibility

In its paraelectric phase KDP is tetragonal (point group $\bar{4}2m$) and so optically uniaxial; the lower phase is orthorhombic ($mm2$) and biaxial. The tensors may be expressed on the basis either of the tetragonal directions (a_1, a_2, c) or of the orthorhombic ones (a, b, c) deduced from the preceding ones by a rotation of 45° around the c axis. The linear optical-susceptibility tensor is of the form (in the lower phase)

$$\begin{pmatrix} \chi_{11} & \chi_{12} & 0 \\ \chi_{12} & \chi_{11} & 0 \\ 0 & 0 & \chi_{33} \end{pmatrix} \equiv \begin{pmatrix} \chi'_{11} & 0 & 0 \\ 0 & \chi'_{22} & 0 \\ 0 & 0 & \chi'_{33} \end{pmatrix} , \tag{1}$$

where the primed quantities refer to the orthorhomic frame.

One has

$$\chi'_{11} = \chi_{11} + \chi_{12} ,$$
$$\chi'_{22} = \chi_{11} - \chi_{12} , \tag{2}$$
$$\chi'_{33} = \chi_{33} .$$

In the upper phase $\chi_{12} = 0$ and $\chi'_{11} = \chi'_{22}$.

As in the Landau theory, the free energy is expanded in ascending powers of the order parameter; one may develop each coefficient of the susceptibility according to its symmetry properties.

$$\chi^F_{11} = \chi^P_{11} + A_{1133} P_3^2 + \cdots ,$$
$$\chi^F_{33} = \chi^P_{33} + A_{3333} P_3^2 + \cdots , \tag{3}$$
$$\chi^F_{12} = A_{123}\ P_3 \ldots ,$$

where the superscripts F and P refer to "ferroelectric" and "paraelectric," respectively, and the A tensors are approximately temperature independent near T_0. Such expansions have already been written by Van der Ziel and Bloembergen.[17] Strictly speaking, they are only valid for a second-order transition and their extension to KDP is not completely rigorous.

The birefringence $\Delta n = n'_1 - n'_2$ which appears in the orthorhombic phase is related linearly to the coefficient χ_{12} and so must be proportional to P_3 (to second order in P_3). More precisely, one has

$$\chi_{12} = \chi'_{11} - \chi'_{22} = (1/4\pi)(n_1'^2 - n_2'^2) \sim 2\bar{n}\Delta n/4\pi \propto P_3 . \tag{4}$$

This birefringence changes its sign with P_3 and so from a 180° domain to the neighboring one; therefore it can be easily measured only in a single-domain sample (or at least inside one domain of a multidomain crystal).

B. Nonlinear optical susceptibility

The forms of the nonlinear susceptibility in the tetragonal and orthorhombic frame, respectively, are the following (lower phase):

$$\begin{pmatrix} 0 & 0 & 0 & \chi_{14} & \chi_{15} & 0 \\ 0 & 0 & 0 & \chi_{15} & \chi_{14} & 0 \\ \chi_{31} & \chi_{31} & \chi_{33} & 0 & 0 & \chi_{36} \end{pmatrix} \equiv \begin{pmatrix} 0 & 0 & 0 & 0 & \chi'_{15} & 0 \\ 0 & 0 & 0 & \chi'_{24} & 0 & 0 \\ \chi'_{31} & \chi'_{32} & \chi'_{33} & 0 & 0 & 0 \end{pmatrix} , \tag{5}$$

with

$$\chi'_{15} = \chi_{14} + \chi_{15}, \quad \chi'_{24} = -\chi_{14} + \chi_{15},$$
$$\chi'_{31} = \chi_{36} + \chi_{31}, \quad \chi'_{32} = -\chi_{36} + \chi_{31} , \tag{6}$$
$$\chi'_{33} = \chi_{33} .$$

In the visible and near-infrared regions the crystal is well transparent and the "Kleinman rule"[22] implies $\chi_{14} = \chi_{36}$, $\chi_{15} = \chi_{31}$. The expansions of these susceptibility coefficients as a function of P_3 are[23]

$$\chi^F_{36} = \chi^F_{14} = \chi^P_{14} + B_{12333} P_3^2 + \cdots ,$$
$$\chi^F_{31} = \chi^F_{15} = B_{1133} P_3 + \cdots , \tag{7}$$
$$\chi^F_{33} = B_{3333} P_3 + \cdots .$$

Actually χ^F_{33} is weak and Van der Ziel and Bloembergen cannot detect its presence in their experiment; owing to the enhancement of the harmonic intensity in the presence of a domain structure we have been able to show that χ_{33} is different from zero, although one order of magnitude smaller than χ_{31}.[21] Nevertheless, the measurements reported in this paper will concern only χ_{31}. In principle, to measure this coefficient one must record the harmonic intensity created by a laser beam directed along the [010] (tetragonal) axis and polarized along [100]. In practice this geometry was found to be not very convenient because it requires a very accurate alignment to prevent interferences between the χ_{31} and χ_{14} coefficients. Furthermore, a large-incident laser peak power is necessary in view of the weakness of the coefficient. Therefore we have chosen another geometry which used the so-called noncollinear-phase-matching condition[24]; this technique consists in the mixing of two beams vibrating at the fundamental frequency ω such that their wave vectors $\vec{k}_1$ and $\vec{k}_1'$ inside the crystal satisfy the relation

