Phonon spectrum in the vicinity of the phase transition from a crystal to a nematic liquid crystal, and the order parameter

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The immediate vicinity of the crystal-nematic liquid crystal phase transition was investigated for the first time by using the long-wave IR absorption spectrum. From the temperature dependence of the integrated intensity of the 24 cm^{-1} phonon bend in the spectrum, we obtain for the order parameter at $T < T_{tr}$ a variation that agrees with the Landau theory.

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The nematic phase of liquid crystals is characterized by a zero value of the translational order parameter, whereas the orientational order parameter of this phase differs from zero.[1] One can therefore expect a characteristic change in the intensities of the long-wave IR absorption bands (particularly of the translational type) on going from the crystalline state (C) to the nematic liquid-crystal (NLC) phase.

In the spectrum of crystalline butoxybenzilidene-amino-benzonitryl (BBAB) $C_4H_9 - O - \langle \bigcirc \rangle - CH = N - \langle \bigcirc \rangle - C \equiv N$, we found an isolated narrow 24 cm^{-1} band, the temperature dependence of which and of the bands close to it was investigated in a wide temperature range (100—400 °K), including the crystalline nematic-liquid crystal, and the isotropic liquid (IL) phases. The long-wave IR absorption spectra were registered with an FIS-21 spectrometer having a slit spectral width 0.5 cm^{-1} in the region 20—40 cm^{-1}. The temperature stabilizati during the study of the immediate vicinity of the transition wave was within $\pm 0.03°$.[2] The 24 cm^{-1} band vanishes on going to the NLC phase (Fig. 1). Figu 2 shows the temperature dependence of the integrated intensity of the 24 cm^{-1} band. The decrease has a clearly pronounced power-law character and is noti able only near the transition point. An analysis of the data shows that the inter sity decreases here like $K(T - T)^\beta$, where $\beta = 0.8$ ($T_{tr} = 336.3°$ K).

To identify the discussed band, we obtained the far IR absorption spectrum of a 10% solution of this substance in carbon tetrachloride. In the vicinity of 24 cm^{-1}, only a weak smeared absorption is observed, similar to that observed in IL. In the Raman scattering spectrum of the crystalline samples, at room temperature, the discussed band is replaced by a weak 29 cm^{-1} line, whereas the higher-frequency lines, for example at 43 cm^{-1}, have an appreciable intensity. This allows us to state that the discussed far-IR 24 cm^{-1} band is due to crystal vibrations, and most readily to vibrations of the translational type.

Crystal—nematic liquid crystal transition is a phase transition of first order.[3] However, the pretransition phenomena in the crystalline phase can apparently possess properties of a second-order transition. Inasmuch as the transition in NLC is accompanied by vanishing of the periodicity of the distances between the molecules, whereas the directions of the dipoles of the neighboring molecules remain parallel, the order parameter (σ) must be related just to the violation of the translational symmetry in the crystal at $T < T_{tr}$.
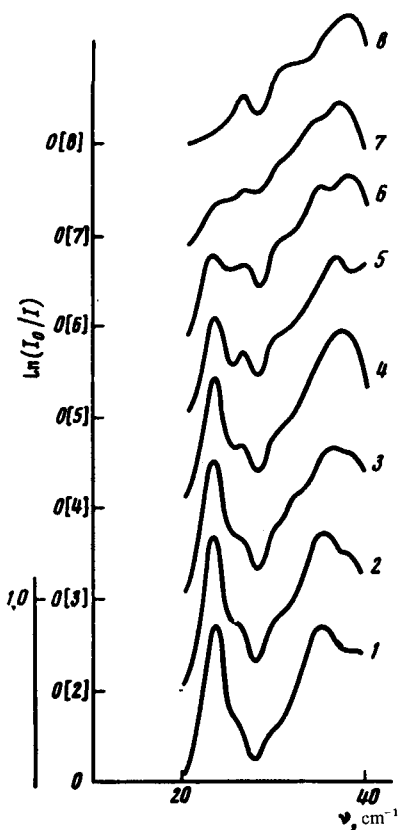

FIG. 1. Absorption spectra of BBA B in the 20—40 cm^{-1} region in the vicinity of the C—NLC transition at temperatures: 1—335.5, 2—335.6, 3—335.7, 4—335.8, 5—335.9, 6—336.0, 7—336.1, 8—336.3 °K.

Expanding the dipole moment μ of the transition in the crystal in powers of $(\tau - \sigma_0)$ about the value of σ_0 (σ_0 is the order parameter at which the "break" between the second-order and first-order transitions takes place) and confining ourselves to the first two terms, we have at $T < T_{tr}$

$$\mu(\sigma) = \mu(\sigma_0) + (\sigma - \sigma_0)\left(\frac{d\mu}{d\sigma}\right)_{\sigma = \sigma_0} .$$

Inasmuch as the discussed band is not observed in NLC, i.e., it does not contain the corresponding optical vibrations, it follows that $\mu \approx 0$ at $T > T_{tr}$. The integrated intensity I of the band at $T < T_{tr}$ is proportional to $\mu^2(\sigma)$, so that

$$I \sim (\sigma - \sigma_0)^2\left(\frac{d\mu}{d\sigma}\right)_{\sigma = \sigma_0} .$$

Consequently, the temperature dependence of the order parameter takes the form

$$\sigma - \sigma_0 = \sqrt{I(T)} \approx (T_{tr} - T)^{\beta/2} .$$

Our experimental data yield $\beta/2 = 0.4 \pm 0.1$, which is close to the value predicted by the Landau theory.[4]
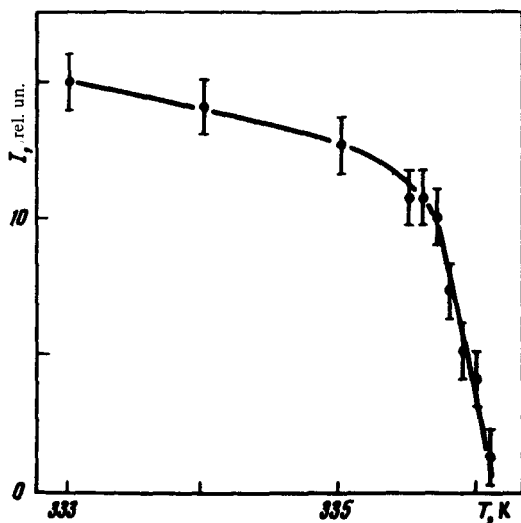

FIG. 2. Temperature dependence of the integrated intensity of the 24 cm^{-1} band in the immediate vicinity of the C $\rightarrow$ NLC phase transition.

The frequency of the discussed band near the phase transition remains strictly constant. Thus, we are dealing not with a "soft mode," but with an optical oscillation whose frequency in the crystal is fixed, and only the absorption intensity is a function of the order parameter.

We note in conclusion that lower temperatures in the interval 140—150°K of this band splits into two components. It appears that a phase transition into a new crystalline modification takes place here. There are no previously published data on this phase transition.

[1]K.K. Kobayashi, Mol. Cryst. Liq. Cryst. **13**, 137 (1971).

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