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Phenomenological model for the structural transition in benzil

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We reconcile apparently contradictory crystallographical and optical results relative to the 83.5 K transition in $(C_6H_5\text{-}CO)_2$ crystals. X-ray data are reinterpreted and shown to be compatible with a monoclinic low-symmetry phase, thus lifting the present uncertainty on the crystal's system below the transition. The spontaneous strain components are deduced from the crystallographical data. From their values, it is pointed out that the orientation of a certain type of boundary between domains is determined by the combined influence of elastic and electrostatic compatibility conditions. On the other hand, the high values at T_c of the strain components disclose the pronounced first-order character of the transition. On this basis, the mechanism of the transition is assumed to proceed through the triggering of an M point instability by a Γ point one. The consequences of this model are analyzed by a discussion of the Landau free energy corresponding to its symmetry characteristics. It accounts for the observed simultaneous occurence of the softening of a Brillouin-zone-center optic mode and of a fourfold expansion of the crystal's primitive unit cell. The qualitative temperature dependences of the soft-mode frequency, the spontaneous strain, and the dielectric constant are also satisfactorily reproduced.

Benzil, $(C_6H_5\text{-}CO)_2$, undergoes a crystalline phase transition at 83.5 K. The room-temperature structure has a rhombohedral symmetry[1,2] corresponding to the $P3_121(D_3^4)$ space group.[3] The transition and the low-temperature phase have recently been studied by means of optical observations in polarized light,[4,5] x-ray diffraction,[6] Raman scattering,[5] specific heat,[7] electron-nuclear double resonance (ENDOR),[8] and dielectric constant measurements.[5] A first-order transition has been conjectured on the basis of the occurence of discontinuities in the spontaneous quantities,[4,6] the observation that the two phases coexist at the transition,[4,5] and the form of the specific-heat anomaly.[7]

The results of various experimental investigations have revealed some apparent contradictions relative to the nature of the symmetry change and to the mechanism of the transition.

Thus, an ambiguity exists on the crystal system of the low-symmetry phase. Optical data are consistent with a monoclinic symmetry, while x-ray diffraction patterns have been demonstrated to imply a triclinic unit cell for it.

On the other hand, Raman scattering measurements have shown that the transition is accompanied by a pronounced softening of the lowest frequency optic mode of the rhombohedral phase. This feature discloses the occurence of an instability of the high-symmetry lattice at the Γ point of the hexagonal Brillouin zone. Such an instability is usually related, on the basis of symmetry[9] and physical[10] considerations, to a transition which will preserve the number of atoms in the crystal's unit cell. Actually, x-ray measurements show a change of the translational symmetry of the crystal at 83.5 K in contradiction with the former expectation.

In the present paper, we establish the mutual consistency of the preceding experimental results through a reinterpretation of the crystallographical data and a phenomenological model for the transition mechanism.

In Sec. I, the available x-ray results are shown to be entirely compatible with the monoclinic symmetry deduced from the macroscopic experiments. The space symmetry of the low-symmetry phase and the numerical values of the spontaneous strain components are derived from the crystallographical data. From these values, consequences are inferred for the orientation of the boundary between domains, and for the order of the transition. Based on a pronounced first-order character, a phenomenological model of the transition is then described and analyzed in Sec. II. Its results are compared to the available experimental data.

I. SPACE SYMMETRY AND SPONTANEOUS STRAIN TENSOR IN THE LOW-SYMMETRY PHASE

Optical conoscopic figures of (0001) hexagonal plates of benzil have shown[4] that below 83.5 K the crystal is biaxial ($2V = 39°$ at 70 K) with an optical plane perpendicular to a binary axis of the initial rhombohedral phase. This axis is also observed to constitute an extinction direction between crossed polarizers[5] in the whole temperature range below the transition. On the other hand, needles parallel to the ternary axis have extinction positions slightly tilted with respect to this axis.[4] Such features are clearly consistent with a monoclinic symmetry of the crystal, since a triclinic one would not preserve the binary axis as a privileged optical direction at all temperatures. In spite of their limited accuracy, these results provide a strong evidence of the claimed monoclinicity[5] because the characteristics of the optical indicatrix are known to be a very sensitive probe of the crystal's symmetry. For instance, similar optical measurements have shown that the room-temperature phase in bismuth titanate is monoclinic[11] while several refinements of the structure through x-ray and neutron-diffraction studies[12,13] have failed to detect any deviation from an orthorhombic symmetry.

Additional evidences have been pointed out[5,8] to support a monoclinic symmetry in benzil as, for instance, the observations of three domain orientations and of two unequivalent types of domain boundary directions.

By contrast to the converging results of the macroscopic observations, an x-ray investigation by Odou *et al.*[6] has led to the assignment of a triclinic symmetry to the low-temperature phase of benzil. Below the transition, these authors have noted a splitting of the Bragg reflections in several planes of the reciprocal lattice, denoting a lowering of the symmetry and the coexistence of several domain orientations in the samples. By a detailed analysis of the splittings occuring at 80 K, in the $(h01)$ and $(0k1)$ planes, they were able to demonstrate that the diffraction patterns cannot be reproduced if one assumes a monoclinic symmetry for the primitive unit cell of the crystal. Instead, an excellent agreement is obtained with a pattern constructed from a triclinic unit cell having the following lattice parameters[14] at 80 K:

$$a_t=(16.576\pm0.005)\ \text{Å},\quad b_t=(16.578\pm0.005)\ \text{Å}\ ,$$
$$c_t=(13.330\pm0.005)\ \text{Å}\ , \tag{1}$$
$$\alpha_t=(88.8\pm0.1)\ ^\circ,\quad \beta_t=(91.0\pm0.1)\ ^\circ\ ,$$
$$\gamma_t=(119.4\pm0.1)\ ^\circ\ .$$