$$\vec{k}_1 + \vec{k}_1' = \vec{k}_2 , \quad (8)$$

where $\vec{k}_2$ is the wave vector of the second-harmonic beam produced. This condition is generally not fulfilled owing to the presence of dispersion. But in an anisotropic medium such as KDP, the ordinary index of refraction n_ω^0 for fundamental frequency may be larger than the extraordinary index $n_{2\omega}^e$ at the harmonic frequency. So $2|\vec{k}_1^0| > |\vec{k}_2^e|$ and there exist some directions for $\vec{k}_1$ and $\vec{k}_1'$ where the relation (8) is satisfied. For example, if $\vec{k}_1$ and $\vec{k}_1'$ lie in the [001] plane and make angles $+\phi$ and $-\phi$, respectively, with the [010] axis, $\vec{k}_2$ points in the [010] direction and phase matching is achieved for an angle φ_{PM} such that (see Fig. 1)

$$\cos\varphi_{PM} = n_{2\omega}^e / n_\omega^0 . \quad (9)$$

If the incident-beam polarizations are both in the (001) plane (ordinary waves) and if the harmonic-wave polarization is perpendicular to this plane (extraordinary wave) one sees that this geometry involves the nonlinear coefficient χ_{31} which is to be measured; one can show[19] that even when the small

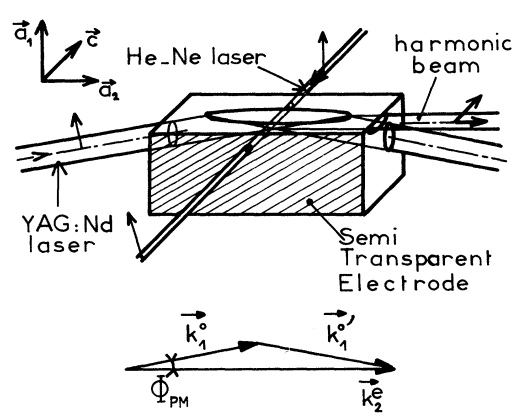

FIG. 1. Experimental arrangement used for the simultaneous measurements of second-harmonic generation and of the birefringence on a KDP single-domain crystal. The lower diagram shows schematically the wave vectors in the noncollinear–phase-matching geometry used for second-harmonic generation in the present experiment. The angle φ_{PM} is about 10° so the Nd:YAG laser beam is totally reflected inside the sample. The birefringence is measured by analyzing the He-Ne laser beam after the sample with a polarizer parallel to [010].

biaxiality is taken into account the SH intensity is proportional to $|\chi_{31}|^2$ to a very good approximation.

III. EXPERIMENTS

A. Experimental setup

1. Sample preparation

The samples of KDP single crystal were cut in the form of long parallelepipeds about 7×16×7 mm in size; the edges were parallel to the $\vec{a}_1$, $\vec{a}_2$, and $\vec{c}$ tetragonal axes. The good quality of some natural (100) faces allowed their direct use after a slight polishing. Semitransparent gold electrodes were evaporated on the (001) faces in order to apply dc fields and to measure the sample capacitance. The low value of the coercive field (<30 V/cm for $T_c - T \sim 1$ °K) and the good mobility of the domain walls which moved easily parallel to themselves in presence of small fields seemed to bear witness to the quality of the samples.

2. Cryostat

The sample temperature was controlled by a specially constructed Dewar. The sample was placed inside a first copper block equipped with four glass windows. This block was itself enclosed in another larger copper cylinder; helium gas was used as a thermostating medium. The system was cooled by liquid nitrogen and insulated by vacuum. The outer part of the Dewar was provided with two large glass windows (80 mm in diameter) perpendicular to the [100] crystal axis. At 90° [perpendicular to [001] direction) a small window (30 mm in diameter) and a microscope allowed the direct observation of the crystal—especially of the domain structure—and the birefringence measurement. The Dewar was rotatable around its vertical axis for angular adjustments. The temperature was controlled by regulating the heating current of a resistor placed in the inner copper cell, with a proportional-integral-derivative regulator and a platinum-resistor sensor. The controller output was approximatively 1 W at 122 °K. The sample temperature was measured by another 4-wires platinum thermometer, the resistance of which was determined with a dc Smith bridge (AOIP-B9OR). The temperature stability was estimated to be better than 0.01 °K for a period of several hours (in the absence of the YAG laser beam). Care was taken to avoid thermal shock on the sample, especially very near T_c, where it may crack easily. The time required to go from 300° to 120 °K was about 5.5 h.

3. Measurements procedure

SHG was achieved with the beam of an acousto-optic Q-switched YAG:Nd laser (Quantronix 112 Å). The pulse width was about 0.4 μsec and the peak power $\lesssim 8$ kW. This beam was polarized with a glan polarizer and focused on the sample with a long-focal-length lens (500 mm). The direction of the incident beam was varied through an angle φ relative to the [010] axis in the (001) plane of the crystal. Noncollinear phase matching was achieved by making the beam reflect inside the crystal on the (100) large face of the sample and adjusting the angle φ to the value φ_{PM} (see Fig. 1).

The harmonic beam produced in the [010] direction was collected by a lens and measured with a photomultiplier (Radio Technique 56 DVP) provided with a gate system synchronized with the laser pulses. Some perturbations in the temperature stability and homogeneity were introduced by the laser beam during SH measurements; in order to evaluate experimentally this effect we have compared the variation of the birefringence near T_c successively with a high-power beam (3 W mean power) pulsed at 1 kHz and the same YAG laser beam in the continuous mode at very low power (<1 mW). The results obtained in both cases were quite similar, but they differ by a translation of the temperature scale of 0.525 ± 0.005 °K. Fortunately, the phase-matching geometry allows SH measurements with relatively weak mean power: They were made with a pulse repetition rate of 40 Hz and a mean power $\lesssim 100$ mW. Then one may estimate the laser heating to be less than 2.5×10^{-2} °K.

