Study of the phase transition of benzil by simultaneous Raman-scattering and domain-structure investigations

J. Sapriel, A. Boudou, and A. Perigaud

Centre National d'Etudes des Télécommunications, 196 rue de Paris, 92220 Bagneux, France

Backward Raman measurements of external modes between 300 and 5 K are reported. For the first time the existence of an underdamped soft optical mode above and below the transition temperature (83.5 K) is evidenced. The soft mode of the high-temperature phase, of E symmetry, possibly induces the transition. Simultaneous studies of the domain structure in the low-temperature phase lead to the identification of W and W' walls. The orientation of the W' walls gives the ratio a/c of the independent components of the spontaneous strain tensor of the low-temperature phase which according to symmetry considerations is ferroelectric as well as ferroelastic. Complementary measurements of 90° Raman scattering and dielectric-constant temperature variations are also reported.

I. INTRODUCTION

Benzil ($C_6H_5COCOC_6H_5$) is a pale yellow organic crystal with large optical nonlinearities[1] which belongs to the class 32 (space group $P3_121$ or $P3_221$) at room temperature. When performing optical measurements on (001) plates of benzil Esherick and Kohler concluded[2] in favor of a reversible low-temperature phase transition at 84 K.

The loss of the threefold axis, suggested by the appearance below 84 K of birefringence[2] in the plane perpendicular to the z axis, might be accompanied by a well-defined ferroelastic domain structure. Such a structure is constituted of planar domain walls, the orientations of which have been determined in Ref. 3 from the symmetries of both the upper and lower phases and from the relative values of the spontaneous strain components.

Besides, previous polarized-Raman-scattering measurements have been performed[4] between 293 and 123 K, but no temperature dependence of the spectra has been noted, which could be related to the proximity of the transition. Another Raman study appeared more recently[5] on the phase transition of benzil under pressure. But the phonon spectra reported showed no indication of the symmetry of the modes and showed very little resemblance to those of Ref. 4.

The preceding considerations have led us to perform direct optical observations on benzil crystals in order to detect the appearance of a domain structure, the study of which constitutes an efficient tool for the determination of the species[6] of the ferroelastic transition as well as the relative magnitude of the spontaneous tensor components. The result of this study confirmed the existence of the transition at the temperature announced by Esherick and Kohler. In addition, we resumed polarized-Raman measurements between

room temperature and 5 K in order to obtain information on the lattice-dynamics aspect of the transition. Actually, these investigations permitted the discovery of soft optical modes in the high- and low-temperature phases.

Our crystals were grown in the laboratory from a saturated solution of benzil in xylene, by a very slow lowering of the temperature from 34.7 to 30.8 °C. High-quality single crystals up to 100 cm³ were obtained with the familiar faces of quartz crystals indicated in Fig. 1 ended by very large parallel m planes facing each other. From these rectangular parallelepiped crystals were prepared with their faces perpendicular to the x, y, z axes of the trigonal system, in keeping with the conventional rules.[7] The cutting of the samples was performed with a miniature saw constituted by a rotating thread dipped in xylene. The parallele-
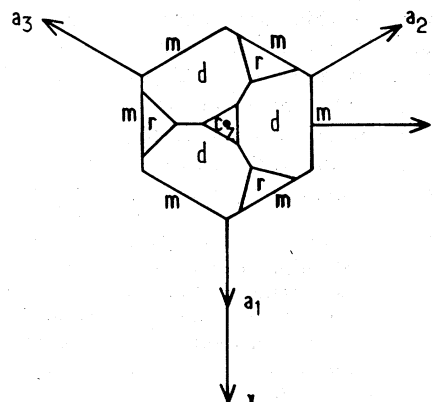

