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Brillouin-scattering investigation of the ferroelastic transition of benzil

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The acoustic properties of benzil are investigated by means of Brillouin scattering in both high- and low-temperature phases. The elastic constants have been measured in the trigonal phase as a function of temperature from 300 to 84 K; it appears that the constant c_{44} is the most sensitive to the phase transition. The transverse acoustic mode of lowest energy which propagates along the x axis is a soft acoustic mode related to the same order parameter as the Brillouin-zone-center E soft optical mode. In the low-temperature monoclinic phase, measurements have been performed in the z direction for the longitudinal and transverse lines: the variation with temperature of the frequency and linewidth of these modes has been observed to be continuous at the phase transition.

I. INTRODUCTION

Benzil $C_6H_5COCOC_6H_5$ is a molecular crystal whose space group is $P321$ at room temperature.[1] Since the discovery of a phase transition by Esherick and Kohler[2] by means of a birefringence study versus temperature, several other investigations have observed the phase change in this crystal around 84 K: EPR,[3] electron-nuclear double resonance (ENDOR),[4] specific heat,[5] crystallographic,[6] and dielectric measurements.[7] Raman scattering experiments[7] have led to the observation of a soft optical mode whose frequency decreases substantially as the transition is approached from above or below. This soft mode is of E symmetry in the high-temperature phase and splits into A and B modes in the less symmetric phase. In the trigonal phase its squared frequency has a linear decrease typical of a Brillouin-zone-center order parameter.

The symmetry of the low-temperature phase was controversial, since contrary to the major studies which assigned a monoclinic class[3,4,7] to benzil below 84 K, x-ray measurements[6] led to the identification of a triclinic unit cell. Actually, the latter data have been shown[8] to be entirely compatible with a monoclinic base-centered C-type Bravais lattice whose primitive unit cell is triclinic. Moreover the volume of this unit cell is four times that of the trigonal unit cell.

In this paper, we present the results of a study of the acoustic properties of benzil related to the phase transition at 84 K. The velocity and attenuation of the acoustic phonons are determined versus temperature by means of Brillouin scattering. Preliminary measurements in the trigonal phase have been presented elsewhere.[9]

In Sec. II the experimental setup is described and the whole set of independent elastic constants is given as a function of temperature. The special feature of the z direction which is invariant in the three types of ferroelastic domains of benzil is pointed out, as well as its interest as an acoustic propagation direction in phase-transition study of this crystal. Finally, the relation between the observed acoustic soft mode and the previously discovered optical soft mode is discussed in Sec. III.

III. EXPERIMENTAL RESULTS

The Brillouin-scattering setup used for this study has a high resolution ($> 10^7$) and a high contrast ($> 10^8$). This is obtained by a tandem arrangement of a triple pass Fabry-Pérot monochromator, followed by a spherical Fabry-Pérot interferometer with a free spectral range of 1.48 GHz and a finesse of 50. The light source is a single frequency argon-ion laser with an output power limited here at 200 mW for $\lambda = 5145$ Å, in order to avoid sample heating. The spectra were recorded by repetitive scanning and stored in a multichannel analyzer.

In the cryostat used, the sample was cooled by a circulation of ^{4}He gas. The temperature of the gas was stabilized by a heater with a P.I.D. amplifier; the accuracy of temperature measurements was better than 1 K.

TABLE I. Correspondence between the scattering geometry and the elastic modulus in class 32 for the two samples of benzil. More details are given in Ref. 13. The samples "*a*" and "*b*" are defined in the text. BS is backscattering and RAS is right-angle scattering.