During the SHG measurements the birefringence of the sample was measured with the aid of an He-Ne laser beam of low power (<0.5 mW) directed along the [001] axis and polarized along the [100] axis. After the crystal the polarization along the [010] axis was analyzed. As the crystal became biaxial the emergent intensity was modulated according to the formula

$$I = I_0 \sin^2\{\pi[\Delta n(T) l/\lambda]\}, \qquad (10)$$

where l is the length crossed by the beam (about 7 mm) and $\lambda = 6328$ Å so that the period of oscillations corresponded to a variation of Δn of about 9×10^{-5}. As the total variation of Δn on a range of a few degrees under T_c was larger than 10^{-2}, the recording of the oscillations provided an accurate measurement of Δn.

These experiments were made in the presence of a static electric field (<2890 V/cm). The temperature was varied step by step because the time necessary to get thermal equilibrium is very long, especially near the transition point, where it may reach more than 2 h. The large electrocaloric effect prevents measurements with a continuous variation of the field at fixed temperature.

In all the experiments we measured the dielectric constant K_3 of the sample at 1 kHz (with an ac field amplitude sufficiently low to avoid heating).

B. Experimental results

1. Comparison between linear and nonlinear susceptibilities

The results obtained for the SH intensity $I^{2\omega}$ and the birefringence Δn for various magnitudes of the field are shown in Figs. 2 and 3. These results were reproducible and no thermal hysteresis was found for the range of fields shown in these figures.

In order to test the assertion of the Sec. II which says that χ_{12}^{ω} and $\chi_{31}^{2\omega}$ are proportional to the order parameter, we have first attempted to examine the proportionality of these two coefficients themselves. Figure 4 shows that the linear law is well verified within the experimental accuracy. One may note that the simultaneity of the measurements eliminates the uncertainties on many parameters such as temperature, dc field, crystal quality, etc...

In the hope of comparing these optical susceptibilities to the electric polarization P_3 directly, we have also tried to make simultaneous measurements of the pyroelectric current i_p produced by the pulses of the laser beam: An easily detectable effect was actually observed. Unfortunately this technique cannot give the $P_3(T)$ curve very near T_c in the case of KDP since

$$i_p = \frac{\partial P}{\partial t} = \frac{\partial P}{\partial T}\frac{dT}{dt} \sim \frac{\partial P}{\partial T}\frac{1}{C_E(T)}\frac{\Delta Q}{\Delta t}, \qquad (11)$$

where $\Delta Q/\Delta t$ is the heat rate for a pulse and $C_E(T)$ is the specific heat at constant field, which shows

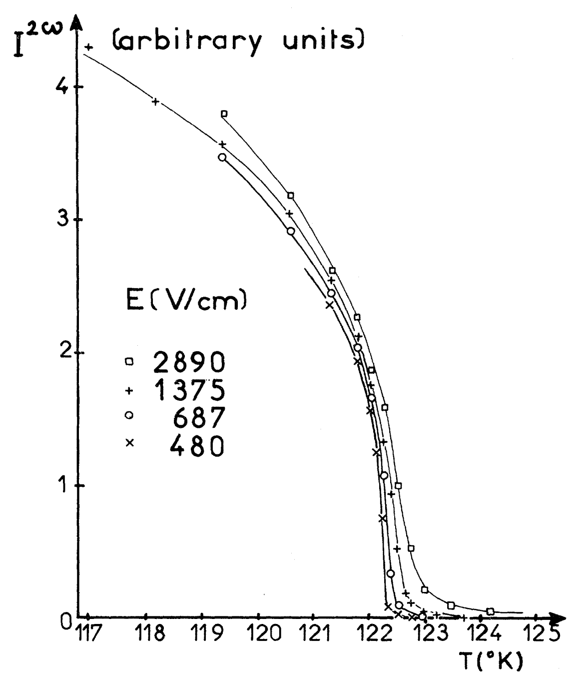

FIG. 2. Second-harmonic intensity $I^{2\omega} \propto |\chi_{31}^{2\omega}|^2$ as a function of the temperature for various dc electric fields. The relative accuracy $\Delta I^{2\omega}/I^{2\omega}$ is about ±5%.

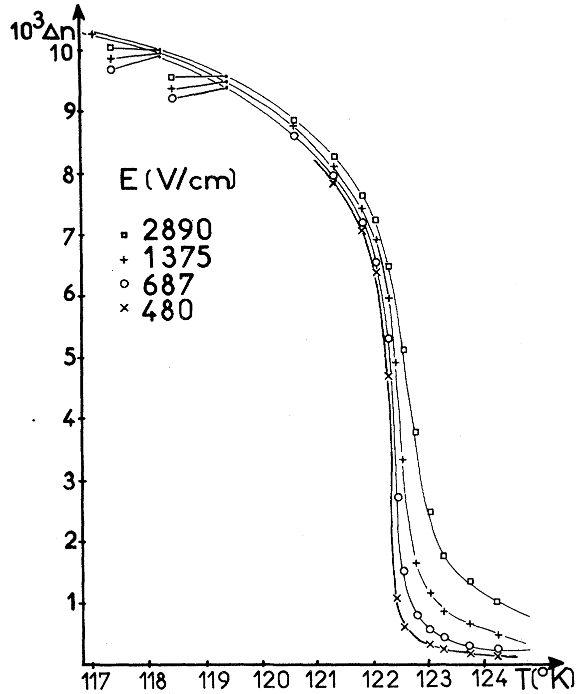

FIG. 3. Birefringence $\Delta n = n_1' - n_2' \propto \chi_{12}^{\omega}$ as a function of the temperature for various dc electric fields. The absolute uncertainties are $\pm 3\times 10^{-5}$ for Δn and ± 0.03 °K for T. These measurements were simultaneous to the second-harmonic generation.

a strong anomaly near T_c. The determination of $P(T)$ from $i_p(T)$ requires an accurate knowledge of $C_E(T)$. Therefore one will be led to compare our optical data to the measurements of the order parameter made by other authors; this will be done in Sec. IV.

