guish between the continuous network model[25] and the molecular model[26] for this alloy, in favor of the former.

The model that I present here is simple enough to allow us to understand vibrational properties on physical grounds; and it is also realistic enough to make possible detailed comparison between theory and experiment. To my knowledge, this is the first time that good agreement between the calculated density of states and experiments is obtained for noncrystalline alloys.

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Critical Angular Fluctuations of Molecules above a Second-Order Smectic-*A* to Smectic-*C* Phase Transition*

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Using light-beating spectroscopy we detect the "soft" mode associated with the second-order smectic-*A* to smectic-*C* phase transition in undecylazoxymethylcinnamate. This mode corresponds to angular fluctuations of molecules with respect to the normal of the layers. In the *A* phase both the amplitude and the relaxation time of these fluctuations diverge with a mean-field critical exponent $\gamma = 1.0 + 0.15$.

Since de Gennes's first suggestion[1] that second-order phase transitions in liquid crystals[2] [smectic-*A* to nematic ($A \to N$) and smectic-*A* to smectic-*C* ($A \to C$)] could be described by critical exponents analogous to superfluids, many experiments have been performed on the $A \to N$ transition. However it is not yet clear if the exponents are always in agreement with scaling arguments. Moreover the second-order nature of the $A \to N$ transition has been questioned on theoretical grounds.[3] In view of this fact, the $A \to C$ transition seems more appealing: (1) Here the direct observation of the order parameter[4] of the C phase is possible using the coupling between light and angular fluctuations, and (2) no one has yet challenged its second-order character. In this Letter we report the first experimental evidence of the critical fluctuations of the C-phase order parameter above a second-order $A \to C$ phase transition. Using quasielastic Rayleigh scattering and light beating spectroscopy we perform both static and dynamic measurements.

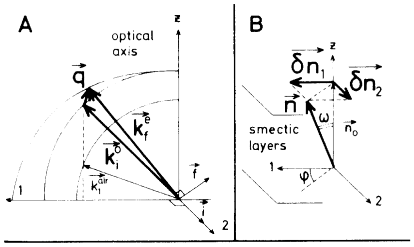

FIG. 1. (a) $\vec{k}_i{}^0$ and $\vec{k}_f{}^e$ are the incident ordinary and the outgoing extraordinary wave vectors of the light; $\vec{q}$ is the momentum transfer. (b) We observe the fluctuations $\delta\vec{n}_2$ orthogonal to the plane $(\vec{q}, \vec{z})$. Contrary to $\delta\vec{n}_1$ this mode of pure tilt ω does not involve any layer undulation or compression.

Let us recall some theoretical predictions. In the C phase de Gennes has introduced[5] a bidimensional heliumlike order parameter $\psi = \omega \exp(i\varphi)$ where ω is the tilt of the molecules and φ defines their azimuthal position [see Fig. 1(b)]. $\langle|\psi|\rangle$ is typically a few tens of degrees[6] and will go to zero at the transition temperature T_{CA}. In the A phase only $\langle|\psi|^2\rangle$ will be nonzero, diverging at T_{CA} for a second-order transition. The fluctuations extend spatially on a coherence length ξ. They contribute to the free energy[7] as an additional term

$$F_E = \tfrac{1}{2} B_\perp(T) |\psi|^2 + \text{terms in } (\nabla\psi)^2 + \text{higher order terms}, \tag{1}$$

where $B_\perp$ is the elastic modulus keeping the molecules normal to the layers. $B_\perp$ goes to zero at T_{CA} with an exponent γ ($\gamma = 1.3$ in helium analogy; $\gamma = 1$ in mean-field approach). Note that ξ varies like $(\Delta T/T)^{-\nu}$ where $\nu \approx \gamma/2$.

Raleigh scattering from thermally excited fluctuations of the director[2] $\vec{n}$ allows a direct measurement of $B_\perp$. In the A phase, angular fluctuations can be due either to layer undulations or to molecular tilt. Choosing a wave vector $\vec{q}$, fluctuations are analyzed in two orthogonal modes $\delta\vec{n}_1$ and $\delta\vec{n}_2$ [$\delta\vec{n}_2$ orthogonal to $(\vec{g}, \vec{Oz})$ plane, see Fig. 1(b)]. It is possible to isolate the tilt fluctuations by detecting only the $\delta\vec{n}_2$ mode: By definition of the axes the layer undulation is confined in direction 1. The mean square amplitude is then