Samples	Scattering geometry	Acoustic propagation	Acoustic polarization	Elastic modulus
a	BS	[100]	L	c_{11}
a,b	BS	[001]	L	c_{33}
a	BS	[010]	T	c_{66}
a,b	BS	[001]	T	c_{44}
b	RAS	[100]	T	$\gamma_3=\frac{1}{2}\{c_{44}+c_{66}-[(c_{44}-c_{66})^2+4c_{14}^2]^{1/2}\}$
a	BS	[010]	L	$\gamma_4=\frac{1}{2}\{c_{11}+c_{44}+[(c_{11}-c_{44})^2+4c_{14}^2]^{1/2}\}$
a	RAS	[011]	L	$\gamma_{13}=\frac{1}{4}\{c_{11}+c_{33}+2(c_{44}-c_{14})$ $+[(c_{11}-c_{33}-2c_{14})^2+4(c_{13}+c_{44}-c_{14})^2]^{1/2}\}$

A. Elastic constant variations in the trigonal phase

Two samples were investigated. Sample "*a*" had its faces perpendicular to the crystallographic axes of the trigonal phase. Sample "*b*" was a rectangular parallelepiped whose edges were parallel to the z axis and to the bisectors of the x and y axes of the high-temperature phase. These samples which were carefully polished allowed the measurement of the set of six independent[10] elastic constants c_{11}, c_{33}, c_{44}, c_{66}, c_{13}, and c_{14} of the trigonal system. Backscattering as well as right-angle Brillouin experiments have been performed. If one takes v and ω^* as the velocity and angular frequency of the acoustic wave, the conservation laws on wave vectors and energy of light and elastic wave give the straightforward expressions[11]:

$$\omega^{*2}=v^2\omega^2(n_s^2+n_i^2)/c^2 \tag{1a}$$

for 90° scattering,

$$\omega^{*2}=v^2\omega^2(n_s+n_i)^2/c^2 \tag{1b}$$

for backscattering, where c is the light velocity in vacuum, ω the photon angular frequency, n_i and n_s the refractive indices of the crystal associated to the incident and scattered optical polarizations, respectively.

At room temperature we measured $n_x=1.679$ and $n_z=1.693$ at 5145 Å and $n_x=1.688$ and $n_z=1.700$ at 4880 Å. The values of v are deduced from Eqs. (1) and the measured Brillouin shift ω^*. The corresponding elastic modulus γ is then deduced $(\gamma=\rho v^2)$. The crystal density ρ is calculated from the lattice parameter data[6] versus temperature. A detailed description of the procedure used for the determination of the acoustic properties of crystals by means of Brillouin scattering is given in Refs. 12 and 13. For each sample labeled *a* or *b* we have indicated in Table I the scattering geometry, the corresponding propagation, and polarization directions of the acoustic waves, the expression of the elastic modulus as a function of the elastic constants c_{ij}; c_{11}, c_{33}, c_{44}, and c_{66} are therefore directly obtained, though c_{14} and c_{13} are deduced from γ_3, γ_4, and γ_{13} determinations. In the γ expressions, the piezoelectric properties, which are rather weak in benzil,[14] have been completely neglected. In Table II are reported the room-temperature values of c_{ij} from our experiments (first column) as well as those obtained in Ref. 14. The ultrasonic values are smaller than the Brillouin-scattering ones by a few percent for all the elastic constants. These discrepancies, which are higher than the experimental uncertainties, could be attributed to the frequency dependence of the acoustic velocities, if differences between samples are completely ruled out.

The temperature variations of the elastic constants c_{ij} between 300 and 84 K are plotted in Fig. 1.

TABLE II. Room-temperature values of the elastic constants of benzil (10^{10} N m^{-2}).