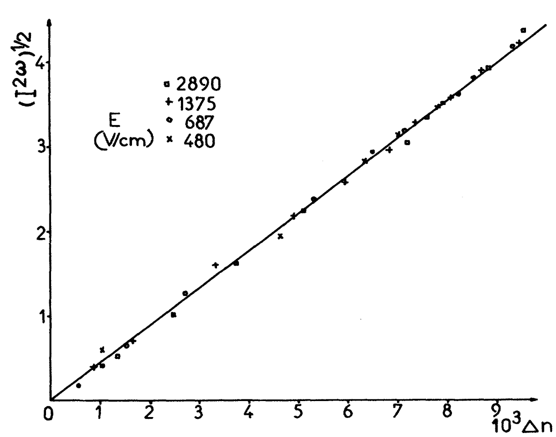

FIG. 4. Plot of $(I^{2\omega})^{1/2}$ vs Δn showing the proportionality between the nonlinear coefficient $\chi_{31}^{2\omega}$ and the linear coefficient χ_{12}^{ω}.

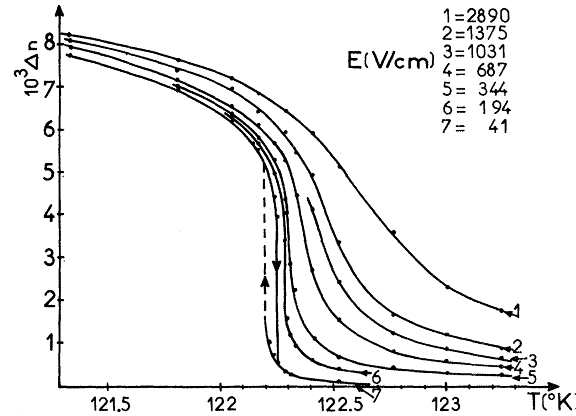

FIG. 5. Birefringence Δn for various fields very near the transition point. The absolute uncertainties are $\pm 3\times 10^{-5}$ for Δn and ± 0.008 °K for T. The arrows show the thermal hysteresis for the 41-V/cm curve. The solid lines have no significance other than that of fitting data.

2. *Birefringence measurements very near* T_c

In order to investigate the region very close to T_c, we have used the birefringence technique alone, thus avoiding the troubles due to the small heating of the sample by the YAG laser. The range of temperature was limited to ± 1 °K around T_c, but the range of dc fields extended from 2890 to 41 V/cm (so low a field was sufficient to produce a single-domain sample).

Figure 5 shows the results obtained. For the highest fields ($E > 344$ V/cm) no thermal hysteresis was found, but for $E = 41$ V/cm a small hysteresis of about 0.06 °K appears unambiguously. In this last case some instructive information was drawn from a direct observation of the crystal between crossed polarizers. When it passed through T_c when heating at a slow rate ($\lesssim 0.03$ °K h), a gradient of birefringence appeared on the crystal leading to a pattern of fringes more and more numerous when the transition was approached; these fringes swept the observed field in following the temperature gradient, but during the transition their orientation changed rapidly and they became parallel to the [100] axis, remaining always well contrasted. Then they recovered their initial orientation and disappeared at a higher temperature. When the temperature was decreased from the higher phase, the fringes pattern could be followed as far as a temperature lower than that of the preceding "reorientation" of the fringes. Then the pattern became misty for a short time after which the normal behavior was recovered.

The dielectric constant showed the same hysteresis effect, its maximum value becoming higher when T was decreased. These observations seem to prove that the KDP transition is first order—although very nearly second order. Nevertheless, the birefringence appears to vary continuously inside the crystal (at least when heating). A tentative explanation of this fact is that, owing to the presence of the spontaneous shear x_6, the coexistence of the ferroelectric and paraelectric phases in the sample leads to internal stresses which tend to "round" the transition; this may explain the rapid reorientation of the fringes which could correspond to a strain gradient along the [100] direction (rather than to a temperature gradient).

For a field of 194 V/cm the hysteresis range is no longer greater than the stability of the temperature regulation and this field must correspond approximatively to the limit of the range where hysteresis is present.

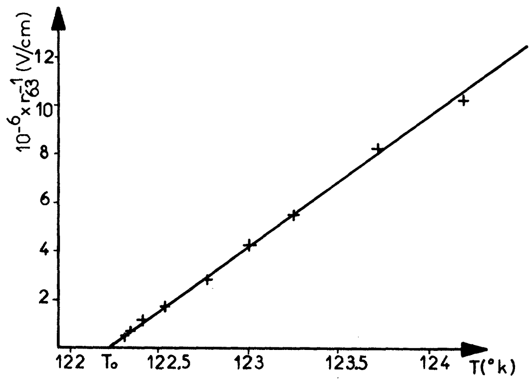

FIG. 7. Plot of the reciprocal of the Pockels coefficient r_{63} as a function of temperature showing the Curie-type behavior.

IV. DISCUSSION OF THE RESULTS

A. Landau phenomenological theory

Following Landau and Devonshire, the Gibbs free energy at constant stress ($\sigma = 0$) can be expanded in a power series of the spontaneous polarization P,[25]

$$F(P, T) = \tfrac{1}{2} a P^2 + \tfrac{1}{4} b P^4 + \tfrac{1}{6} c P^6 + \tfrac{1}{8} d P^8 + \cdots - EP , \tag{12}$$

where $a = a'(T - T_0)$ and the other coefficients are temperature independent.

