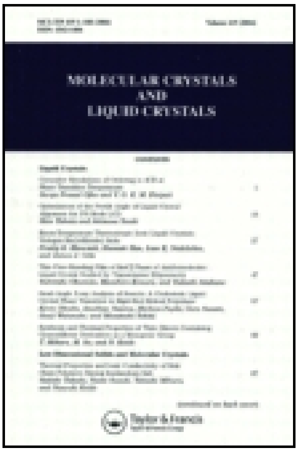

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Weak Crystalization in Liquid Crystals: Experimental Evidence

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WEAK CRYSTALLIZATION IN LIQUID CRYSTALS: EXPERIMENTAL EVIDENCE

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Abstract. The heat oapaoity in the isotropio phase and the latent heat on the IN transition line have been measured in binary liquid orystal mixtures by high-resolution adiabatio oalorimetry. It shown that an anomalous behaviour of the entropy jump on the IN phase transition line in the vioinity of the INA triple point is defined only by an partioular behaviour of the orystallization fluotuations in the isotropio phase. The oontribution of the orystallization fluotuations to the heat oapaoity is oomparable with the pretransitional heat oapaoity of the nematio fluotuations in the isotropio phase.

Keywords: phase transition, crystallization fluctuations, liquid crystal, isotropic phase, heat capacity, latent heat

The orystallization phase transitions in ordinary liquids are strongly first order. A latent heat of suoh transitions is muoh larger than unity ($\Delta H_{cr}/RT_{cr}=\Delta S_{cr}/RT_{cr}\gg 1$). Therefore fluotuations of the orystal order parameter are rather small, and their oontribution to thermodynamio values is not observable experimentally.

In liquid orystals the situation is different. First, the interaotion of the orystal lattioe with the orientational ordering leads to a lattioe of lower dimensionality whioh turns out to be preferable. In partioular, the smeotio phases A and C are systems with one dimensional orystal lattioes. Seoondly, the orystallization transitions are weakly first order, the latent heat being of the order of unity ($\Delta H_{cr}/RT_{cr}\sim 1$). Therefore one oan expeot that the orystallization fluctuations could be observed experimentally. Moreover, a variety of transitions in liquid crystals allows us to study the crystallization with different effective dimensionality of the phase space for fluctuations.

The spectrum of a uniaxial mode in the vicinity of the characteristic wave vector q_o of a smectic lattice can be expressed in the form[1]

$$\Delta(q) = \Delta + \xi_o^2(q - q_o)^2$$

where $\Delta=\Delta_o+\tau$, $\tau=(T-T_{IN})/T_{IN}$, Δ_o characterizes the nematic phase width, ξ_o is the bare correlation radius. The phase space for the smectic fluctuations in the isotropic phase in reciprocal space is a spherical shell of radius q_o and width dq. This phase space is effectively one-dimensional. This is so because only the component of the wave vector normal to the surface of the sphere changes the energy. Other components are degenerate in energy. This leads to large fluctuations.

The entropy of smectic fluctuations in the isotropic phase in low-order perturbation theory can be expressed in the form

$$(S_{sm})_I/R = A\tilde{\Delta}^{-0.5} ,$$

where R is the universal gas constant, A=const, and $\tilde{\Delta}$ is renormalized inverse smectic susceptibility . When orientational ordering appears in the nematic phase, the phase space for the smectic fluctuations is strongly suppressed. Therefore the entropy of the smectic fluctuations at the IN transition has a jump which can be expressed in the form

$$(\delta S_{sm})_{IN}/R = A\tilde{\Delta}_{IN}^{-0.5}(1 - \xi_{o\parallel}^2/2\xi_{o\perp}^2\tilde{\Delta}_{IN}) \approx A\tilde{\Delta}_{IN}^{-0.5} \qquad (1).$$

Here $\tilde{\Lambda}_{IN}$ is the inverse smectic susceptibility at the IN transition, $\xi_{o\parallel}$ and $\xi_{o\perp}$ are respectively the transverse and longitudinal bare correlation radii.

Thus the contribution of the smectic fluctuations to the entropy jump displays an anomalous behaviour when a nematic phase width decreases.

The contribution of the smectic fluctuations to the specific heat in the isotropic phase can be obtained from the smectic fluctuation entropy

$$\delta C_{sm}/R = A/2\tilde{\Lambda}^{-1.5}\partial\tilde{\Lambda}/\partial\tau = =A/2\tilde{\Lambda}^{-1.5}(1 - A_1\tilde{\Lambda}^{-1.5})^{-1} \qquad (2).$$

Note that the behaviour of the specific heat of the smectic fluctuations is unusual, with the critical exponent in first approximation equal to $\alpha = 1.5$ (for the second order transitions $\alpha=0.5$)!.