FIG. 1. External shape of benzil crystals, showing the familiar faces of quartz. The coordinate axes x, y, z are represented with respect to the hexagonal axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$. The faces m, d, r, c are parallel, respectively, to the atomic planes $(10\bar{1}0)$, $(10\bar{1}2)$, $(10\bar{1}1)$, and (0001).
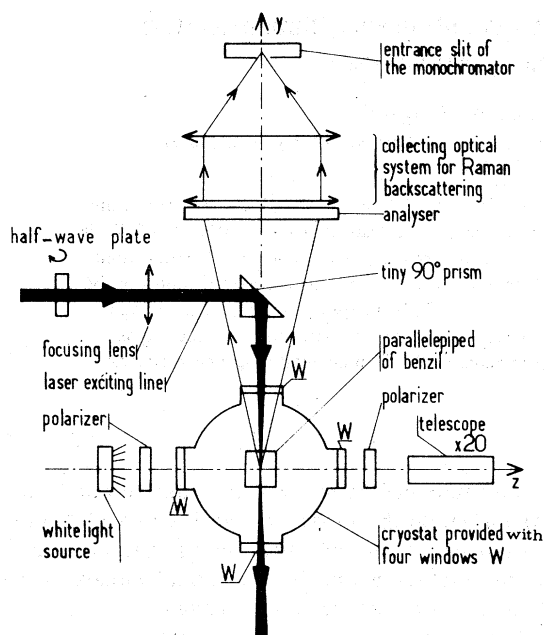
FIG. 2. Experimental setup for simultaneous Raman and domain-structure studies vs temperature in benzil. In the case of the figure, Raman spectra are obtained from backscattering (y direction) while the domain structure is observed in the z direction by means of a telescope with a magnification of 20.

pipeds were polished by abrading the surfaces on a soft paper damped with xylene.

Our experimental setup is sketched in Fig. 2 and is conceived in order to perform simultaneous Raman measurements in a backscattering geometry, perpendicular to the direction of the domain structure optical observations. The benzil crystal was positioned in a little copper box, the dimensions of which are scarcely larger than those of the sample in order to avoid any stress when lowering the temperature. This box was held inside the cryostat and was provided with four apertures at right angles in order to permit simultaneous domain observations and Raman-scattering studies. The benzil crystal was cooled by a con-

tinuous flow of gaseous helium which allowed a homogeneous temperature regulated to better than 0.1 K during all the measurement time. In the experimental conditions described above, the crystal remained undamaged after several tens of phase-transition cycles.

II. DOMAIN STRUCTURE OF BENZIL LOW-TEMPERATURE PHASE

The loss of the threefold axis of the point group 32 can only give rise to the classes 2 or 1 if one considers that the point group of the low-temperature phase is a subgroup of the prototype phase. Actually, it can easily be checked by means of crossed polarizers that proper directions for optical vibrations in a single domain of the low-temperature phase of benzil are parallel to one of the three equivalent x axes of the prototype structure. This indicates a transition to the monoclinic system, in agreement with the fact that, in the low-temperature phase, the optic plane is perpendicular[2] to x. The crystal therefore belongs to the $32F2$ species and according to symmetry considerations[6] ferroelectricity and ferroelasticity completely couple in the low-temperature phase. There are three orientation states giving rise to three types of domains (called 1,2,3) differing in spontaneous strain tensor $\overset{\leftrightarrow}{S}$ as well as in spontaneous polarization $\vec{P}_s$ (Table I). The different domains are deduced one from the other by a 120° rotation around the z axis.

In a twinned crystal at least two orientation states coexist. The domain boundaries are two directions of plane solutions of the equation $(S_{ij} - S'_{ij})x_i x_j = 0$, $\overset{\leftrightarrow}{S}$ and $\overset{\leftrightarrow}{S}'$ being the spontaneous strain tensors of the two orientation states under consideration.[3] The results are reported in Table II where the equations of the domain walls are given as functions of the coordinates x, y, z of the prototype phase. Two types of domain walls can be distinguished. W walls which are prominent planes of fixed indices and W' walls the orientations of which depend on the relative magnitude of the components of the spontaneous strain tensor.[3]

TABLE I. Spontaneous polarization $\vec{P}_s$ and spontaneous strain tensor $\overset{\leftrightarrow}{S}$ associated with different orientation states D_1, D_2, D_3 in benzil in the ferroic phase. In the case of D_1, X is parallel to the monoclinic axis; D_2 and D_3 are deduced from D_1, respectively, by a $-120°$ and a $+120°$ rotation around the z axis of the prototypic phase. The direction of $\vec{P}_s$ is given by its unit vector and $\overset{\leftrightarrow}{S}$ is expressed in matrix form.