However, in concluding on the basis of this result that the crystal itself had the triclinic symmetry, the former authors seem to have overlooked the fact that a triclinic unit cell can generate a monoclinic lattice. The necessary and sufficient conditions for it are: $a_t=b_t$ and $(90^\circ-\alpha_t)=(\beta_t-90^\circ)$. The resulting Bravais lattice is a base-centered C-type lattice for whom a nonprimitive monoclinic unit cell exists, defined by (Fig. 1)

$$\vec{a}_m=(\vec{a}_t-\vec{b}_t),\quad \vec{b}_m=(\vec{a}_t+\vec{b}_t),\quad \vec{c}_m=\vec{c}_t\ , \tag{2}$$

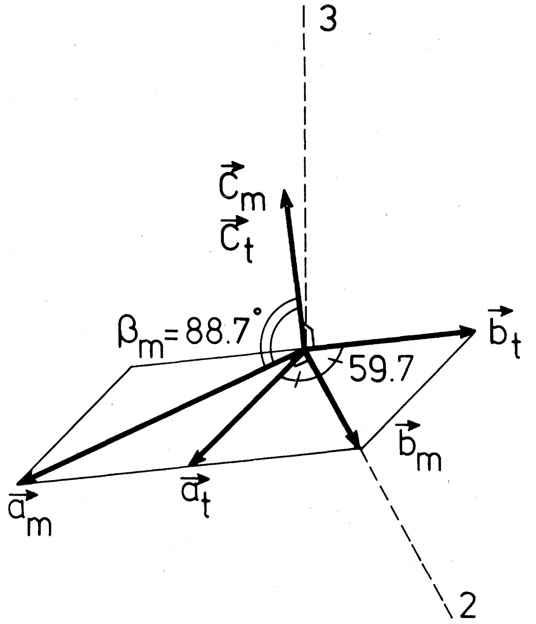

FIG. 1. Relative orientations of the triclinic unit cell $(\vec{a}_t,\vec{b}_t,\vec{c}_t)$, and of the monoclinic unit cell $(\vec{a}_m,\vec{b}_m,\vec{c}_m)$ describing the Bravais lattice of the low-symmetry phase in benzil. $\vec{b}_m$ coincides with the preserved binary axis of the rhombohedral phase, while 3 is the ternary axis which disappears at the transition. The angles indicated correspond to a temperature of 80 K.

with the binary axis along $\vec{b}_m$.

It appears in Eq. (1) that, within the accuracy of the experimental results, the above conditions are indeed fulfilled in benzil, thus establishing that the low-symmetry phase is crystallographically monoclinic. Besides, an additional evidence of this symmetry lies in the fact that the distortion of the hexagonal cell has been noted[6] to correspond to a rotation of the (0001) plane around $(\vec{a}_t+\vec{b}_t)$, a direction which coincides with the one assigned to the preserved binary axis.

The parameters calculated for the monoclinic cell are:

$$\begin{aligned} a_m&=a_t\sqrt{2}(1-\cos\gamma_t)^{1/2}=28.62\ \text{Å}\ ,\\ b_m&=a_t\sqrt{2}(1+\cos\gamma_t)^{1/2}=16.72\ \text{Å}\ ,\\ c_m&=c_t=13.33\ \text{Å}\ ,\\ \beta_m&=\arccos[\sqrt{2}\cos\beta_t/(1-\cos\gamma_t)^{1/2}]=88.7\ ^\circ\ . \end{aligned} \tag{3}$$

In the light of the preceding deductions, the available crystallographic data allow a complete specification of the space group of the low-symmetry phase in benzil. Odou *et al.* have stressed that Weissenberg photographs taken at 74 K show a doubling of the periodicity of the crystal along the two translations of the hexagonal lattice in the (0001) plane, thus resulting in a fourfold expansion of the primitive unit cell. As these translations remain of equal length, the distortion towards a monoclinic lattice can be shown[15] to lead necessarily to a *C*-type Bravais lattice, consistently with the result inferred above.

We have considered the possibility that the change observed in the crystal's periodicity was due to a doubling along a single of the former crystallographical directions. The appearance of a fourfold unit-cell expansion would have then been produced by the presence, in the samples, of domains rotated by 120° with respect to each other. This possibility can clearly be ruled out since the resulting lattice would be of the *P*-type[15] with a monoclinic primitive unit cell, in contradition with Odou's analysis of the diffraction patterns.

The average space symmetry of the polydomain samples has been identified as $P321$, showing that the monoclinic phase has no mirror planes. This establishes its point symmetry as 2. An identical assignment had previously been made[5] on the basis of the macroscopic measurements and of a group-subgroup relationship between the point symmetries of the two phases. The transition being of first order, the latter assumption did not necessarily hold beforehand[9] though it is ultimately found to be verified on the basis of the crystallographical data.

In conclusion, the space-symmetry change in benzil can be unambiguously deduced to be from $P3_121$ to $C2$ since the latter group is the only one belonging to the class 2 and to the Bravais lattice type *C*. This symmetry change involves a lowering of both the translational symmetry and the point symmetry of the crystal.