The phase space for the smectic fluctuations in the nematic phase near the NC transition is two toroids of radius $q_{o\perp}$. This phase space is effectively two-dimensional. There are two components of the wave vector which change the energy.Again a two-dimensional phase space give rise to large fluctuations.

In this case the entropy of the smectic fluctuations has logarithmic dependence on the inverse susceptibility[2]

$$(S_{sm})_N \sim -\ln\tilde{\Lambda}.$$

The fluctuational part of the specific heat can be expressed in the form

$$\delta C_{sm}/R \sim \tilde{\Lambda}^{-1}\partial\tilde{\Lambda}/\partial\tau \qquad (3)$$

with the critical exponent α = 1 !.

To observe the smectic fluctuations in the isotropic phase we have investigated the behaviour of a latent heat on the IN transition line and the isobaric specific heat

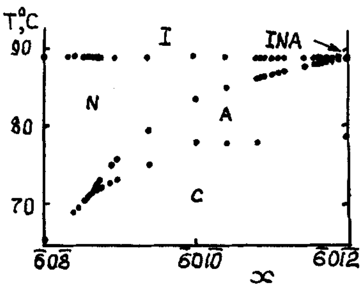

Fig. 1.

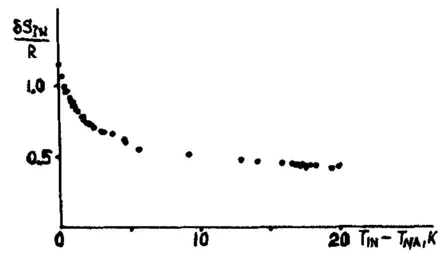

Fig. 2.

in the isotropic phase in binary liquid crystal mixtures. The measurements were performed by high -resolution adiabatic calorimetry.

The phase diagram of binary mixtures is shown in Fig. 1. On the phase diagram there is the INA triple point. It allows us to investigate the behaviour of the thermodynamic values as a function of the nematic phase width.

In Fig. 2 the behaviour of the entropy jump in units of R on the IN phase transition line is shown. The entropy jump increases anomalously as the nematic phase width decreases. The size of the jump is formed by two contributions, one connected with the nematic order parameter jump at the IN transition, the other connected with the jump of the smectic fluctuation entropy:

$$\delta S_{IN}/R = \alpha(\delta Q)^2_{IN} + (\delta S_{Sm})_{IN}/R.$$

It had been shown experimentally[9] that the nematic order parameter jump is practically independent of the nematic phase width. Thus the anomalous behaviour on the entropy jump on the IN transition line is due only to the particular behaviour of the smectic fluctuations.

The entropy jump as a function of the renormalized inverse smectic susceptibility is shown in Fig.3. The solid curve is the approximation of the experimental data

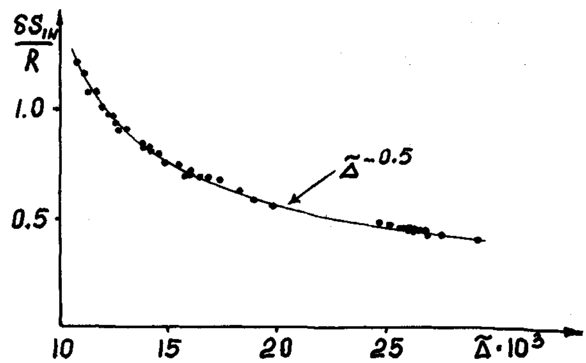

Fig.3.

by Eq.1. We have obtained very good agreement between experimental data and the theory. It is the direct experimental evidence of the smectic (crystallization) fluctuations in the isotropic phase.

In Fig. 4 the behaviour of the specific heat in units of R near the IN transition is shown for three mixtures. The nematic phase width for them changes from OK to 23K. The anomalous part of the specific heat in the isotropic phase is formed by the specific heat of the nematic order parameter fluctuations and that of smectic fluctuations:

$$\delta C = \delta C_N + \delta C_{sm}.$$

It is very difficult to separate these two contributions because the smectic fluctuation specific heat usually plays the role of the background for the pretransitional specific heat of the nematic fluctuations in the isotropic phase.

We have proposed the special procedure of fitting. The cross-sections of the specific heat curves in the isotropic phase at constant distances from the IN line (dashed lines in Fig.4) have been performed. They (without the regular part of the specific heat) are shown in Fig.5.