$\vec{P}_s$ direction	D_1 $(1,0,0)$	D_2 $-\frac{1}{2}(1,\sqrt{3},0)$	D_3 $\frac{1}{2}(\bar{1},\sqrt{3},0)$
$\overset{\leftrightarrow}{S}$ components	$\begin{pmatrix} a & 0 & 0 \\ & -a & c \\ & & 0 \end{pmatrix}$	$\begin{pmatrix} -a/2 & \sqrt{3}a/2 & \sqrt{3}c/2 \\ & a/2 & -c/2 \\ & & 0 \end{pmatrix}$	$\begin{pmatrix} -a/2 & -\sqrt{3}a/2 & -\sqrt{3}c/2 \\ & a/2 & -c/2 \\ & & 0 \end{pmatrix}$

TABLE II. Domain–wall orientations in benzil. In the species $32F2$ the W walls are neutral though the W' walls are charged. In each row are given the set of mutually perpendicular planar walls separating two adjacent domains (indicated in the first column). The coordinates x, y, z refer to the orthogonal system of the prototype phase; a and c are the components of the strain tensor (see Table I).

Domains under consideration	W wall equations	W' wall equations
$D_2 \leftrightarrow D_3$	$x = 0$	$z = -ay/c$
$D_1 \leftrightarrow D_2$	$x = \sqrt{3}\,y$	$a\,(\sqrt{3}\,x + y) - 2cz = 0$
$D_1 \leftrightarrow D_3$	$x = -\sqrt{3}\,y$	$a\,(\sqrt{3}\,x - y) + 2cz = 0$

It can be noted that the equations of the walls are identical[8] to those given for $Pb_3(PO_4)_2$, a pure ferroelastic belonging to different $3mF2/m$ species. This is a consequence of the result which asserts that the ferroelastic domain structure only depends on the Laue classes of the prototype (L_p) and ferroelastic (L_f) phases (in this case L_p is $\bar{3}m$ and L_f is $2/m$). The equations of the domain walls do not depend on the spontaneous polarization $\vec{P}_s$.[3,9] But the existence of $\vec{P}_s$ leads to the creation of electrical charges on the surface of the wall of density $\vec{P}_s \vec{n}$, $\vec{n}$ being the unit vector of the normal to the wall external to the domain under consideration. It can readily be demonstrated that the electrical charges in both sides of a wall, owing to two different $\vec{P}_s$ and $\vec{P}'_s$ vectors of the two adjacent domains, exactly compensate on W walls, but add in the case of W' walls when one considers the $32F2$ species. W walls are therefore neutral and W' walls charged in the case of benzil.

We performed domain-structure observations between two rotating polarizers. When the temperature was lowered down to 83.5 K, domain structures appeared. The domain walls, which separate two regions of different optical contrast between the couple of polarizers, were visualized by their traces on the crystal faces. When observing the faces perpendicular to z, we noted traces parallel to the y axis of the prototype phase and along the two equivalent directions deduced from y by 120° rotations around z. Besides, traces parallel to the z axis were seen on the faces (100) and (010). These traces correspond undoubtedly to the W walls, in conformity with the results of Table II. W' walls occur less frequently, probably because of their electrical charge. Yet, we observe them sometimes under certain conditions (a fast crossing of the transition temperature seems to favor their occurrence). The traces on the (001) planes are along one of the three equivalent x directions of the prototype phase. The trace inclinations on (010) faces,

for instance, give the ratio a/c. If we call θ the angle of the W' planes with the x axis, we obtain from the equations of Table II $a/c = (2\tan\theta)/\sqrt{3}$. We measured $\theta = 17.9°$, value which gives $a/c = 0.32 \pm 0.02$. The W'-walls inclinations appeared, according to our observations, to be constant with temperature. This feature is characteristic of a constant ratio a/c and is due to the fact that a and c are both proportional to the same power α of the order parameter (α is equal or superior to 1 according as the transition is proper or improper[10]).