With respect to the reciprocal lattice of the high-symmetry phase, the superlattice associated with the change in the translational symmetry is generated by the two vectors $(0\ \frac{1}{2}\ 0)$ and $(\frac{1}{2}\ 0\ 0)$ which belong to the star of $\vec{k}$ vectors[16] corresponding to the *M* point of the hexagonal Brillouin zone.[17] This star has three arms: $(\frac{1}{2}\ 0\ 0)$, $(0\ \frac{1}{2}\ 0)$ and $(\frac{1}{2}\ \frac{1}{2}\ 0)$. The observed fourfold unit-cell expansion involves at least two of them.

The change in point symmetry $32 \rightarrow 2$ has been noted to imply[5] simultaneously ferroelectric and ferroelastic[18] properties for the monoclinic phase. The ferroelasticity is characterized by the onset of a spontaneous strain tensor.[19] For the considered point-symmetry change, this tensor has two independent components[19] which can be denoted $(\frac{1}{2})(e_{11}-e_{22})$, and e_{23}, if they are referred to a standard[20] frame of axes of the high-symmetry phase. The first component measures the deformation in the (0001) plane of the crystal, while e_{23} represents the shear in the plane perpendicular to the preserved binary axis.

The values of the spontaneous strain components below a ferroelastic transition can always be deduced from the lattice parameters of the distorted phase, provided that the point-symmetry and the translational-symmetry changes are known for this transition.[21] In the present case, we have at 80 K,

$$(\tfrac{1}{2})(e_{11}-e_{22}) = \frac{b_m - a_m/\sqrt{3}}{b_m + a_m/\sqrt{3}} = (6 \pm 1) \times 10^{-3} \ ,$$

$$e_{23} = (\tfrac{1}{2}) \cos\beta_m = (11 \pm 1) \times 10^{-3} \ . \tag{4}$$

Their variations as a function of the temperature cannot be entirely deduced from the available data. However, e_{23} is approximately[22] proportional to the angle $(\pi/2 - \beta_t^*)$ which has been measured by Odou[6] between 10 K and T_c. The results show that e_{23} will reach at low temperature a value of about 3×10^{-2} which is considerably higher than the spontaneous strain measured in most ferroelastics studied up to now.[19] In particular, it is 20 times larger than the spontaneous strain in a standard ferroelastic like gadolinium molybdate.[23]

More important is the fact that the residual value at T_c is still 8×10^{-3}, which implies that the onset of the monoclinic phase is associated to large discontinuous displacements of atoms in the structure. Consistently, the upward jump occuring at T_c in the spontaneous birefringence[4] is of the order of 10^{-3}, twice as large as the saturation value of this quantity in gadolinium molybdate.[23]

In this aspect, which is essential to the model developed in the Sec. II, the phase transition in benzil appears as a strongly first order one, in agreement with the specific-heat measurements.[7]

On the other hand, the ratio of the two strain components in Eq. (4) has been related[5] to the orientation of one type of domain boundaries in the low-symmetry phase. In this phase, two domains were noted[5] to be separated either by a planar boundary perpendicular to a binary axis of the rhombohedral phase, or by a planar boundary containing this axis and making an angle Θ with the (0001) plane. If the directions of the boundaries are assumed to be determined by a strain compatibility between adjacent domains,[24,25] the angle Θ is expected to obey the following relation:

$$|\tan\Theta_0| = \frac{(\frac{1}{2})(e_{11}-e_{22})}{e_{23}} \ . \tag{5}$$

The value of $\tan\Theta_0$ deduced from Eqs. (4) and (5) is (0.54 ± 0.14) while the experimental value[5] is (0.32 ± 0.02). The measured angle Θ is therefore significantly smaller than the calculated one Θ_0. This situation is surprising because relation (5) is remarkably fulfilled in lead phosphate,[25] a material undergoing a symmetry change ($\bar{3}m \rightarrow 2/m$) corresponding to identical ferroelastic characteristics,[19] and whose strain components also possess large values.[26]

One possible cause of the discrepancy appears to be the fact that, unlike lead phosphate, benzil is a ferroelectric crystal, and the directions of the considered "oblique" boundaries are not necessarily determined by a strain compatibility between domains. Actually, these boundaries bear an electric charge distribution[5] of density $P_s \sin\Theta$ where P_s is the spontaneous polarization. The electrostatic energy of the crystal is not a minimum for the Θ_0 orientation, and it decreases when Θ is lowered, with an approximate linear dependence on $(\Theta-\Theta_0)$. By contrast, the elastic energy is a minimum at Θ_0, and it increases when Θ deviates from Θ_0, with an initial quadratic dependence on $(\Theta-\Theta_0)$. Accordingly, the minimum of the total energy determines an equilibrium orientation $\Theta < \Theta_0$ for the boundary, in agreement with the trend observed experimentally.

An order of magnitude of the quantities defining the preceding equilibrium can be estimated by expressing the dependence of the variations E_t of the total energy per unit volume in the form

$$E_t \approx E_s(\Theta-\Theta_0)^2 + E_p(\Theta-\Theta_0) \ , \qquad (6)$$

which corresponds to the qualitative description indicated above, and where E_s and E_p are, respectively, the elastic and electrostatic energies per unit volume associated with the onset of the spontaneous strain and of the spontaneous polarization. The knowledge of the elastic constants of benzil[27] together with Eq. (4) determines the value of $E_s \approx 5 \times 10^5$ J/m^3. On the other hand, $E_p = P_s^2/2\epsilon_0\epsilon_r$, with $\epsilon_r \sim 3$.[27] From Eq. (6), and the experimental value of $(\Theta-\Theta_0)$, we deduce $P_s \sim (0.5 \pm 0.3)$ μCb/cm^2. Another value of P_s can be obtained by assuming that its ratio to the spontaneous strain components is equal to the room-temperature values of the relevant piezoelectric coefficients.[27] This relation is known to hold for the transitions having the polarization as their order parameter.[28] As shown in Sec. II, benzil does not comply with this condition. Nevertheless, the relation is likely to supply a correct order of magnitude for P_s. We obtain from it $P_s \sim 0.1$ μCb/cm^2. These estimations of the spontaneous polarization in benzil appear to be of the same order of magnitude as the one determined for other organic ferroelectrics, for instance 0.5 μCb/cm^2 for tanane.[29]