In order to compare our data with the Landau theory we assume, as in Sec. II, that the birefringence Δn is proportional to P; then Eq. (12) and the equilibrium condition $\partial F / \partial P = 0$ lead to

$$E = (a/A)\Delta n + (b/A^3)\Delta n^3 + (c/A^5)\Delta n^5 + \cdots , \tag{13}$$

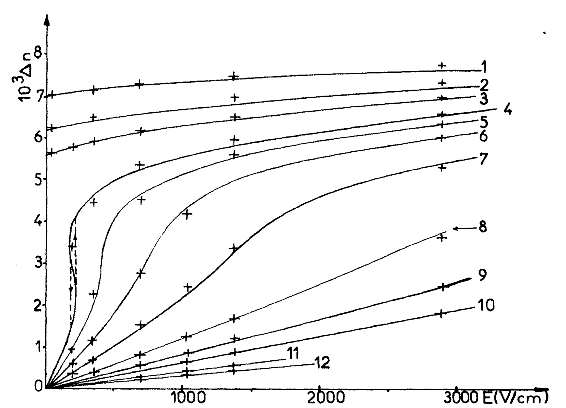

FIG. 6. Birefringence Δn as a function of the applied field for various temperatures T: 1, 121.81 °K; 2, 122.05 °K; 3, 122.17 °K; 4, 127.29 °K; 5, 122.34 °K; 6, 122.41 °K; 7, 122.53 °K; 8, 122.75 °K; 9, 122.99 °K; 10, 123.23 °K; 11, 123.79 °K; 12, 124.19 °K. The solid lines are obtained from the Landau theory with $a' = 3.9 \times 10^{-3}$ esu and the set (2) of parameters [see formula (19) in the text].

where A is temperature independent.

From the set of data $\Delta n = f(T)$ for various E (Fig. 5) one may plot the set $\Delta n = f(E)$ for various T (Fig. 6). We shall study successively the linear and the nonlinear parts of these curves.

1. Linear part

It represents the usual linear electro-optic effect obtained at low fields, and Δn can be related to the r_{63}^{σ} Pockels coefficient

$$\Delta n = -n_1^3 r_{63}^{\sigma} E_3 ; \tag{14}$$

so

$$\left(\frac{\partial(\Delta n)}{\partial E}\right)_{E=0} = -n_1^3 r_{63}^{\sigma} \sim \frac{AK_3}{4\pi} \propto \frac{1}{T - T_0} , \tag{15}$$

where K_3 is the dielectric constant along the $\vec{c}$ axis. This term must show the Curie-type divergence when $T \rightarrow T_0$.

The obtained experimental results are plotted in Fig. 7 and are actually well described by a relation of the form

$$r_{63}^{\sigma} = \frac{5.6 \pm 0.1}{T - T_0} \times 10^{-5} \text{ esu } (T_0 = 122.195\ °\text{K}) . \tag{16}$$

The ratio r_{63}^{σ}/K_3 is then found to be $(1.72 \pm 0.04) \times 10^{-8}$ esu if one takes the value $K_3 = 3255\ °\text{K}/(T - T_0)$ as is usually done. This result is in very good agreement with the previous data of Zwicker and Sherrer.[16] It implies that A is indeed temperature independent or, in other words, that the hypothesis $\Delta n \propto P_3$ is valid.

2. Nonlinear part

This part is defined as

$$E_{\text{NL}} = E - (a/A)\Delta n . \tag{17}$$

In the Landau description it is temperature dependent and depends on Δn only. Figure 8 shows that

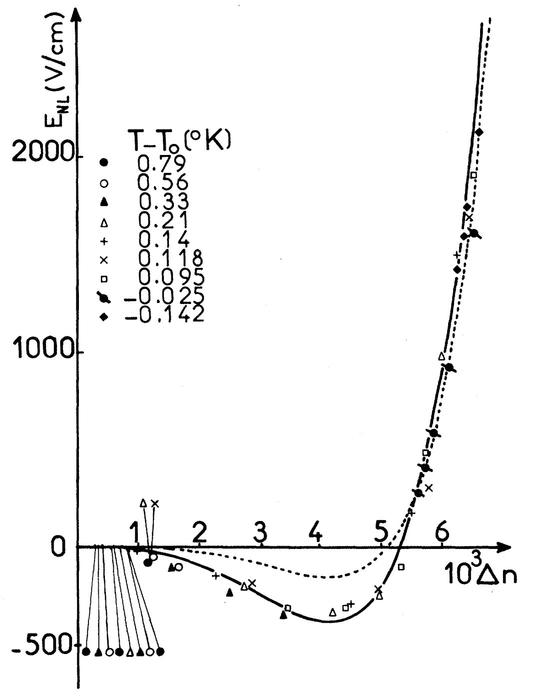

FIG. 8. Nonlinear part E_{NL} of the curves $E = f(\Delta n, T)$. The lines are the predictions of the Landau theory: dashed line with the set (1) of parameters; solid line with the set (2).

this is indeed the case within experimental uncertainties.

We have tried to fit the curve $E_{NL}(\Delta n)$ with various odd polynomial expansions. Following Benepe and Reese[2] we have first taken $c = 0$ in Eq. (12), keeping only b and $d \neq 0$. A least-square fit leads to the set (called set 1) (in esu)

$$b = (-0.54 \pm 0.06) \times 10^{-11} ,$$

$$c = 0 \text{ (fixed)} , \tag{18}$$

$$d = (+2.85 \pm 0.10) \times 10^{-27} .$$

These values are not very different from those found by Benepe and Reese ($b = -0.44 \times 10^{-11}$ and $d = +2.96 \times 10^{-27}$) in fitting the $P(T)$ curve at zero field only. One may see, however, that the fit is not very good near $E_{NL} = 0$.