We have also examined the possibility that the low-temperature phase of benzil is triclinic instead of monoclinic through the domain structure. Yet in this case the theory predicts 6 domains of different kinds[3] instead of the 3 actually observed, and the number of permissible domain wall orientations would be 12, instead of the 6 really found at low temperature. Additional impermissible walls would also appear which have never been seen in our experiments.

It is worth noticing that we have also been able to observe along the z direction of the crystal when we approached the transition very slowly, the coexistence of the two phases with moving boundaries, whose traces on the (001) plane were approximately parallel to the y directions. Sometimes, we succeeded in stabilizing a structure where one phase was surrounded by the other. These observations constitute an indication of the first-order nature of the transition, which is confirmed by the fact that the angle between the optic axes increases from 0° to 24° at the phase[2] transition. Besides, the very weak values of the hysteresis (< 0.1 K) and the latent heat[2] (< 0.04 cal g^{-1}) attest that the transition is weakly first order.

The number and the sizes of the domains in the crystal varied from one experiment to another. But sometimes it was possible to obtain a single (or nearly single) region in the crystal, large enough to perform polarized-Raman measurements.

III. TEMPERATURE DEPENDENCE OF THE EXTERNAL RAMAN MODES

A. Study of the prototype phase

We restricted our study to the low-frequency modes, i.e., below 100 cm^{-1} due to intermolecular vibrations. There are three molecules of site symmetry 2, in the unit cell, arranged spirally along the z axis.[11] As the unit cell belongs to the point group 32, the Raman tensors have the well-known form[12]

$$A_1 \qquad\qquad E(x) \qquad\qquad E(y)$$

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}.$$

$E(x)$ and $E(y)$ correspond to vibrations parallel to the x and y axes, respectively, and are also infrared active. The $A_2(z)$ modes[13] polarized along z are only infrared active.

Group-theory considerations[13] applied to benzil give a total number n of external modes equal to 15 (2 of type A_1, 3 of type A_2 and 5 doubly degenerate of type E). The polar modes E split into LO and TO modes which we label E_L and E_T. About 500 mW of a Coherent Radiation CR3 Ar$^+$ laser ($\lambda = 5145$ Å) was focused in the sample which was observed in backscattering configurations in the x and y directions. We avoided in the prototype phase the use of the z direction for the light propagation where the optical activity[14] could introduce important modifications of the laser beam polarization. These precautions become meaningless in the ferroelastic phase where the effect of the optical activity is negligible with respect to the birefringence.[7] The spectra were detected through a T800 Coderg triple monochromator ended by a cooled 56 TVP Radiotechnique multiplier with magnetic defocusing and a dc detection (602 Keithley electrometer). The resolution given by the Rayleigh linewidth was of the order of 0.6 cm^{-1}.

In Table III we reported the frequencies of the optical Raman modes. A_1 modes corresponds to $y(xx)\bar{y}$, $y(zz)\bar{y}$, $x(yy)\bar{x}$, and $x(zz)\bar{x}$ scattering geometries; E_T modes are given by $y(xx)\bar{y}$ and E_L by $y(xz)\bar{y}$, $x(yy)\bar{x}$, and $x(yz)\bar{x}$ configurations. Thus backscattering allows the distinctions between longitudinal and transverse modes, which are not possible[4] in 90° scattering. As it can be seen in Table III the splitting LO-TO is very weak. Besides, the values of A_1 and E modes are in fairly good agreement with those published in Ref. 4. The E mode situated at 47.5 cm^{-1} begins to be clear below 100 K when the broadness of the adjacent

TABLE III. Frequencies of the Raman-active phonons in the 32 phase of benzil with their assignments, at room temperature. The fifth E mode, situated at 47.5 can be seen only below 100 K. Besides the 28.8 line has a thermal behaviour of a second-order vibration and could be considered as the difference between the two A_1 modes[4] at 37.6 and 68.8.