A precise quantitative comparison between the observed and calculated values of Θ would require a direct experimental determination of P_s, as well as more accurate lattice-parameter measurements in the low-symmetry phase. Such a comparison would be useful to find out if the suggested mechanism accounts entirely, or only partly, for the orientation of the boundary.

II. MECHANISM OF THE TRANSITION

In the Landau theory of crystalline phase transitions, the high-symmetry phase becomes unstable at T_c with respect to a single degree of freedom (possibly degenerate) $\{\eta_i\}$, which is the order parameter of the transition. The set $\{\eta_i\}$ spans an irreducible representation $\Gamma_n(k^*)$ of the high-symmetry space group, where k^* is a star of $\vec{k}$ vectors of the first Brillouin zone,[16] and n specifies a small representation τ_n of the group of the $\vec{k}$ vector. The change, occuring at the transition, in the translational periodicity of the crystal is directly related to k^*.[15] On the other hand, the instability of the high-symmetry phase at T_c results from the fact that in the order-parameter expansion,[9,16] the quadratic term $(\frac{1}{2}a)(\Sigma\eta_i^2)$ has a coefficient $a \sim (T-T_c)$ becoming negative below T_c. Whenever $\{\eta_i\}$ is a set of atomic displacements associated to a certain normal mode of the crystal, the preceding coefficient is proportional to the square of the frequency of this mode.[10]

Thus, in the framework of the theory, both the symmetry change and the "soft" vibrational mode are related to the same $\Gamma_n(k^*)$. As stressed above, this situation is not realized in benzil since a doubly degenerate mode having $k^* = 0$ and the E symmetry[17] is observed[5] to soften in the rhombohedral phase, with a linear decrease of its squared frequency, while the translational symmetry has been shown in Sec. I, to correspond to the star of the M point of the Brillouin zone $[k_M^* = (0\,\frac{1}{2}\,0)]$.

However, the conditions of the Landau theory are only rigorous when a transition is of second order. For a first-order one, as the transition in benzil, other situations can arise. In particular, it has been suggested by Holakovsky[30] that an instability with respect to one degree of freedom $\{\zeta_i\}$ could be "triggered" by another instability with respect to $\{\eta_i\}$, the two sets having different symmetry properties. In such a mechanism, a coupling is assumed to exist between ζ and η of the form $-\delta(\eta\zeta^2)$. As a consequence, the quadratic contribution of ζ to the free-energy expansion, $(\frac{1}{2}\alpha)\zeta^2$, is renormalized by the coupling as $(\frac{1}{2}\alpha-\delta\eta)\zeta^2$. If the transition, provoked by an instability with respect to η, is a first-order one, and involves a sufficiently large value of $(\delta\eta)$, the coefficient of ζ^2 will become negative, thus resulting in an instability with respect to ζ, and in the onset of spontaneous values for both η and ζ.

In this model, the soft vibrational mode of the high-symmetry phase remains related to the "primary" order parameter $\{\eta_i\}$. By contrast, the space group of the low-symmetry phase is the intersection of the symmetries determined separately by the $\{\eta_i\}$ and the $\{\zeta_i\}$.[30]

Such a model appears well adapted to the experimental situation in benzil. The primary order parameter $\{\eta_i\}$ can be associated to the E symmetry at $k^*=0$, while the triggered one $\{\zeta_i\}$ can be chosen to correspond to $k_M^*=(0\,\frac{1}{2}\,0)$. Consistently, symmetry considerations[31] show that an order parameter having the E symmetry determines the presence of a cubic polynomial in the free-energy expansion and therefore necessarily induces a transition of first order.[9] In addition, the fact that the transition provokes large atomic displacements gives ground to the possibility of making $(\delta\eta)$ large enough to trigger the instability of ζ without needing an unrealistically large value for the coupling coefficient δ.

Let us now work out the specific symmetry and thermodynamical characteristics of the model in benzil and compare its results to the experimental data.

The set $\{\eta_x;\eta_y\}$ of atomic displacements related to the soft-optic mode is not the only relevant physical quantity possessing the E symmetry. Other important quantities are the two sets of strain components $\{(\frac{1}{2})(e_{11}-e_{22});e_{12}\}$, $\{e_{23};e_{13}\}$, and the components $\{P_x;P_y\}$ of the dielectric polarization in the (0001) plane. A linear coupling is allowed between any two of these quantities. In the following discussion, we will first restrict ourselves to the consideration of a single set of E-symmetry quantities coinciding with the primary order parameter $\{\eta_x;\eta_y\}$. The effect of the preceding coupling will then be examined. We can note that the equitranslational symmetry change determined by the E symmetry is towards the monoclinic group $C2$ if the first component only acquires a spontaneous value (i.e., $\eta_x\neq 0$), while it is towards a triclinic phase otherwise (i.e., $\eta_y\neq 0$).