If one relaxes the condition $c = 0$, the best least-square fit gives (set 2) (in esu)

$$b = (-1.85 \pm 0.25) \times 10^{-11} ,$$

$$c = (+3.50 \pm 0.5) \times 10^{-19} , \tag{19}$$

$$d = (+0.87 \pm 0.5) \times 10^{-27} .$$

The comparison between these two sets of parameters shows that the values depend rather strongly on the assumption that $c = 0$ and this explains (partly) the discrepancies found between the values given by different authors (see Table I).

If the above, given values must not be taken too seriously; one may see in Fig. 8 that the coefficient b is unambiguously negative, but weak (i.e., the energy $\frac{1}{4} bP^4$ is more important than the other terms only for a small range of field and of temperature around T_c). In the Landau picture this negative b value leads to a first-order phase transition,[25] and this is consistent with our observations of thermal hysteresis. The first-order character has already been recognized by various authors,[2–6] but Brody and Cummins[9] have not observed evidence of discontinuity in their careful study of the elastic anomaly very near T_c.

From the sets of parameters (1) and (2) and from the Curie constant ($C = 3255$ °K) one may calculate the shape of the spontaneous polarization at zero field. Following the notations of Merz and Fatuzzo[25] for the critical temperature T_c and the maximum thermal hysteresis $T_1 - T_0$ one gets

TABLE I. Comparison of the values of the parameters (in esu) of the Landau free-energy expansion obtained by various authors.

	$10^{11}b$	$10^{19}c$	$10^{27}d$	$T_c - T_0$
Present work				
Set (1)	-0.54 ± 0.05	0	$+2.85 \pm 0.10$	0.017
Set (2)	-1.85 ± 0.25	$+3.3 \pm 0.5$	$+0.87 \pm 0.5$	0.045
Benepe and Reese (Ref. 2)	-0.44	0	$+2.96$	0.012
Strukov *et al* (Ref. 4)	-1.9	$+6.3$	0	0.03
Sidnenko and Gladkii (Ref. 5)	-3.0 ± 0.8	$+6.5 \pm 1.1$	0	
	-0.5 ± 0.3	0	$+3.8 \pm 0.4$	
Kobayashi *et al.* (Ref. 3)	-11.9	$+11$	0	0.67

$$P_c^2=(4/3d)[-\tfrac{1}{3}c+(\tfrac{1}{9}c^2-\tfrac{3}{8}bd)^{1/2}]\ ,$$
$$T_c-T_0=-(1/a)(+bP_c^2+cP_c^4+dP_c^6)\ ; \quad (20)$$
$$P_1^2=(1/3d)[-c+(c^2-3bd)^{1/2}]\ ,$$
$$T_1-T_0=-(1/a')(bP_1^2+cP_1^4+dP_1^6)\ ; \quad (21)$$
$$P_c=1.95\ \mu C/cm^2\ ,\quad T_c-T_0=0.017\ ^\circ K\ ,$$
$$P_1=1.69\ \mu C/cm^2\ ,\quad T_1-T_0=0.045\ ^\circ K\ , \quad (22)$$

for set (1);

$$P_c=2.05\ \mu C/cm^2\ ,\quad T_c-T_0=0.055\ ^\circ K\ ,$$
$$P_1=1.8\ \mu C/cm^2\ ,\quad T_1-T_0=0.062\ ^\circ K\ , \quad (23)$$

for set (2).

A comparison between our data (extrapolated to $E=0$) (Table II), those of Benepe and Reese,[2] those of Strukov *et al.*,[4] and the calculated value of P with the set (2) of parameters is shown in Fig. 9. One may note that only the value of T_c is adjusted between the various curves (the coefficient A relating Δn and P was fixed by the ratio r_{63}/K_3 and the value of the Curie constant). Both our data and those of Benepe and Reese are in relatively good agreement with the Landau form (with the parameters given).

Recently, Bastie *et al.*[26] have made very precise measurements of the spontaneous shear x_6 by a γ-ray diffractometry technique in a multidomain sample. In the vicinity of T_c this quantity is found to be well proportional to Δn and to the $P(T)$ values of Benepe and Reese.

To conclude, one may confirm that no significant departures from the phenomenological theory are found in the KDP transition if it is interpreted as a first-order one.[27] Reese[29] and Strukov *et al.*[30] have

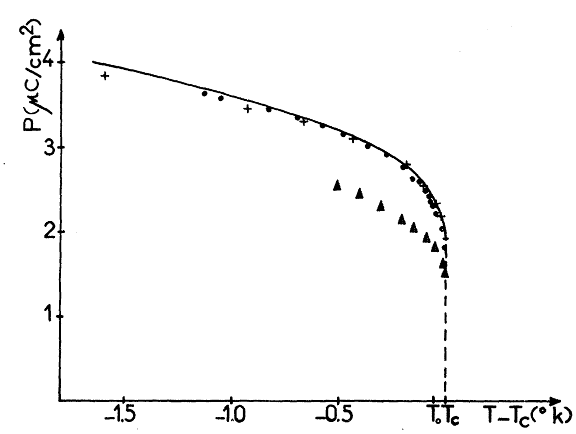

FIG. 9. Spontaneous polarization at zero field as a function of the temperature: +, from our birefringence data extrapolated at zero field; ●, from Benepe and Reese (Ref. 2); ▴, from Strukov *et al.* (Ref. 4); dashed line, from Landau theory with the set (2) of parameters. All the data have been fitted to have the same value of T_c.

TABLE II. Values of Δn extrapolated to zero field from our birefringence measurements. P_s is calculated from $\Delta n = AP_s$ with $A=2.22\times10^{-3}$ cm$^2/\mu$C, as deduced from the ratio r_{63}/K_{31} [See Eq. (16)]. (For $T=T_c$ the extrapolation is not very accurate.)