Modes	Frequencies (cm$^{-1} \pm 0.2$)
A_1	28.8; 37.6; 68.8
E_{TO}	15.1; 37.9; 57. ; 82.5
E_{LO}	15.3; 38. ; 57.8; 82.5

lines diminishes.

When cooling from 300 to 84 K the lowest-frequency E modes decrease markedly from 15.5 to 8 cm^{-1} (Fig. 3). This is actually a behavior of a soft optical mode inducing a phase transition from 32 without modification of the number of atoms in the unit cell.[15] We have plotted the frequency ν of the E_T in the $y(xx)\bar{y}$ geometry versus temperature (right-hand side of Fig. 4). The square of the frequency has a linear behavior in this temperature range (M-N portion of the curve of Fig. 5). We have also observed that the lowest-frequency E_L mode, given by the scattering geometry $y(zx)\bar{y}$, undergoes a very similar behavior, the distance between these two E_L and E_T modes remaining small (less than 0.5 cm^{-1}). Thus, our observa-
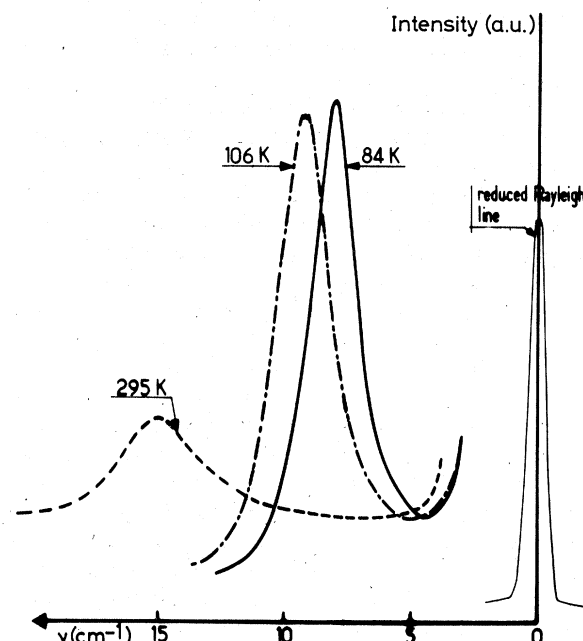

FIG. 3. Frequency variations of the soft E_T mode line in the high-temperature phase of benzil [$y(xx)\bar{y}$ scattering geometry].
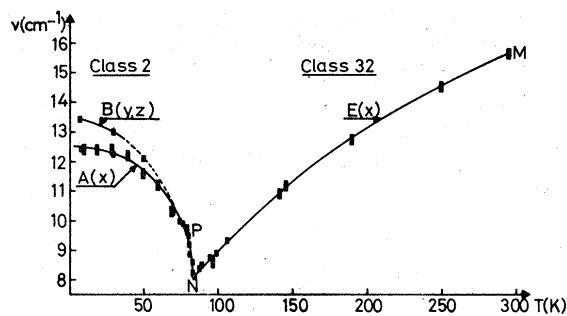
FIG. 4. Frequency dependence of the soft modes between 300 and 5 K in benzil: $E(x) \to y(xx)\bar{y}$; $A(x) \to y(xx)\bar{y}$; $B(y,z) \to y(zx)\bar{y}$.

tions agree with the assumption of Ref. 4, concerning the weakness of the splitting LO-TO, which characterizes a crystalline phase where the anisotropy forces predominate over the long-range electrostatic forces.