The triggered order parameter $\{\zeta_i\}$ spans an irreducible representation of $P3_121$ at the M point of the hexagonal Brillouin zone. At this point, there are[17] two distinct representations $\Gamma_1(k_M^*)$ and $\Gamma_2(k_M^*)$, both three dimensional. $\{\zeta_i\}$ therefore has three components $(\zeta_1,\zeta_2,\zeta_3)$, each one being associated[32] to a different arm of the star k_M^*. These two representations correspond to physically distinct situations. The first one only determines the presence of a cubic term in the free-energy expansion.[32] However, it cannot be distinguished from the second one on the basis of the available symmetry characteristics of benzil. For the sake of simplifying the algebraic discussion, we will assume that $\{\zeta_i\}$ spans $\Gamma_2(k_M^*)$.[33]

The preceding assumptions specify entirely the transition free-energy expansion.[16] A standard group theoretical procedure[16,32] leads to the following form for it:

$$F=(\tfrac{1}{2}a)(\eta_x^2+\eta_y^2)-(\tfrac{1}{3}b)(\eta_x^2-3\eta_y^2)\eta_x+(\tfrac{1}{4}c)(\eta_x^2+\eta_y^2)^2+(\tfrac{1}{2}\alpha)(\Sigma\,\zeta_i^2)+(\tfrac{1}{4}\beta_1)\left|\sum\zeta_i^4\right|+(\tfrac{1}{2}\beta_2)\left|\sum_{i<j}\zeta_i^2\zeta_j^2\right|$$
$$+\delta\{\eta_x(2\zeta_1^2-\zeta_2^2-\zeta_3^2)+\eta_y\sqrt{3}(\zeta_2^2-\zeta_3^2)\}\ . \tag{7}$$

The first order of the transition can be accounted for by the presence of the cubic polynomials, and therefore no term of degree higher than four has been considered. In agreement with the "primary" character of the $\{\eta_i\}$ parameters we have $a\sim(T-T_0)$, while the other coefficients are assumed to be temperature independent and positive.

It is worth noting that the $\{\eta_x,\eta_y\}$ set also gives rise[31] to a term of the form

$$\left(\eta_x\frac{\partial\eta_y}{\partial z}-\eta_y\frac{\partial\eta_x}{\partial z}\right)$$

(Lifschitz invariant[34]), whose presence in the free energy of a transition has been related[34,35] to the occurence of a " modulated" phase sandwiched between the high- and low-symmetry crystalline phases. However, in benzil, the considered transition is of first order and it leads to a low-symmetry phase where the preceding term will vanish by symmetry ($\eta_y=0$). In such a case, it has been shown[31,35] that the modulated phase will generally be absent and that the Lifschitz invariant can be omitted. Besides, no experimental evidence is available at present for the occurence of a modulated phase in this material.

To specify the triggering mechanism in benzil let us examine the renormalized ζ_i quadratic terms. These are

$$\zeta_1^2(\tfrac{1}{2}\alpha+2\delta\eta_x),\quad \zeta_2^2[\tfrac{1}{2}\alpha-\delta\eta_x+\delta\eta_y(3)^{1/2}]\ ,$$
$$\zeta_3^2[\tfrac{1}{2}\alpha-\delta\eta_x-\delta\eta_y(3)^{1/2}]\ . \tag{8}$$

The ζ_i quartic terms are identical for the three components. As stressed above, the observed monoclinic symmetry requires $\eta_y=0$. Reporting this condition in Eq. (8) shows that according to the sign of η_x a triggering can affect either the ζ_1 component alone ($\eta_x<0$) or the set $\{\zeta_2,\zeta_3\}(\eta_x>0)$. In the first case, the symmetry resulting from the simultaneous onset of ζ_1 and η_x would be monoclinic with a P-type Bravais lattice and a double unit cell. In the second case corresponding to $\zeta_2=\zeta_3\neq 0$, and $\eta_x\neq 0$, the symmetry is $C2$ with a fourfold expansion of the unit cell in the (0001) plane.

The symmetry change observed experimentally is consistent with the model for $\eta_x>0$. The algebraic discussion can therefore be restricted to this case, by setting, in the free-energy expansion, $\eta_y=\zeta_1=0$, $\zeta_2=\zeta_3$, and $\eta_x>0$.[36] In order to deal with dimensionless variables and coefficients let us also put

$$\Phi=\frac{2(\beta_1+\beta_2)}{\alpha^2}F,\quad \zeta=\left(\frac{\beta_1+\beta_2}{\alpha}\right)^{1/2}\zeta_2\ ,$$
$$\eta=\left(\frac{2\delta}{\alpha}\right)\eta_x,\quad \lambda=\frac{4\delta^3}{\alpha(\beta_1+\beta_2)b}\ , \tag{9}$$
$$\nu=\frac{\alpha c}{2b\delta},\quad t=\left(\frac{a(T)\delta}{b\alpha}-\lambda\right)\ .$$

The expansion takes the simpler form

$$\Phi=(1/\lambda)\{(t+\lambda)\eta^2-\tfrac{1}{3}\eta^3+(\tfrac{1}{4}\nu)\eta^4\}$$
$$+2\zeta^2+\zeta^4-2\eta\zeta^2\ . \tag{10}$$

It only depends on two positive coefficients λ and ν, and on the "reduced" temperature t. At each temperature, the stable phase of the crystal corresponds to the absolute minimum of Φ. It implies, in particular, the cancellation of the first derivatives

$$\frac{\partial\Phi}{\partial\eta}=\left(\frac{1}{\lambda}\right)\{2(t+\lambda)\eta-\eta^2+\nu\eta^3\}-2\zeta^2=0\ ,$$
$$\frac{\partial\Phi}{\partial\zeta}=4\zeta(1+\zeta^2-\eta)=0\ . \tag{11}$$