T_c-T	$10^3\,\Delta n$	P_s (μC/cm^2)
1.595	8.56	3.85
0.922	7.68	3.46
0.663	7.32	3.30
0.430	6.88	3.09
0.180	6.17	2.78
0.100	5.66	2.55
0.040	5.16	2.32
0.020	4.85	2.18
0.000	(4.30 ± 0.2)	(1.90 ± 0.1)

also noted that the phenomenological law $C_v \sim (T_0 - T)^{-1/2}$ in the ferroelectric phase seems also well obeyed. This may be related to the fact—already noted by Brody and Cummins[9]—that the parameter b is so weak that the transition is nearly a tricritical one and then the Landau picture gives a good description.[28]

B. Statistical theory

The phenomenological theory, although it seems able to give a good macroscopic insight of the transition, does not give any idea of microscopic mechanism. The first attempt to relate the onset of ferroelectricity to the ordering of atoms in KDP was made by Slater.[10] He assumed that each proton had two equilibrium positions along the O-O bond and that at any temperature there were two and only two protons "close" to a PO_4 tetrahedron ("ice rule"). Among the six different possible configurations two are orientated (giving rise to a dipolar moment parallel or antiparallel to the $\vec{c}$ axis), the others are not polarized and correspond to an energy $+\epsilon_0$ greater than the proceeding ones. The statistical treatment of such a system leads to a ferroelectric transition [at $T_0=(\epsilon_0/K)\ln 2$] of a strange type: The polarization jumps abruptly to its maximum value at T_0 but the susceptibility becomes infinite at this point.

Some refinements of this theory have been made to further improve the agreement with experimental observations. Takagi[11] gave a finite energy ϵ_1 to the configurations with three or one protons close to a PO_4; Senko[12] introduced a parameter β to take the long-range dipolar coupling into account. This modified Slater model has been investigated by SUS and was recently discussed by Reese and by Brody *et al.*[9] in relation to calorimetric and elastic constant measurements.

The free energy in the SUS model has the following form:

$$F(p,T)=-NkT\,\{(\beta/kT)p^2+\ln[(1-p^2)(\cosh^2\lambda$$

$$+2\Theta_1 \cosh\lambda + \Theta)] + 2p\,(\tanh^{-1}p - \lambda)\}, \quad (24)$$

with

$$p = \frac{\tanh\lambda(1+\Theta_1/\cosh\lambda)}{1+2\Theta_1/\cosh\lambda+\Theta/\cosh^2\lambda}, \qquad \Theta = e^{-\epsilon_0/kT} - \tfrac{1}{2}, \quad \Theta_1 = e^{-\epsilon_1/kT}. \quad (25)$$

A first question which may be asked is how is this free energy related to that of Landau.

One can expand (24) in ascending powers of p,

$$F(p, T) = (2NkT/V)(\tfrac{1}{2}c_2 p^2 + \tfrac{1}{4}c_4 p^4 + \cdots). \quad (26)$$

The calculations of the c_n are straightforward but cumbersome, and in order to simplify, we have made the hypothesis that $\Theta_1 \ll \Theta < 1$; so one gets

$$\begin{aligned} c_2 &= (\Theta+\Theta_1)/(1+\Theta_1) - \beta/kT, \\ c_4 &= -\Theta^2(1+\tfrac{2}{3}\Theta) + \tfrac{1}{2}\Theta_1(1-\Theta+3\Theta^2+5\Theta^3) \\ &\quad + 4\Theta_1^2\Theta(1-3\Theta_1^2) + O(\Theta_1^3), \\ c_6 &= 2\Theta^3(1+\tfrac{3}{2}\Theta+\tfrac{3}{5}\Theta^2) + \tfrac{3}{8}\Theta_1(1-\Theta+2\Theta^2-10\Theta^3 \\ &\quad -35\Theta^4-21\Theta^5) + O(\Theta_1^2), \\ c_8 &= 5\Theta^4(1+\tfrac{12}{5}\Theta+2\Theta^2+\tfrac{4}{7}\Theta^3) + \tfrac{51}{112}\Theta_1 + \cdots O(\Theta\Theta_1). \end{aligned} \quad (27)$$

The temperature T_0 is defined by $c_2(T_0)=0$, but, in contrast with the Landau theory, all the c_n are temperature dependent. One may easily see that (i) if $\Theta_1=\beta=0$ (Slater initial hypothesis), when $\Theta \to 0$ *all* the $c_n \to 0$ (the transition may be called of "infinite order"). One notes also that $C_4 < 0$ in the neighborhood of $T=T_0$. (ii) If $\beta=0$ but $\Theta_1 \neq 0$ (Takagi hypothesis), the transition appears when $\Theta(T_0) = -\Theta_1(T_0)$; c_4 is then $\sim \frac{1}{2}\Theta_1(T_0) > 0$ when $T \sim T_0$ and the transition is second order. (iii) If $\beta \neq 0$ but $\Theta_1 = 0$, T_0 is defined by $\Theta(T_0) = \beta/kT_0 > 0$, $c_4(T_0)$ is <0 and the transition is first order. (iv) If β and $\Theta_1 \neq 0$, the transition may be either first or second order according to the relative value of β, ϵ_0, and ϵ_1.

There exists in the space ϵ_0, ϵ_1, β a surface separating the ordered and disordered regions, and on this surface a line of tricritical points separating the first- and second-order regions (see Fig. 10). The possibility of tricritical points in the SUS model is clearly seen on the expansion [Eqs. (26) and (27)] where the c_4 term appears as the sum of a negative term and of positive ones; it vanishes when $\Theta_1 \sim \Theta^2$, which is possible when $\Theta_1 \ll \Theta \ll 1$.