B. Temperature dependence of the soft modes in the low-temperature phase

In the monoclinic phase A_1 modes of the prototype phase transform to $A(x)$, E modes to $A(x)$ $+B(z,y)$, the Raman A and B tensors having the following form[12]:

$$
\begin{pmatrix} A(x) \\ a\ 0\ 0 \\ 0\ b\ d \\ 0\ d\ c \end{pmatrix} \qquad
\begin{pmatrix} B(y,z) \\ 0\ e\ f \\ e\ 0\ 0 \\ f\ 0\ 0 \end{pmatrix}.
$$

A_2 modes which were only infrared active in the trigonal phase give $B(z,y)$ Raman active modes. On the whole, there are 15 external modes. If one considers that all these modes are polar, i.e., split into longitudinal and transverse components, the identification of the complete set of Raman lines in such a relatively narrow frequency range ($\sim$90 cm^{-1}) appears as uncertain. Moreover, the eventuality of a weak proportion of undesirable domains does not make the task easier in the sense
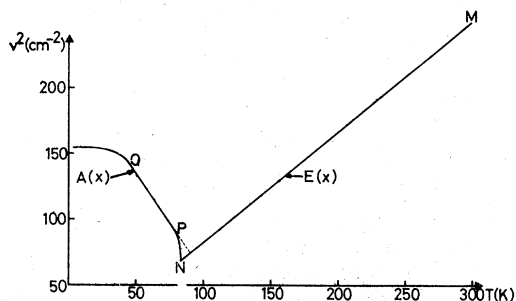

FIG. 5. Square frequency dependence of the soft modes. MN is the high-temperature phase. PQ is the linear part of the curve $\nu^2 = f(T)$ in the low-temperature phase.
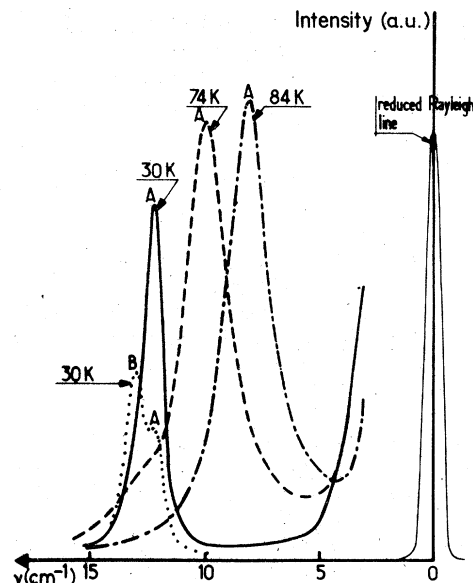

FIG. 6. Frequency variations of the soft modes lines in the low-temperature phase of benzil. $A \to y(xx)\bar{y}$; $B \to y(zx)\bar{y}$.

that it introduces changes in the light polarizations and also possible frequency shifts on the lines due to the phonon dispersion[16] in this biaxial crystal, due to the reflections and refractions of the incident beam on the domain boundaries.[3]

We therefore focused our attention only on the two lowest frequencies $A(x)$ and $B(x)$ which come from the splitting of the soft E mode already studied in the trigonal phase.

In Fig. 6 we have reported the $A(x)$ line of lowest frequency, from 84 to 30 K. Moreover the relative position of the $B(y,z)$ and $A(x)$ lines at 30 K are given by the dotted line at the left side of Fig. 6, issued from a prevalent B symmetry [scattering geometry $y(zx)\bar{y}$].