This system determines three distinct phases. Phase I ($\eta=\zeta=0$) is the rhombohedral phase, stable above 83.5 K. Phase II ($\eta_{\text{II}}\neq 0$; $\zeta=0$) is a monoclinic phase of space-symmetry $C2$, having the same primitive translations as phase I. This phase corresponds to the absence of triggering of ζ. In this case, it would onset below a first-order transition occuring at the reduced temperature $t_{\text{II}}=\{(1/9\nu)-\lambda\}$. The variations of η_{II} are expressed by

$$\eta_{\text{II}}=(1/2\nu)\{1+[1-8\nu(t+\lambda)]^{1/2}\}\ . \tag{12}$$

Phase III ($\eta_s\neq 0$, $\zeta_s\neq 0$) is the monoclinic phase observed experimentally. Its range of stability, as well as the equilibrium values of η_s and ζ_s are determined by the following equations deduced from Eqs. (10) and (11):

$$\zeta^2=\eta-1>0\ ,$$
$$\Phi(\eta)=(1/\lambda)\{t\eta^2-\tfrac{1}{3}\eta^3+(\tfrac{1}{4}\nu)\eta^4\}+\{2\eta-1\}\ . \tag{13}$$

The form of η_s corresponding to the minimum of $\Phi(\eta)$, cannot be conveniently expressed algebraically. However, if we neglect the term $\{2\eta-1\}$ the function $\Phi(\eta)$ reduces to the usual free energy describing a first-order transition,[9] for which the temperature of the transition is $t_{\text{III}}=(1/9\nu)$, and the variations of the order parameter are given by the expression

$$\eta_{\text{III}}=(1/2\nu)\{1+[1-8\nu t]^{1/2}\}\ . \tag{14}$$

In addition, as shown by Eq. (13), this solution has to comply with the condition $\eta_{\text{III}}>1$.

The influence of the term $\{2\eta-1\}$ is a destabilizing one for phase III, since it raises the free-energy of the crystal for $\eta_s>1$. By contrast, the free energy in Eq. (13) is lower than the free energy of phase II, and one can easily establish that whenever $\eta_s>1$ is fulfilled, phase III is more stable than phase II. This condition imposes $\nu<\nu_0(\lambda)$, where the upper limit $\nu_0(\lambda)$ is an increasing function of λ. For $\lambda<<1$, we have $\nu_0(\lambda)\sim 0.67$ while for $\lambda\sim 1$ we obtain $\nu_0(\lambda)\sim 0.87$. If $\nu>\nu_0(\lambda)$, a transition will occur first towards phase II. If $\nu<\nu_0(\lambda)$, phase III constitutes the stable low-symmetry phase of the crystal. The reduced temperature t_c and the equilibrium value of η_s comply with the conditions

$$t_{\text{II}}<t_c<t_{\text{III}}\quad\text{and}\quad \eta_{\text{II}}<\eta_s<\eta_{\text{III}}\ . \tag{15}$$

Thus, an effect of the triggering is an upward shift of the transition temperature ($t_{\text{II}}<t_c$). Besides for $|t|>>\lambda$ (i.e., for negative temperatures $t<<-\lambda$), we have $\eta_s\sim\eta_{\text{II}}\sim\eta_{\text{III}}$. At higher temperatures, the magnitude of the difference between η_s and η_{III} increases with the value of λ. This coefficient is unlikely to be large as it is proportional to the third power of the coupling coefficient δ. We have investigated numerically the minima of $\Phi(\eta)$, for $\lambda\sim 1$, and $\lambda<<1$. In both cases the temperature dependence of η_s resembles closely that of η_{III} (Fig. 2).

Let us now examine qualitatively the influence of the linear coupling between η and the macroscopic components possessing an E symmetry. Such a coupling has been studied by various authors[10,37,38] and its effects are well known.

In the first place, the relevant strain and polarization components acquire spontaneous values proportional to η_s. The temperature dependence of all these quantities is therefore expected to be the same. On the other hand, the coupling provokes an upward shift of the transition temperature whose magnitude increases with the strength of the coupling. Finally, a softening of certain components of the elasticity and inverse dielectric susceptibility tensors occur at the shifted temperature of the transition. The equilibrium states of the crystal can be determined from the free energy Eq. (7) by replacing in it the T_0 temperature in $a\sim(T-T_0)$ by its shifted value T_1.

Likewise, the quadratic coupling of the macroscopic quantities to the triggered parameters $\{\zeta_i\}$ only leads to modified values for the β_i and δ coefficients in Eq. (7). Thus, the results of the preceding algebraic discussion are entirely preserved, within a substitution of the expansions coefficients, and they can be used in order to predict the variations of η_s as well as the shape of the anomalies in the mechanical and dielectric properties.