The contribution of the nematic fluctuations to the anomaly of the specific heat depends only on a distance from the IN transition. Therefore the temperature dependence of each cross-section is defined only by the behaviour of the smectic fluctuation specific heat. If the contribution of the nematic fluctuation specific

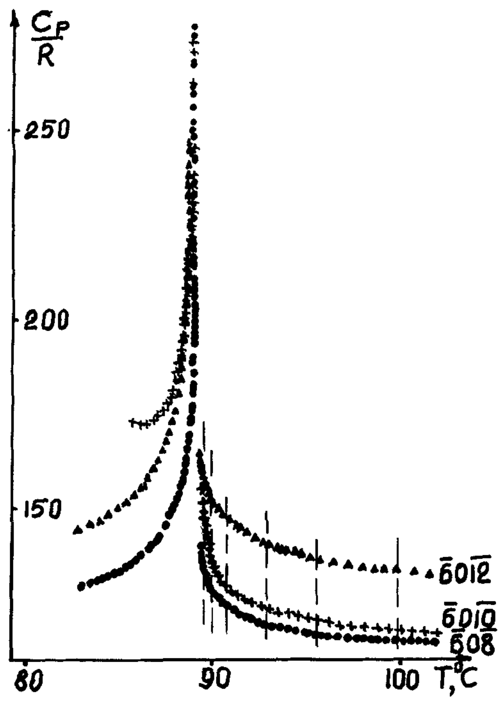

Fig. 4.

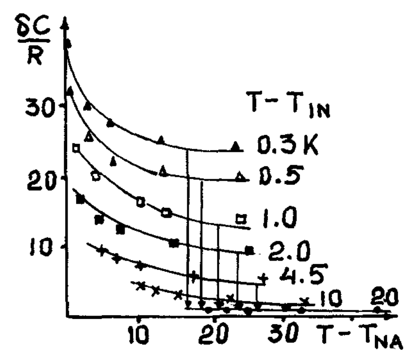

Fig. 5.

heat is subtracted from the each cross-section (as shown by the arrows in Fig.5) we will obtain a universal behaviour of the contribution of the smectic fluctuations to the specific heat.

In Fig.6 the behaviour of the contribution of the smectic fluctuations to the specific heat is shown which

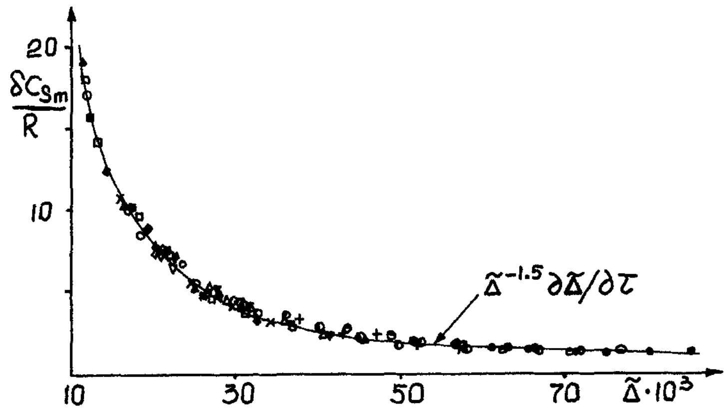

Fig. 6.

is obtained by such procedure. The solid curve is approximation by the Eq. 2. Very good agreement is observed. The approximations of the experimental data on $(\delta S_{sm})_{IN}/R$ and $(\delta C_{sm})/R$ were obtained with the same

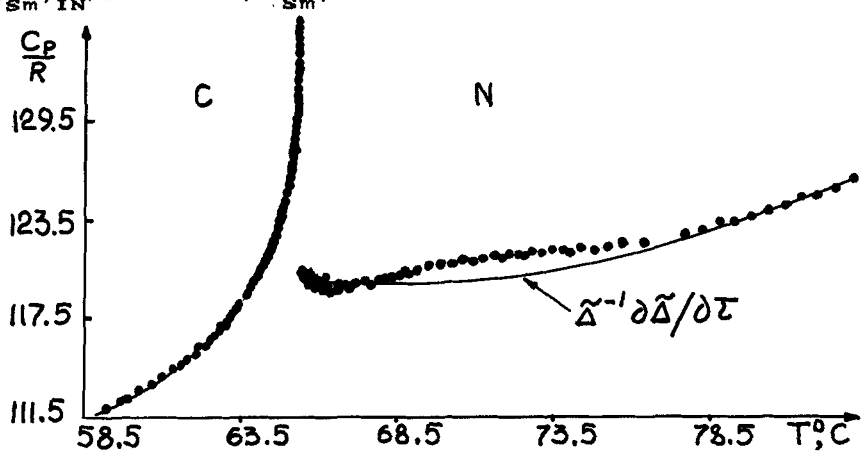

Fig. 7.

adjustable parameters. Note that the vicinity of the INA triple point the contributions of the smectic fluctuations and nematic to the heat capacity in the isotropic phase are comparable.

The behaviour of the specific heat on the NC transition is shown in Fig.7. The solid line is the approximation by Eq.(3). Appearance on the specific heat curve for $T>T_{NC}$ of the "hump" which size increases when the distance from the NAC multicritical point decreases, must be yet explained.

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