We have plotted (left-hand side of Fig. 4) the frequencies of $A(x)$ and $B(y,x)$ modes versus temperature between 84 and 5 K. It can be noted that these two lines come closer, till they merge, when the temperature approaches the transition. Simultaneous optical observations, described in the previous paragraph, indicated that the domain structure appeared on cooling as soon as the minimum (point N of Fig. 4) is reached. The squared frequencies of the soft $A(x)$ modes are plotted on the left side of Fig. 5. The behavior is linear between 45 and 80 K (points Q and P). The linewidth of the soft $E(x)$ and $A(x)$ modes are represented in Fig. 7. Except for a small singularity near 84 K, they show a regular decrease from 3.5 to 0.6 cm^{-1} when the temperature is lowered from 300 to 5 K. These soft modes can thus be considered as underdamped.
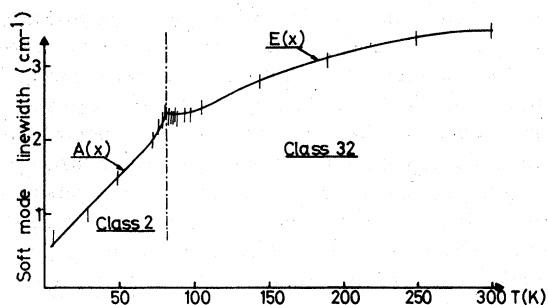
FIG. 7. Linewidth of the soft modes in benzil in both high- and low-temperature phases.

IV. COMPLEMENTARY MEASUREMENTS AND DISCUSSION

In this paper we have studied two aspects of the phase transition of benzil which occurs according to observations at 83.5 ± 0.5 K. The first aspect is concerned in the domain structure, particularly the domain wall orientations. W walls were identified as well as W' walls. In the case of W' walls, the measurements of their orientations with respect to the x axis, gave us a constant ratio a/c of the spontaneous strain components all over the low-temperature phase. The second part of this study has been devoted to polarized Raman measurements all over the range 5–300 K. The chief result obtained is the discovery of soft optical modes above and below the transition temperature. These modes have been identified and their frequencies as well as their width have been determined versus temperature.

Optical observations, i.e., number of domains of different kinds, number, and orientations of the domain walls, position of the optical plane and de-

termination of the proper directions, for polarized vibrations (cf. Sec. I) had led us to the conclusion that the low-temperature phase of benzil is monoclinic. Our polarized-Raman measurements seem to be consistent with this point group which was confirmed by EPR results[17] as well as ENDOR study.[18]

Now let us examine some aspects related to the existence of the soft optical mode E in the high-temperature phase.

A. Relation between the softening of this mode and the variations of the dielectric constant

We have recorded (Fig. 8) the variations of the dielectric constant versus temperature from 10 to 230 K of a plate of benzil perpendicular to the x axis. A very small dielectric peak is observed (about $\frac{5}{1000}$ enhancement with respect to the mean value of the high-temperature phase). The maximum of the dielectric constant is situated at 82.5 ± 1 K and is in good accordance with the transition temperature obtained by Raman scattering and domain-structure observations. The variations of the dielectric constant which are negligible with respect to the softening of the E mode can be predicted from our Raman-scattering measurements through the generalized Lyddane-Sachs-Teller relation.[19]

$$\prod_{n-1} \frac{\omega_L^2(\alpha)}{\omega_T^2(\alpha)} = \frac{\epsilon_{\alpha\alpha}^0}{\epsilon_{\alpha\alpha}^\infty}, \qquad (1)$$