Elastic constant	Brillouin measurements (this work)	Ultrasonic results (Ref. 14)
c_{11}	1.123	1.092
c_{33}	0.856	0.823
c_{44}	0.115	0.108
c_{66}	0.288	0.274
c_{13}	0.335	0.326
c_{14}	−0.061	−0.051

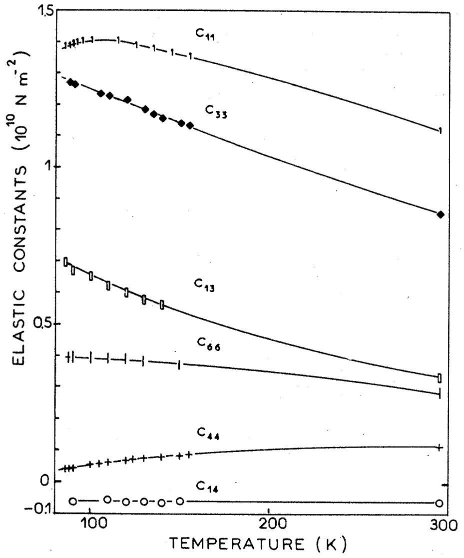

FIG. 1. Elastic constant variations vs temperature in the trigonal phase.

Among them, the elastic constant c_{44} is the most sensitive to the phase transition and softens markedly when the critical temperature is approached from above. This constant corresponds to the unpolarized transverse-acoustic wave propagating in the z direction. Nevertheless it is not obvious that this mode is the softer that can be encountered in the benzil crystal since c_{44} is contained in the velocity expression of many other modes. The velocities v of the three acoustic waves which propagate along the direction parallel to the unit vector $\vec{s}$ are obtained from the secular equation[11–13]:

$$\det|c_{ijkl}s_js_l - \rho v^2\delta_{ik}| = 0 \ , \quad i,j,k,l = 1,2,3 \ ,$$

where c_{ijkl} are the rigidity tensor components. There are one quasilongitudinal and two quasitransverse-acoustic waves whose velocity are designated, respectively, by v_{L}, v_{T_1}, and v_{T_2} ($v_{\mathrm{L}} > v_{\mathrm{T}_1} > v_{\mathrm{T}_2}$). One usually defines the slowness of an acoustic mode as the inverse $1/v$ of its velocity. We have plotted the slowness curves for the three modes L, T_1, and T_2 in the principal planes xy, yz, and xz [Figs. 2(a), 2(b), and 2(c)] in polar coordinates and for three values of the temperature $T = 295$, 150, and 85 K. In these curves the radius vector is parallel to the propagation direction and its modulus is equal to the slowness value for the corresponding acoustic wave. Figures 2(a), 2(b), and 2(c) show that the velocity of the longitudinal waves increases when approaching T_c. In the plane xy, the curves corresponding to T_1 and T_2 are well separated. The modulus of T_1 hardens

