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Mössbauer Investigations of Liquid Crystalline Systems

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Abstract—Mössbauer spectra of solutions of diacetylferrocene in 4,4′-di-*n*-heptyloxyazoxybenzene and 4,4′-di-*n*-octyloxyazoxybenzene possessing the nematic and smectic mesophases have been investigated.

Gamma-resonance was observed in both phases; its existence in the nematic mesophase can be explained by the preservation of smectic structure fragments –cybotactic groups. The dependence of Mössbauer effect probability and of the asymmetry of quadrupole doublets diacetylferrocene in the oriented 4,4′-di-*n*-heptyloxyazoxybenzene solutions versus the angle between the applied external magnetic field and the γ-ray beam were studied for. Under the assumption of " cone of planes " structure of the oriented system the angle of the slope of heptyloxyazoxybenzene molecules in smectic layers was determined $(40 \pm 15)°$.

First applications of γ-resonance spectroscopy (GRS) to liquid crystalline (LC) systems were described in Ref. 1. Mössbauer effect (ME) was observed[1] when the label of Fe^{57} was introduced in more ordered of LC phases, namely in the smectic phase. Possibilities of using the ME for investigation of liquid crystals were discussed in two subsequent theoretical papers.[2,3]

Our investigation was undertaken in order to extend the circle of LC systems studied by means of GRS and to attempt to observe the γ-resonance in less ordered LC phases (particularly in the nematic phase).

The 5% (by weight) solutions of diacetylferrocene (DAF) in 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB) and 4,4′-di-*n*-octyloxy-

azoxybenzene (OOAB)—the first homologs of alkyloxyazoxybenzenes possessing both nematic and smectic LC phases—were chosen for our investigations. The first of the mentioned systems has been already investigated in Ref. 1, but—what is of importance—at a higher concentration of DAF (7% by weight).

Temperatures of the phase transitions of DAF + HOAB and DAF + OOAB systems were determined before and after the γ-resonance experiments by thermomicroscopic analysis (TMA) at the D. A. Furmanov Pedagogical Institute. There were found only minor differences in TMA data obtained before and after the GRS-measurements.

In the same laboratory it was found that, for our sample, the formation of the separate phase of DAF was absent although such a phase appears during the cooling of the isotropic melt at higher (i.e. >6%) DAF concentrations.

GR-spectra were treated using the computer BESM-3 and the programme developed by Yu. M. Ostanevich of the Joint Institute of Nuclear Research. Here and below, δ is isomer shift, Δ—quadrupole splitting, Γ—width of lines, $\alpha f'$—total area of GR-spectra, $A = S_+/S_- = S_\pi/S_\sigma$—asymmetry of quadrupole splitting, $S_+ = S_\pi$ and $S_- = S_\sigma$ are areas of lines corresponding to the larger and the smaller energy of γ-transition (one can assume that, for DAF like ferrocene, $q > 0$).[4]

When studying the temperature dependence of $\alpha f'$ the isotropic solutions of DAF in HOAB and OOAB slowly cooled down to the room temperatures were carefully powdered in the agate mortar (in order to avoid possible orientation effects) and then placed in the hermetic teflon cuvette inside the thermostatic oven keeping the temperature constant to within $\pm 0.5°$ during the measurements of the spectrum, i.e. 10–12 h.

The investigation of GR-spectra has been made during the heating of systems from the room temperature up to the temperatures corresponding to the isotropic liquid phase and during the cooling from the isotropic liquid phase down to the room temperature.

Temperature dependence of $\alpha f'$ and A for DAF solutions in HOAB and OOAB are presented on Figs. 1 and 2. The temperatures of the TMA-defined phase transitions are shown too.

GR-spectra of DAF + OOAB systems at 25 °C (crystal phase) and

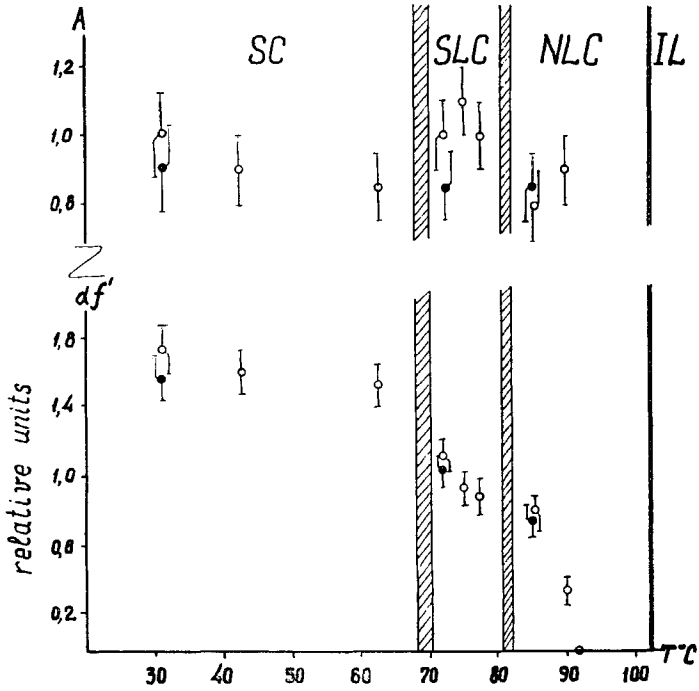

Figure 1. Temperature dependence $\alpha f'$ and A in DAF + HOAB system (○—heating, ●—cooling).