$$\langle|\delta n_2(q)|^2\rangle = kT(B_\perp + K_2 q_1{}^2 + K_3 q_z{}^2)^{-1}, \tag{2}$$

where K_2 and K_3 are twist and bend nematiclike elastic constants. Formula (2) was also recently obtained below the $N \to A$ transition by Birecki *et al.*[8] The $\delta\vec{n}_2$ mode induces fluctuations of the dielectric tensor which give rise to a scattered intensity[9]

$$I_2 \sim \epsilon_a{}^2 \langle|\delta n_2(q)|^2\rangle (1 + q^2\xi^2)^{-1}, \tag{3}$$

where ϵ_a is the dielectric anisotropy at optical frequencies and the denominator is the well-known Ornstein-Zernike form for correlation functions. In fact we always choose the wave vector q small enough to fulfill both conditions:

$$q\xi < 1, \tag{4}$$

and

$$K_2 q_1{}^2 + K_3 q_z{}^2 < B_\perp. \tag{5}$$

I_2 then is directly proportional to $\epsilon_a{}^2 B_\perp{}^{-1}$. In principle ϵ_a should also show a pretransitional behavior. In fact, as stated by Galerne's birefringence measurements[6], ϵ_a remains constant within ± 2% our temperature range. The tilt fluctuations are relaxed by the elastic torque $-B_\perp\omega$ in balance with a viscous torque $\eta\partial\omega/\partial t$ (η is a viscosity coefficient). The damping rate is then $\tau_c{}^{-1} = B_\perp/\eta$, which varies in the same way as I_2 if η is regular.

Our experimental setup is described by Delaye.[10] We use undecylazoxymethylcinnamate,

$$\mathrm{C_{11}H_{23}CO_2C(CH_3)CH{-}O{-}N_2O{-}OCHC(CH_3)CO_2C_{11}H_{23}},$$

which presents the following phases:

crystalline-(68°C)-S_C-(78.1°C)-S_A-(87.6°C)-isotropic.

In the C phase the molecules are really tilted in the layers; at the $A \to C$ transition the latent heat peak is smaller than 10^{-2} cal/g. We prepare sealed homeotropic samples by coating glass plates with silane agents[11] and check their alignment by conoscopic methods for sample thickness up to 400 μm. The sample is maintained in a temperature controlled oven[10] of stability ± 1 mK. We measure the temperature by comparing a MINCO platinum resistance (S 1061-2) situated in the oven to a Leeds & Northrup standard with a Guidline ac four terminal bridge (model 9975). An He-Ne laser illuminates a 600-μm-diam spot on the sample; the laser power is adjusted during the experiment from 50 μW to 15 mW and measured by a Spectra Physics cell (model 404). The scattering geometry [Fig. 1(a)] is chosen to select the $\delta\vec{n}_2$ mode. The values of q_z (2×10^3 cm^{-1}) and q_1 ($<7\times10^2$ cm^{1}) satisfy the conditions (4) and (5) all over the temperature range. With the ordinary incident polarization the dc component of the dielectric torque induced by the laser field on the molecules has zero value. The scattered light, detected over less than one coherence area, is measured by a fourteen-stage cooled photomultiplier. The choice of small q_1 assigns a strong local oscillator intensity I_0, much larger than I_2, giving in the beating process on the phototube a heterodyne regime. A digital clipped real-time correlator is used to build the autocorrelation function $C(\tau)$ of photopulses. τ_C is directly computed from exponential decay of $C(\tau)$ (with 10% uncertainty) while I_2 can be deduced from the zero-delayed value $C(0)$. In fact intensity measurements require two corrections: (1) a calibration of $C(0)$ when the mean count rate $\bar{n}$ per correlator's sample time varies; (2) a normalization at constant incident laser power. This results in a ± 15% uncertainty.