Experimental results show that the KDP transition point lies in the first-order region but in the near vicinity of the tricritical line. A direct comparison of expansions (12) and (26) leads to

$$a = a'(T-T_0) = \frac{2Nk}{VP_m^2}c_2'(T-T_0), \quad c_2' = \left(\frac{\partial c_2}{\partial T}\right)_{T=T_0}, \qquad b = (2NkT/VP_m^4)c_4, \quad c = 2NkT/VP_m^6, \cdots, \quad (28)$$

where $P_m \doteq NM/V$ is the maximum value of P; this value is not precisely known (the maximum value reported is 5.2 $\mu C/cm^2$). We have not tried to extract the parameters ϵ_0, ϵ_1, β from the preceding equations because this procedure involves complicated and somewhat meaningless calculations with regard to the uncertainties on the b, c, d coefficients. We have preferred to choose a set of parameters approximately fitting the Brody-Cummins data and to see to what extent it fits our present results. Taking

$$\epsilon_0/k = 48\ ^\circ K, \quad \epsilon_1/k = 350\ ^\circ K, \quad \beta/k = 26.5\ ^\circ K, \quad (29)$$

one has

$$c_2' = 0.59, \quad c_4 = 0.005, \quad c_6 = +0.032. \quad (30)$$

If one takes $a = 3.9\times10^{-3}$ esu and $T_0 = 122.195\ ^\circ K$, one obtains $P_m \sim 7\ \mu C/cm^2$, $b = -0.9\times10^{-11}$, $c = +1.3\times10^{-19}$.

Furthermore, one may show that the b and c coefficients vary slowly with temperature near T_0 ($\Delta b/b \sim \Delta c/c \sim 5\%$ for $\Delta T = 1\ ^\circ K$) for the present set of parameters. One notes (as Brody and Cummins) that the main shortcoming of the SUS theory is to predict too high a value for P_m.

If one allows for the presence of a lattice contribution χ_L to the dielectric susceptibility in addition to that related to the proton ordering,[13] one has

$$a' = \frac{2Nk}{VP_m^2}c_2'\frac{1}{\zeta} \quad \text{with} \quad \zeta = 1 + \frac{2\chi_L N\beta}{VP_m^2}. \quad (31)$$

For the same value of a' and of the parameters ϵ_0, ϵ_1, β, one now obtains $P_m \sim 5.5\ \mu C/cm^2$ if $\chi_L \sim 2.2$. Although it is not very high, it seems rather difficult to explain such a value for χ_L.

The comparison between the SUS theory and our experimental results is summarized in Fig. 11 (for 0- and 1375-V/cm dc applied field).

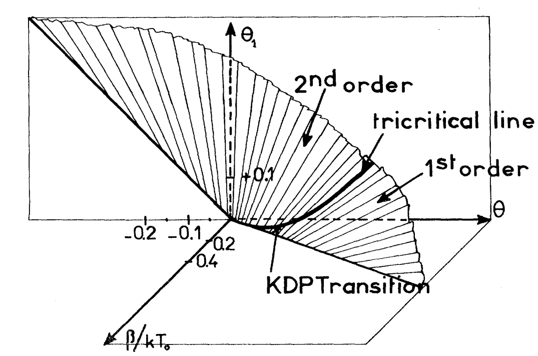

FIG. 10. Schematic diagram of the transition character according to the values of the various parameters of the SUS theory. The origin ($\Theta_1 = \Theta = \beta = 0$) corresponds to Slater's original approximation.

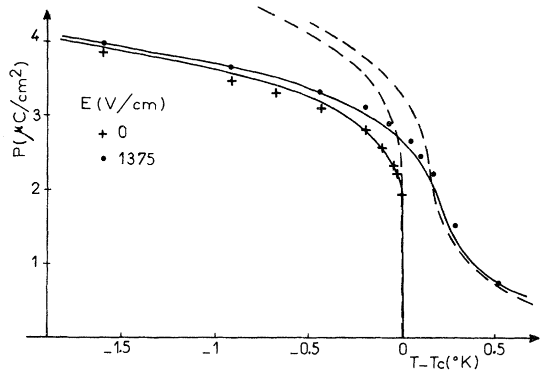

FIG. 11. Comparison of SUS theory with the spontaneous polarization deduced from our birefringence data (for dc fields $E=0$ and $E=1375$ V/cm). The lines are calculated by taking $\epsilon_0/k=48\,°K$, $\epsilon_1/k=350\,°K$, $\beta/k=26.5\,°K$. Solid lines with $\chi_L=2.2$ ($P_m=5.5\ \mu C/cm^2$). Dashed lines with $\chi_L=0$ ($P_m\sim 7\ \mu C/cm^2$).

V. CONCLUSION

We have shown in this work that the phenomenological relations between the linear and nonlinear optical susceptibility coefficients χ_{12}^{ω} and $\chi_{31}^{2\omega}$ are well proportional, and a comparison with the most recent data on the spontaneous polarization P_3 and spontaneous shear x_6 indicates that they are also proportional to the order parameter. The birefringence technique provides a convenient method of investigating the phase transition under applied dc field, and our observations confirm the first-order character of the KDP transition.

A quantitative description of the variation of the order parameter with the temperature near T_c in the framework of the Landau theory needs the introduction of fourth-, sixth-, and eighth-degree terms in P; this indicates that the transition is not far from the "tricritical" situation. No major departures from the Landau theory are present in our observations.

The statistical theory of SUS has the merit of providing a mechanism able to explain qualitatively the possibility of a near-tricritical transition. A quantitative agreement may nevertheless be obtained, but only by the introduction of too many unknown coefficients to be really meaningful. It seems obvious now, in view of the recent light-scattering experimental results,[14,15,31,32] that dynamical aspects must be taken into account in a microscopic picture of the transition. But the proton mode is coupled to the optic and acoustic modes and this makes the calculation of the spontaneous polarization too complicated to allow a comparison with the present data.

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