92 °C (nematic phase) are shown on Fig. 3. According to our data, Mössbauer effect is observable in both smectic and nematic LC phases. δ, Δ and Γ values are not changed in the cycle of heating and cooling of the samples.

All through the studied interval of temperatures for both systems $\delta = 0.65$ mm/sec (relatively to $Na_2[Fe(CN)_5NO].2H_2O$) and $\Delta = 2.15$ mm/sec, which correspond to pure DAF. From Figs. 1 and 2 one can see that within the accuracy of experiments $\alpha f'$ and A values are also not changed in the samples upon cooling and heating.†

The possibility of the observation of γ-resonance in the nematic

† The experiments when cooling the samples from the isotropic liquid phase followed the experiments with the heated sample. Part of the heated samples can evaporate because of the insufficient hermeticity of the cuvette and the $\alpha f'$ values of cooled samples can decrease in comparison with the $\alpha f'$ of heated samples.

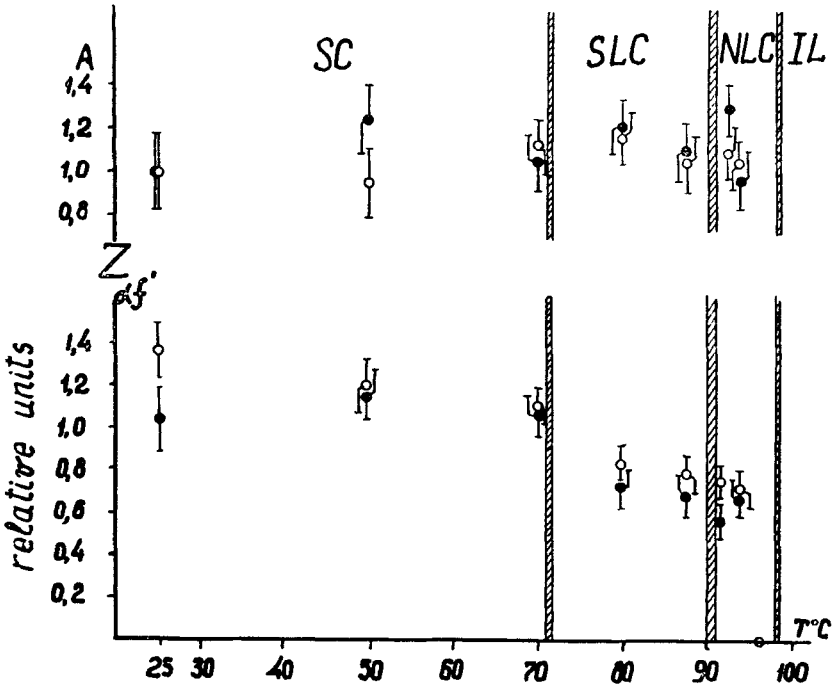

Figure 2. Temperature dependence $\alpha f'$ and A in DAF + OOAB system (○—heating, ●—cooling).

phase of the studied systems can be explained by the existence of pseudolayer ordering of the nematic phase of LC.

Indeed, in Refs. 5 and 6 it was shown by means of roentgenography and optical modelling that in the liquid crystals possessing both nematic and smectic phases the transition from smectic to nematic phase does not lead to a complete disappearence of the smectic layers (i.e. to their destruction to single molecules)—the formation of pseudolayers takes place (so-called cybotactic groups)—the fragments of the layer structure. The sizes of such fragments diminish gradually with the rising temperature.

The large errors in A values $\pm(0.15 \div 0.20)$ do not permit one to find the changes caused by the orientation of LC matrixes when the nematic phase is in contact with the cuvette walls.[7] The situation can be more favourable if the label enriched by Mössbauer isotopes is introduced in the LC, possessing a nematic phase.