In the A phase we actually detect a Rayleigh signal of damping time $\tau_C\sim30$ μsec, 100 mK above T_C. We first confirm that this signal cannot be due to layer undulations[12]: This made has zero cross section in our geometry and is quenched by a $q_z\neq0$ component. Moreover the corresponding damping time is strongly q_1 dependent while in our experiment changing the q_1 component from 3×10^2 cm^{-1} to 1.5×10^3 cm^{-1} does not cause any significant variation of measured damping time. In view of this q_1 behavior and of the polarization rules [$(\vec{k}_e{}^i, \vec{k}_0{}^f)$ and $(\vec{k}_0{}^i, \vec{k}_e{}^f)$ geometries show the same signal, while nothing is visible between parallel polarizers] we conclude that the observed Rayleigh scattering is caused by tilt fluctuations. When we sweep the temperature, τ_C and I_2 increase with decreasing temperature as expected. T_{CA} is defined with an accuracy $\Delta T=\pm2$ mK by the sudden appearance of a strong scattered intensity characteristic of the C phase. We observe a T_{CA} drift (0.15 to 2 mK/h) which will be corrected during the experiment. Sweeping the temperature upwards we measure τ_C and N_2 versus ΔT. In fact two reasons restrict our temperature range to $\Delta T=350$ mK: (1) For large ΔT, I_2/I_0 goes down to a few times 10^{-3} leading to a low signal-to-noise ratio even for long accumulation time. To compensate for this effect we increase the laser power and correct the corresponding sample heating (< 30 mK for 15 mW). (2) Correlated after pulses in our phototube (a few tenths of a percent of incoming pulses in the microsecond range) overshadow our signal for $\Delta T>350$ mK.

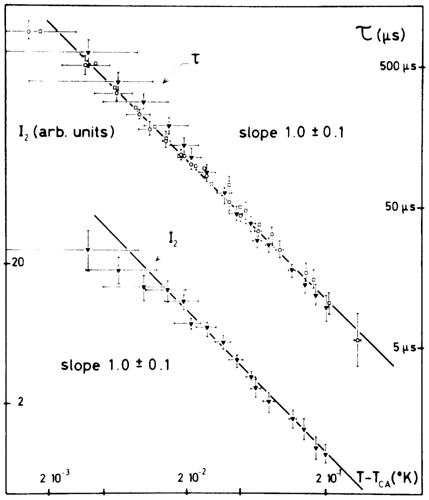

FIG. 2. Divergence of intensity I_2 and damping times τ of the "soft" mode versus ΔT. The trianges, squares, and circles correspond to different samples with T_c varying from 78.624 to 77.465°K.

The experimental data pertaining to $I_2(\Delta T)$ and $\tau_C(\Delta T)$ are plotted on a log-log scale and compared for various samples in Fig. 2. Between 20 and 200 mK, I_2 decreases by an order of magnitude and the corresponding plot is a straight line of slope $\gamma=1.0\pm0.15$. Near T_{CA} the points are no longer aligned; this could be due to a nonnegligible smectic-C contribution or could hide some crossover, but we cannot yet give a conclusive interpretation. The τ_C data are more accurate: For different samples $\tau_C(\Delta T)$ is found to follow a power law over two decades, going from 600 μsec for $\Delta T=3$ mK to 6 μsec for $\Delta T=300$ mK. The associated slope is also 1.0 ± 0.1. The comparison between the two plots does not suggest any critical behavior of η; an Arrhenius dependence with an activation energy ~0.5 eV produces, in our experimental range, only a 2% variation in η, which is well within experimental uncertainty. The exponents for I_2 and τ_C are compatible with a mean-field model.

In conclusion we have seen the first experimental evidence of critical angular fluctuations of the molecules in the layers in the smectic-A phase close to an $A \to C$ second-order transition. We observe the divergence of the corresponding Rayleigh intensity and the thermodynamic slowing down of the associated relaxation time from 350 mK to a few millikelvins near the transition. Both correspond to the same critical exponent $\gamma = 1.00 \pm 0.1_5$.[13] This result indicates a regular behavior of the associated viscosity and shows a better agreement with a mean-field model than with a heliumlike one in our temperature range. An improved apparatus can extend the measurements closer to T_{CA} and allow observation of an eventual "crossover" to a critical regime. The interferometric measurement of tilt angle by Galerne[6] is promising in that way. Note that our experiment is not sensitive to molecular rotations which would correspond to much higher frequencies; it thus cannot be conclusive on McMillan model[4] validity.

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Core Excitons in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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Inelastic electron scattering spectra of nitrogen, sulfur, and carbon core excitations in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are presented. The spectra exhibit sharp excitonic transitions to final states localized on separate TTF^+ or $TCNQ^-$ ions followed at higher energies by a continuum of transitions to free-electron states. In contrast to prior photoemission experiments, we find no evidence for neutral molecules in the bulk of TTF-TCNQ.

The well-known organic metal tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is unique in that it contains two distince one-dimensional stacks of donor and acceptor molecules with conduction bands of comparable bandwidth due to similar intermolecular separations.[1] Techniques which probe low-energy excitations of this crystal are unable to distinguish between the two conducting chains. However, we have measured transitions from core states to low-lying final