where α is the direction of a principal axis, ω_L and ω_T are the frequencies of the longitudinal and transverse modes polarized along α, ϵ^0 is the static dielectric constant, and ϵ^∞ is the high-frequency dielectric constant.
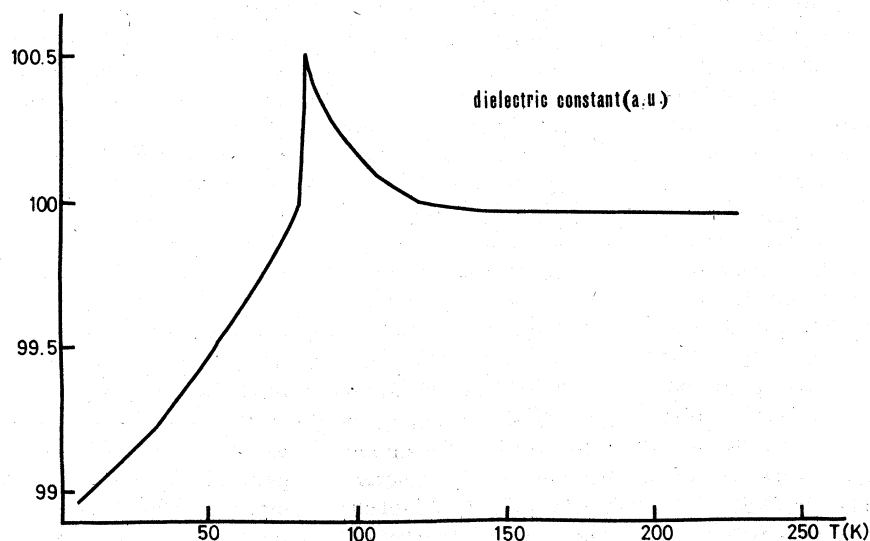

FIG. 8. Low-frequency (1.592 sec^{-1}) dielectric constant variations vs temperature observed on the x-cut plate of benzil.

The only Raman modes which vary strongly with temperature in the high-temperature phase are the lowest-frequency E_T and E_L modes (see Sec. III A). Besides, these modes are very close to one another at every temperature.

If we call $\Delta\omega$ and $\Delta\epsilon$ the frequency and dielectric-constant variations associated with a temperature variation ΔT, one obtains from (1)

$$\frac{1}{\epsilon_{\alpha\alpha}^0}\frac{\Delta\epsilon_{\alpha\alpha}^0}{\Delta T} = \frac{2}{\omega_L}\frac{\Delta\omega_L}{\Delta T} - \frac{2}{\omega_T}\frac{\Delta\omega_T}{\Delta T}, \qquad (1')$$

where the two terms of the second member of (1′) practically compensate one another and this explains the very small value observed for $(1/\epsilon_{\alpha\alpha}^0)(\Delta\epsilon_{\alpha\alpha}^0/\Delta T)$ (Fig. 8).

B. Role of this soft mode in the transition

We have found a soft E mode at the center of the Brillouin zone in the high-temperature phase by means of Raman backscattering. We have also performed additional Raman measurements at 90° which have confirmed the existence of the variations of this mode. This mode has the right symmetry to induce a proper transition[15] (without change in the number of atoms in the unit cell).

Nevertheless, right now new results on the crystallographic study of benzil are being published which set a problem since they announce a transition at 83 K accompanied by a quadrupling of the unit cell.[20] The existence of another soft mode situated at the zone boundary of the Brillouin zone in the high-temperature phase, could be assumed in the case of a quadrupling of the unit cell. This mode would be Raman active in the low-temperature phase and would soften more than the E mode already observed, if it really induced the transition at 83.5 K. We have therefore intensively searched for this eventuality by means of Raman scattering in all geometrical configurations.

Nevertheless no additional line appeared in the spectral range comprised between the A mode (issued from the E mode, in the low-temperature phase) and the Rayleigh line. Besides, an order-disorder transition occuring at 83.5 K seems unlikely when one considers the main features of the high-temperature phase Raman spectra. Indeed, the width of the Rayleigh and Raman lines are too weak to support such an assumption.

Thus it is not possible till now to conclude if the soft E mode induces the transition or not. This question might stimulate complementary Brillouin and neutron measurements. In the case where the transition is induced by the observed soft E mode, one can expect[21,22] a soft acoustical mode the velocity of which tends to zero at 83.5 K. Following Aubry and Pick[22] this mode is associated with a transverse acoustic wave propagating along the x axis.

Switching of the domains with an electric field or by means of a mechanical stress has still not been performed and would also characterize this transition which according to symmetry considerations is ferroelectric as well as ferroelastic.

ACKNOWLEDGMENTS

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