However, as suggested by several recent experi-

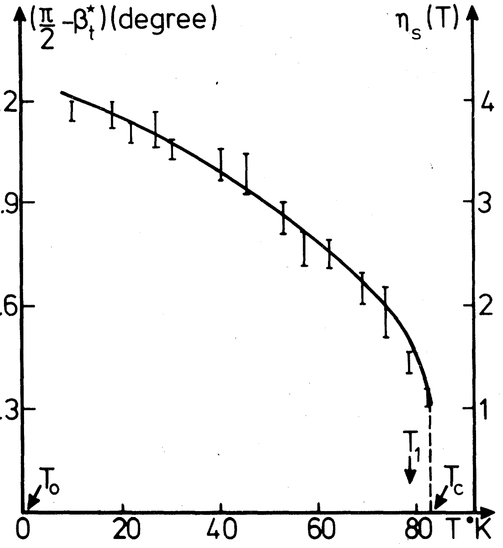

FIG. 2. Solid line: calculated variations of the primary order parameter η_s for values of the model parameters $\lambda = 10^{-3}$ and $\nu = 0.65$, which are close to the limit of stability of phase III. The experimental values are those of the angle $(\frac{1}{2}\Pi - \beta_t^*)$ in Ref. 6. The variations are made to coincide at 83.5 and 10 K. $T_0 = 0$ K is the temperature of vanishing of the frequency of the soft mode relative to η. T_1 is the temperature at which certain elastic and dielectric inverse susceptibilities vanish.

mental studies[39,40] of materials in which a similar linear coupling is active, the modifications of the expansion coefficients should not be considered when one calculates the frequency of the soft mode associated to η. Due to the high frequency of this mode, the homogeneous strain coupled to it will not follow the oscillations and will appear as clamped. Therefore, the squared frequency of the soft mode of the high-symmetry phase, extrapolated below the transition, is expected to vanish at the unshifted temperature T_0. Similarly, the coupling to the macroscopic quantities will also be ineffective in the dynamical properties relative to the ζ parameter. By contrast, the coupling between η and ζ is likely to be active both in the static and the dynamic behavior of the crystal.

Figure 2 shows the variations calculated for $\eta_s(T)$ in the framework of the preceding assumptions. Figure 3 reproduces the variations determined for the squared frequencies of the modes associated to η and ζ (see Appendix). We have also outlined the qualitative behavior predicted for the elastic and dielectric constants. A fitting of the curves has been performed in order to obtain a coincidence with the experimental points at T_c, and the same amplitude in the variations of $\eta_s(T)$ between 0 K and T_c as those indicated[6] for $(\frac{1}{2}\Pi - \beta_t^*)$. In addition, we have imposed $T_0 = 0$ K in agreement with the Raman data.

The fitting discloses that the difference between T_0 and T_1 is of the order of 75–80 K (Fig. 2) indicating that the coupling between η and the macroscopic quantities is strong. This coupling is most likely to involve the strain components since these have large spontaneous values, and that conversely, small anomalies are detected in the dielectric constant of the material.[5] The additional shift due to the triggering of ζ is only a few degrees, showing that this triggering, though essential to explain the symmetry characteristics of the transition, does not influence sensitively the behavior of the other physical quantities. The share of the transition free energy, stored in the spontaneous components $\{\zeta_i\}$ appears to be an order of magnitude smaller than the one stored in the spontaneous components of the primary order parameter and of the ferroelastic strain.

At a first-order transition involving large atomic displacements, terms of degree higher than four, which have been omitted from the free energy, are likely to play a significant role in the temperature dependence of the physical quantities below the transition. Only a qualitative agreement is therefore expected between the results of the present model and the experimental data for benzil.

As shown by Fig. 2, the x-ray data[6] for $(\frac{1}{2}\Pi - \beta_t^*)$ are in good quantitative agreement with the theoretical curve for $\eta_s(T)$. The behavior of the soft mode is more qualitatively accounted for. The calculated curve (Fig. 3) which is only fitted to the experimental point at T_c reproduces well the experimental values in the whole range of temperatures. However, below 50 K, the B mode is predicted to lie under the A mode, in contradiction with the experimental data.[5] Such a discrepancy cannot be attributed to the simplifications of the model. Actually, the stronger temperature dependence of the A mode which results from the model is consistent with the fact that this mode is related to the onset of the observed monoclinic phase, while the B mode, related to a triclinic symmetry, is secondarily influenced by the transition. Thus, the stronger temperature dependence which is found experimentally for the B mode seems anomalous. Considering the difficulties, pointed out in Ref. 5, of obtaining polarized Raman data in a polydomain low-symmetry phase, the experimental identification of the mode symmetry would need to be confirmed.

The temperature dependence of the dielectric constant, predicted from the model, has approximately the same shape as the one which is usual for a first-order ferroelectric transition[28] (Fig. 3). It differs from it by the magnitude of the anomaly which depends on the strength of the coupling between η and P. One can obtain a very small relative variation by choosing the sign and magnitude of the coupling

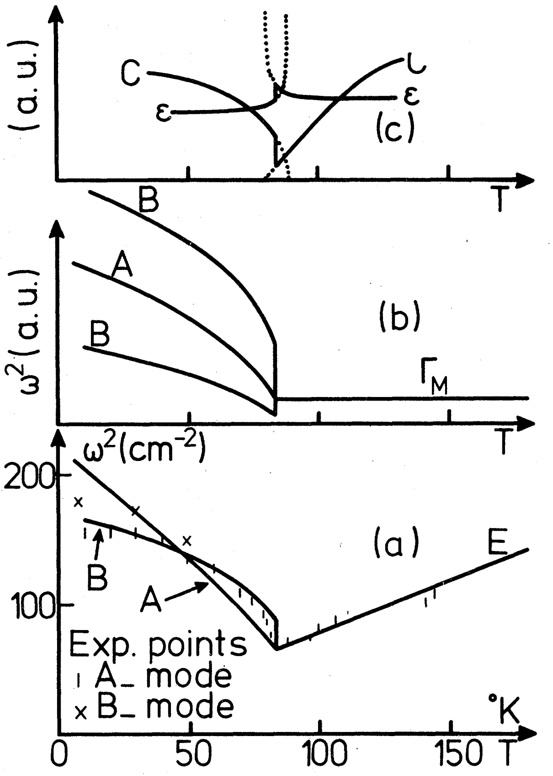

FIG. 3. (a) Calculated and observed behavior of the soft mode relative to η. The experimental data are reproduced from Ref. 5. The model parameters are the same as in Fig. 2. (b) Predicted variations for the modes relative to the $\{\zeta_i\}$ set of parameters. (c) Qualitative behavior predicted for the dielectric constant ϵ_x and the particular combination of elastic constants which softens near T_c. The dotted part of the curves is reproduced to show the temperature of divergence or vanishing of these functions.

