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VIBRATIONAL DENSITY OF STATES OF AMORPHOUS AND CRYSTALLINE LIQUID CRYSTAL SUBSTANCES

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Abstract. - We have measured by the TOF neutron spectroscopy method the amplitude-weighted frequency distribution function of the glassy and crystalline phases of the EBBA, MBBA and PAA compounds. Evident changes in the vibrational density of states in the frequency range up to 300 cm$^{-1}$ are observed when passing from the amorphous to ordered crystalline phases. The partly deuterated $d_6$-PAA spectrum have shown that these vibrations are due to translational and librational motions of the whole molecule and due to low frequency oscillations of the end groups of the molecule.

Liquid crystal (LC) substances dependent on their thermal history may form different solid modifications. The PAA, MBBA and EBBA compounds are the most frequently studied LC substances and they are known to have different polymorphic crystalline phases, see ref.(1-3) and refs therein. By the fast cooling of the mesophase of these substances a glassy state (GLC) is formed. The X-ray and neutron diffraction methods as well as optical spectroscopy ones were used to investigate these GLC materials(2-6). It has been shown that the molecular structure and order parameter of the GLC are similar as in the nematic phase of LC. The GLC state is metastable at low temperatures and may be transformed into the ordered crystalline phases without the melting of the substance. This transformation can be stopped by the lowering of the temperature. So, any intermediate partly ordered state may be studied. Since the GLC systems exist at low temperatures, where the anharmonic effects and multiphonon scattering processes are strongly reduced, they are more suitable for dynamical studies, than LC systems. Here we present the amplitude-weighted frequency distribution function $G_{H}(E)$ of the GLC and crystalline states of the most popular LC substances.

The inelastic incoherent neutron scattering (IINS) spectra have been measured using the KDSOG inverted geometry time-of-flight spectrometer at the IBN pulsed reactor of the JINR Dubna(8). The samples of EBBA, MBBA and PAA were poured in the aluminum containers of about 0.8 mm thick and with the 180 x 160 mm rectangular cross section. The GLC phases were produced by the dip in liquid nitrogen of the container placed at the bottom of the helium cryostat. The IINS spectra have been measured at 5 K at seven scattering angles from 30° to 150° every 20° simultaneously. Recently some of the IINS spectra from the MBBA sample were published(9).

The measured IINS spectra have been transformed into the $G_{H}(E)$ function according to the one-phonon incoherent scattering cross section formula. Such approximation is justified by the fact that IINS spectra of molecular crystals below 300 cm$^{-1}$

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measured at 5 K agree well with calculated ones \(^{(10,11)}\). The resolution function of the KDSOG spectrometer in the mentioned frequency range does not disturb significantly the \(G_H(E)\) function. The singularities of this function correspond to those of the function of phonon density of states \(^{(10-12)}\). So, we believe that the spectra presented here reflect the behaviour of the vibrational density of states in different phases of the LC substances.

The \(G_H(E)\) functions of the MBBA and EBBA compounds are shown in Figs. 1 and 2, respectively. One can see that the transition from the GLC structure to crystalline order does not change significantly the \(G_H(E)\) functions. Thus the large changes in vibrational spectra of the different solid modifications measured by the optical spectroscopy methods \(^{(3-6)}\) are due to the loss of spatial coherency of vibrations and not to significant changes of the vibrational density of states.
Fig. 3.: The $G_{\delta}(E)$ functions of the PAA (p-azoxyanisol) compound:

A is the sample obtained from the nematic LC phase of the normal d-PAA (CH$_3$-PAA) by the fast cooling.

B is the stable crystalline sample of the d-PAA and partly deuterated d$_2$-PAA (CD$_3$-PAA).

The PAA spectra will be discussed in detail in the separate publication by A.V.Bielushkin, E.L.Bokhenkov, A.I.Kolesnikov, I.Natkaniec, E.F.Sheka and S.Urban.

The essential changes of $G_H(E)$ after the transition to the crystalline state occur in low frequency region ($E < 300$ cm$^{-1}$). Vibrational density of states of the GLC substances seems to be a linear function of frequency at $E \to 0$. In Fig.1 the slope of this function fitted to the spectrum of the sample cooled from isotropic liquid is compared with the spectra of other solid modifications. The distinct maxima in the spectra of crystalline samples at the $E \approx 100$ cm$^{-1}$ should correspond to the internal molecular vibrations. These low frequency bands undergo a considerable broadening when passing to the GLC state.

The comparison of the spectra of normal and partly deuterated samples of crystalline PAA (see Fig.3) show us that the lattice vibrations of this substance cut-off at about 140 cm$^{-1}$. The internal vibrations of this molecule in the frequency range below 300 cm$^{-1}$ belong mainly to the oscillations of the end-CH$_3$ groups. We hope that the study of the IINS spectra of partly deuterated LC substances will help in the assignment of these oscillations and will serve to the better understanding of molecular conformations in different modifications of these substances.

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