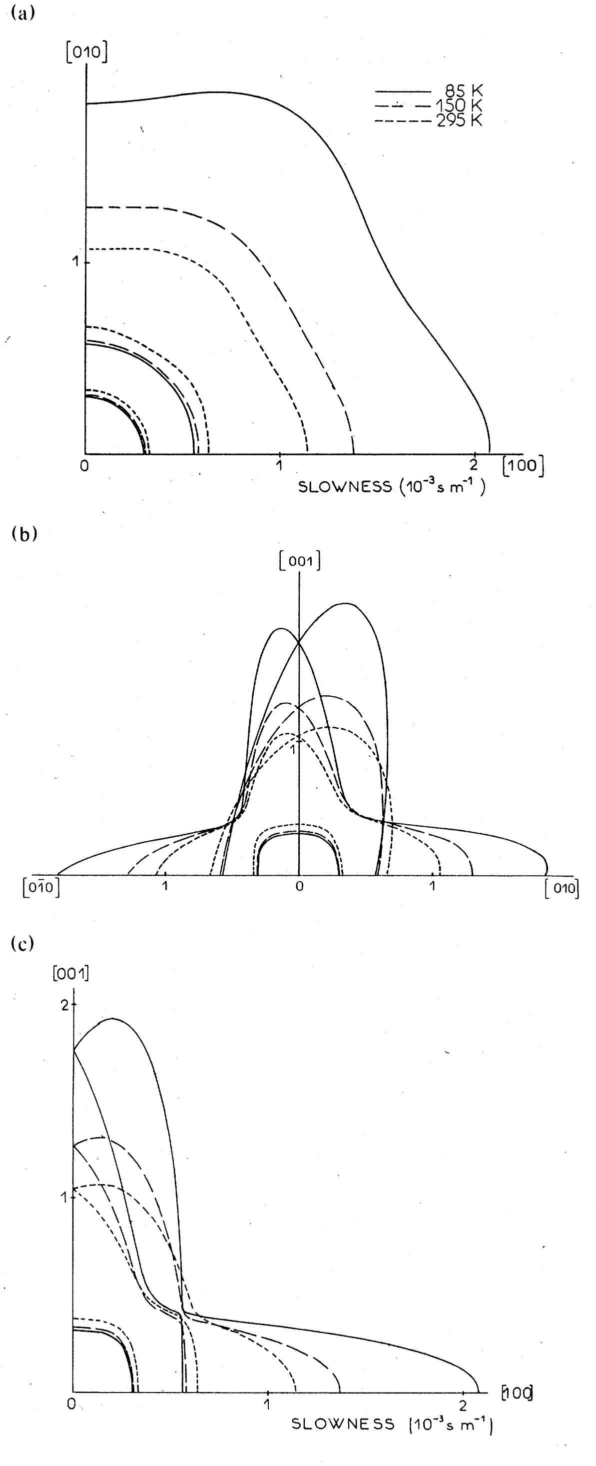

FIG. 2. Slowness curves $1/v$ in benzil in the high-symmetry phase at three temperatures 295, 150, and 85 K (polar coordinates) $1/v_{\mathrm{L}} < 1/v_{\mathrm{T}_1} < 1/v_{\mathrm{T}_2}$ (L: longitudinal, T_1 and T_2: transverse). (a) Slowness curves in the xy plane. (b) Slowness curves in the yz plane. (c) Slowness curves in the xz plane.

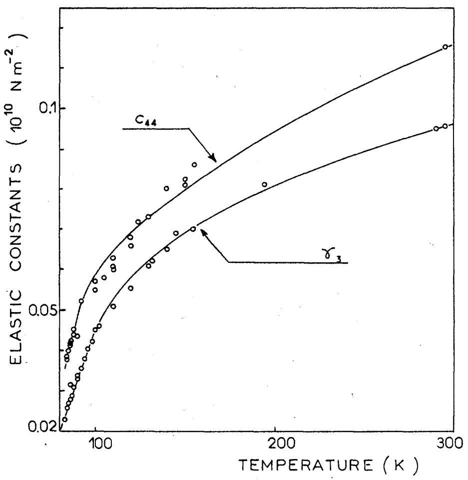

FIG. 3. Comparison between the softening of the elastic moduli c_{44} and γ_3 which are associated to transverse acoustic waves propagating, respectively, along the z and x axes.

though the one of T_2 softens markedly. Overlaps of T_1 and T_2 slowness curves are observed in Figs. 2(b) and 2(c); it can be noted that the directions $\vec{s}(s_1=0,s_2,s_3)$ and $\vec{s}'(s_1'=0,\ s_2'=-s_2,\ s_3'=s_3)$ are obviously nonequivalent in the plane yz as can be checked in Fig. 2(c). When the transition temperature is approached from above, the softer mode among all those considered is the transverse acoustic mode T_2 propagating along x and approximately polarized along y. Its modulus γ_3 is expressed by

$$\gamma_3=\frac{1}{2}\{c_{44}+c_{66}-[(c_{66}-c_{44})^2+4c_{14}^2]^{1/2}\} \ .$$

It is clear according to the c_{ij} values plotted in Fig. 1 that the variation of γ_3 versus temperature is chiefly due to the behavior of c_{44} and that γ_3 is always inferior to c_{44} ($c_{66} > c_{44}$ in the whole temperature range 300–84 K). The c_{44} and γ_3 variations are plotted in Fig. 3. In the vicinity of T_c the elastic moduli γ_3 and c_{44} undergo linear variations which intersect the temperature axis at approximately the same temperature $T_0 \simeq 64 \pm 2$ K (Fig. 4). These two modes exhibit approximately the same behavior with respect to the transition; γ_3 seems more interesting to study as it presents the most marked softening. However, as we will show in Sec. II B, c_{44} is easier to measure in the low-temperature phase.