coefficient in a way to almost cancel the effect of the piezoelectric coupling. The experimental plot seems consistent with such a situation.[5] By contrast, it is expected that a pronounced softening will take place for the combinations of elastic constants $(C_{11}-C_{12})$ and C_{44}, which are referred to standard axes[20] of the rhombohedral phase. On the other hand, the vibrational mode related to ζ is Raman inactive and temperature independent in the upper phase. At T_c, it splits into one A-symmetry and two B-symmetry modes with jumps whose signs depend critically on the model's parameters. A rapid increase of each component is then predicted to take place below T_c (Fig. 3). In the low-symmetry phase, the Raman spectra should contain new lines whose frequencies are likely to be substantially higher than that of the soft mode related to η. This could explain why no extra lines have been observed in the low-frequency part of the Raman spectra.[5] As shown in the Appendix, the squared frequencies of the lines associated to the triggered parameter are proportional to ζ_s^2. Accordingly, they should have the same temperature dependence as the intensities of the superlattice reflections.[41]

III. CONCLUSION

In the present paper, an interpretation has been given of the experimental results relative to the phase transition in benzil.

In the first place, the characteristics of the low-symmetry phase have been established. The space group has been identified as $C2$, in agreement with both the crystallographical and the optical results. The values of the spontaneous strain components, of the order of 10^{-2}, have been derived from the crystallographical data, and the order of magnitude of the spontaneous polarization has been estimated to be $\sim 0.1\ \mu\text{Cb/cm}^2$. In addition, the effect of the electrostatic compatibility between domains on the orientation of certain domain boundaries has been pointed out.

On the other hand, the main features of the 83.5 K transition were explained satisfactorily on the basis of a model involving a primary order parameter associated to a Brillouin-zone-center optic mode, and a secondary one corresponding to $\vec{k}_m = (0\ \frac{1}{2}\ 0)$. The instability of the latter one is triggered by a nonlinear coupling to the primary one. In addition, the primary parameter appears to be strongly coupled to homogeneous strain components and only weakly coupled to polarization ones.

Similar models had been developed previously for the phase transitions in the boracites,[42] in bismuth titanate,[43] and in Rochelle salt.[44] However, in the former materials either part of the x-ray data, or the lattice dynamical behavior is unknown. These data are both available in benzil and therefore, in this material, the veracity of the model appears to be more firmly established.

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APPENDIX

The soft-mode temperature dependence is obtained from the second derivatives of the free energy Eq.

(7) with respect to the various components of the primary and triggered order parameters. In the low-temperature phase, the A-normal modes correspond to η_x and $(1/\sqrt{2})(\zeta_2+\zeta_3)$, while the B ones are associated to η_y, ζ_1, and $(1/\sqrt{2})(\zeta_2-\zeta_3)$. With the notations of Eqs. (7) and (9) and putting $t'=[t+(\delta/b\alpha)a(T_0-T_1)]$, we have for $T>T_c$,

$$\{\eta_x;\eta_y\}(E \text{ mode}):\ \omega^2\sim(b\alpha/2\delta)(2\lambda+2t')\ ,$$

$$\{\zeta_i\}(\Gamma_M(k^*) \text{ mode}):\ \omega^2\sim\alpha\ .$$

Below T_c, we obtain

$$\eta_x(A \text{ mode}):\ \omega^2\sim\left(\frac{b\alpha}{2\delta}\right)(2t'-2\eta+3\nu\eta^2)\ ,$$

$\eta_y(B$ mode):

$$\omega^2\sim\left(\frac{b\alpha}{2\delta}\right)\left(2t'+2\eta+\nu\eta^2-\frac{4\lambda(\beta_1+\beta_2)}{(\beta_1-\beta_2)}\right)\ ,$$

$$\zeta_1(B \text{ mode}):\ \omega^2\sim\alpha\left[3+2\left(\frac{\beta_1+2\beta_2}{\beta_1+\beta_2}\right)(\eta-1)\right]\ ,$$

$\left(\frac{1}{\sqrt{2}}\right)(\zeta_2+\zeta_3)(A$ mode):

$$\omega^2\sim2\alpha(\eta-1)\left(1-\frac{2\lambda}{[2(t'+\lambda)-2\eta+3\nu\eta^2]}\right)\ ,$$

$\left(\frac{1}{\sqrt{2}}\right)(\zeta_2-\zeta_3)(B$ mode):

$$\omega^2\sim\alpha\frac{(\beta_1-\beta_2)}{(\beta_1+\beta_2)}(\eta-1)$$

$$\times\left(1-\frac{(\beta_1+\beta_2)}{(\beta_1-\beta_2)}\times\frac{12\lambda}{[2(t'+\lambda)+2\eta+\nu\eta^2]}\right)\ .$$

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