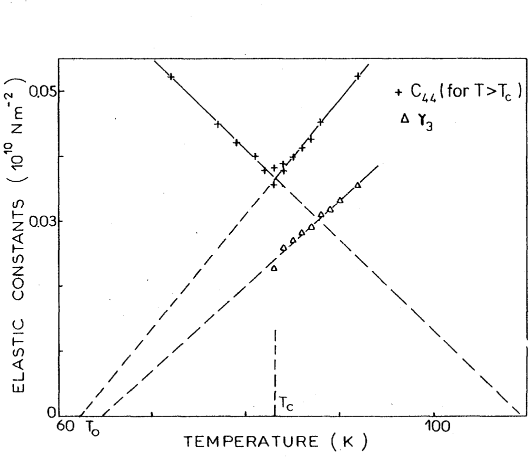

FIG. 4. Linear approximation of the c_{44} and γ_3 variations in the vicinity of the critical temperature T_c.

B. Brillouin measurements in the monoclinic phase

Below 84 K, benzil belongs to the monoclinic point group 2. In this phase the crystal is ferroelectric as well as ferroelastic. The ferroelastic domain structure has been studied elsewhere.[7–15] It is characterized by three types of orientation states[15,16] of the crystal which can be deduced one from the other by a ± 120° rotation with respect to the z axis of the high-temperature phase. The scattering spectra are therefore composed of different Brillouin lines correponding to the contribution of the various orientation states: in each of them the acoustic phonons involved are associated to propagation directions which are generally nonequivalent with respect to the crystal axes. The overlapping observed between the Brillouin lines makes very hard the identification of the acoustic modes. Nevertheless the z axis of these different domains are all parallel to the z axis of the high-symmetry phase. It can be shown that this direction is the only one which is common to all the

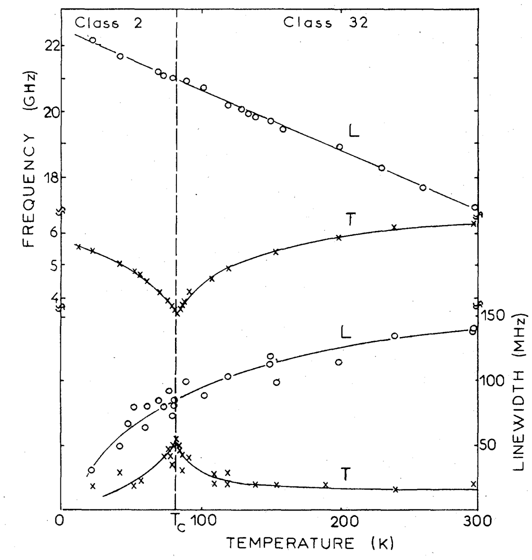

FIG. 5. Acoustic propagation along the z axis. Frequency shift and linewidth of the Brillouin lines in the two phases of benzil. L: longitudinal; T: transverse.

TABLE III. Correspondence between the acoustic modes propagating along the z axis in the trigonal and monoclinic phases.

Trigonal phase Elastic modulus	Trigonal phase Acoustic polarization	Monoclinic phase Acoustic polarization	Monoclinic phase Elastic modulus
c_{33}	L	QL	$\gamma_{\mathrm{QL}}=\frac{1}{2}\{c_{33}+c_{44}+[(c_{33}-c_{44})^2+4c_{34}^2]^{1/2}\}$
c_{44}	T	T	$\gamma_{\mathrm{T}}=c_{55}$
		QT	$\gamma_{\mathrm{QT}}=\frac{1}{2}\{c_{33}+c_{44}-[(c_{33}-c_{44})^2+4c_{34}^2]^{1/2}\}$

domains.[17] Besides, backscattering in this direction gives three acoustic modes: one is pure transverse T and the two others are quasilongitudinal QL and quasitransverse QT. The correspondence between the moduli of the modes in the 32 and 2 phases is given in Table III, for the propagation along the z axis. It can be seen that the degenerate transverse-acoustic wave of the trigonal phase splits into T and QT below 84 K, though the longitudinal mode transforms into a quasilongitudinal mode QL. It is clear from Fig. 5 that the transition has no effect upon the longitudinal mode. On the other hand the transverse wave undergoes a softening on both sides of the critical temperature T_c and its linewidth broadens when approaching T_c from above and below.

From the continuity of the frequency of the longitudinal mode along the z axis and the expression of γ in both phases, it can be seen that c_{34} is very weak at the transition. Besides, the investigations in the low-temperature phase between 84 and 5 K have evidenced only one transverse line of Lorentzian shape. As the calculation indicates that both transverse and quasitransverse modes would have almost the same intensity, this shows that $\gamma_{\mathrm{QT}} \simeq \gamma_{\mathrm{T}}$, i.e., $c_{44} \simeq c_{55}$; in the low-temperature phase, the splitting is then too small to allow the separation of the two components.

III. DISCUSSION AND CONCLUSION

The soft optical mode E which has been observed in Raman scattering is related to a Brillouin-zone-center order parameter[18,19] for a transition $32 \rightarrow 2$ occurring without a change in the number of atoms in the unit cell. Symmetry considerations[18] show that such an order parameter detemines the presence of a cubic polynomial in the free-energy expansion and therefore induces necessarily a first-order transition. The first-order character of this transition is revealed by several experiments: discontinuity of the spontaneous birefringence[2] and crystallographic parameters,[6] coexistence of the two phases in the vicinity of T_c,[7] form of the specific-heat anomaly.[5] Nevertheless we have not observed, in the limit of the accuracy of the measurements, any discontinuity in the Brillouin shift in the vicinity of the phase transition. In the case where the transition is induced by the zone-center parameter of symmetry E one can expect a soft acoustical mode, the velocity of which tends to zero at T_c, for a second-order transition. Following Aubry and Pick,[20] when dealing with a $32 \rightarrow 2$ transition, the soft acoustical mode must be one of the transverse modes propagating along the x direction of the trigonal phase. Acccording to our observations in benzil, this mode is precisely the most sensitive to the transition. On the other hand, the frequency of the optic E mode, which has been followed by means of Raman scattering,[7] would go to zero at a temperature $T_0' = 0$ K. The fact that $T_0' < T_0$, i.e., that the acoustic mode softens more than the optic mode in the vicinity of the transition, is probably a consequence of a coupling[21,22] between the two modes. A detailed analysis of this coupling is not the purpose of this work, but the size of the difference $T_0' - T_0$ gives an estimate of the coupling strength. A phenomenological model based chiefly on the experimental results of Refs. 6 and 7 has introduced two[8] order parameters to explain the phase transition of benzil. The primary one, which is related to the displacements involved in the E soft optical mode, triggers the secondary order parameter, responsible for the unit-cell multiplication, through a nonlinear coupling. The latter order parameter is expected at the Brillouin-zone edge corresponding to $\vec{k}_m = (0, \frac{1}{2}, 0)$.

The present study thus gives the first experimental evidence of a zone-center soft acoustic mode related to the same primary order parameter as the Raman- and infrared-active E soft optical mode of the trigonal phase, the two soft modes being linearly coupled one to another. It appeared during this study that the acoustic softening is chiefly due to the elastic constant c_{44} whose variations have been followed in both phases in spite of the blurring due to the ferroelastic domain structure below T_c.

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