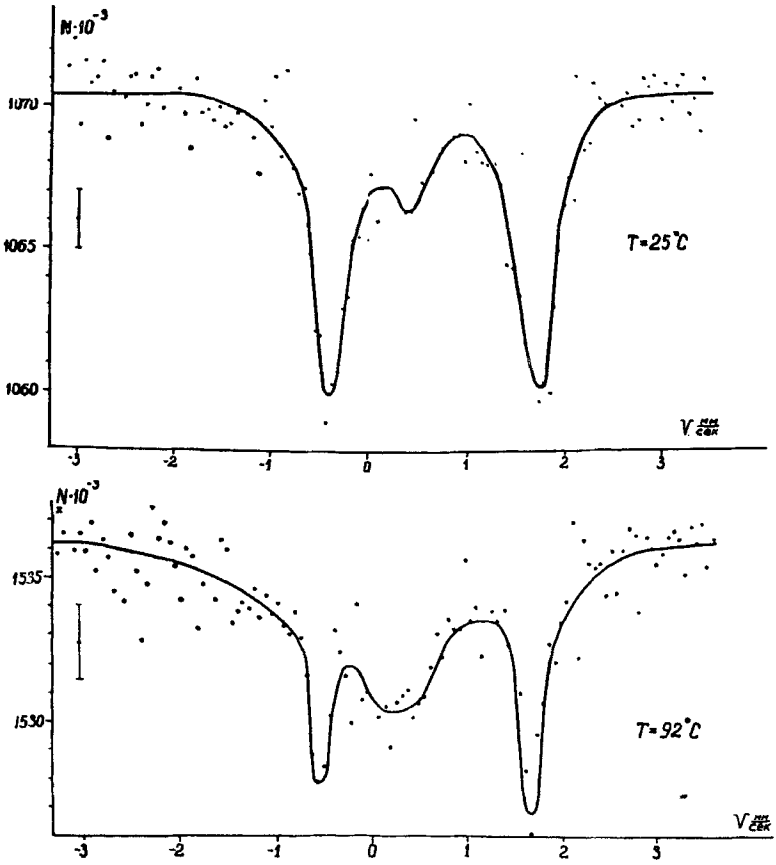

Figure 3. Mössbauer spectra of a solution of DAF in OOAB at $T = 25$ °C (crystal phase) and $T = 92$ °C (nematic phase). The smaller centre line is due to the Fe in the Be disc of the NaI(Tl) scintillation crystal.

Such orienting external factors as magnetic and electric fields lead to the formation of oriented structures of LC,[7,8] e.g. the orientation of the smectic HOAB in the direct magnetic fields leads to the formation of a " cone of planes " structure (Fig. 4c).[6]

On Fig. 5 one can see the changes of $\alpha f'$† and A of DAF + HOAB solution oriented by the magnetic field of 2000 G with the angle θ

† The sample used in experiments on the orientation of DAF + HOAB system by the external field was thinner than in $\alpha f'$ (T) measurements. Values of $\alpha f'$ shown on Fig. 5 are recalculated to the thickness of the sample in $\alpha f'$ (T) experiments.

between the directions of the orienting field and of the γ-beam. The orientation of LC matrix was performed in the isotropic liquid phase ($T \approx 110$ °C) along the directions normal and parallel to the plane of cuvette. GR-spectra of the oriented samples were obtained at room temperature (samples were cooled in the magnetic field); the angles between the axis of the cuvette and the γ-beam varied from 0° to 45° (angle θ between the directions of the field and γ-beam varied from 0° to 90°). The GR-spectrum of DAF + HOAB solution in the oriented smectic phase (at 72 °C) has been obtained for comparison. The measuring of GR-spectra at room temperature brings more distinct spectra and permits also conclusions about the orientation of LC matrix in the smectic phase which is conserved upon the cooling of samples down to room temperature.[1]

The changes of the effective thickness and of the solid angle with the rotation of oriented sample around the direction of γ-beam were taken into account by comparison of $\alpha f'$ changes for the investigated LC system and the calibrating sample of $Na_2[Fe(CN)_5NO].2H_2O$.

One can notice from Fig. 5 that in the DAF + HOAB system oriented by the magnetic field the variation of θ from 0° to 90°

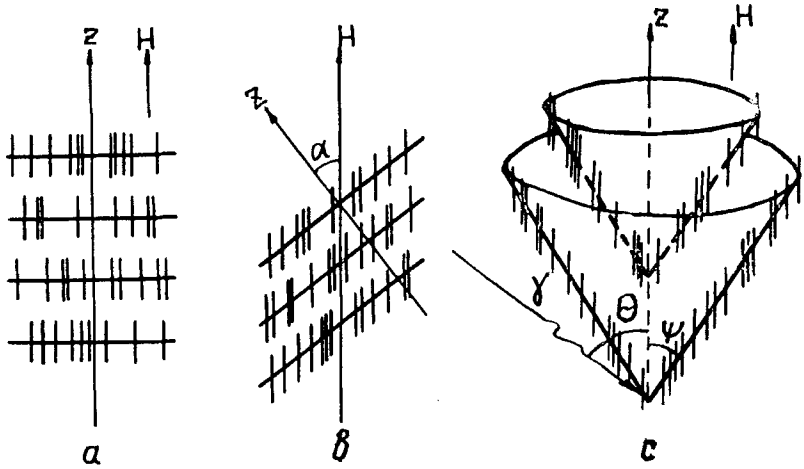

Figure 4. Possible structure of the smectic liquid crystals oriented by magnetic field. a, b—" one-rank " structure; α is the angle of slope of the normal to the smectic LC layers relative to the direction of the orienting field; c—" cone of planes " structure; θ is the angle between the directions of the orienting field and γ-rays beam, Ψ is the apex angle of a cone.

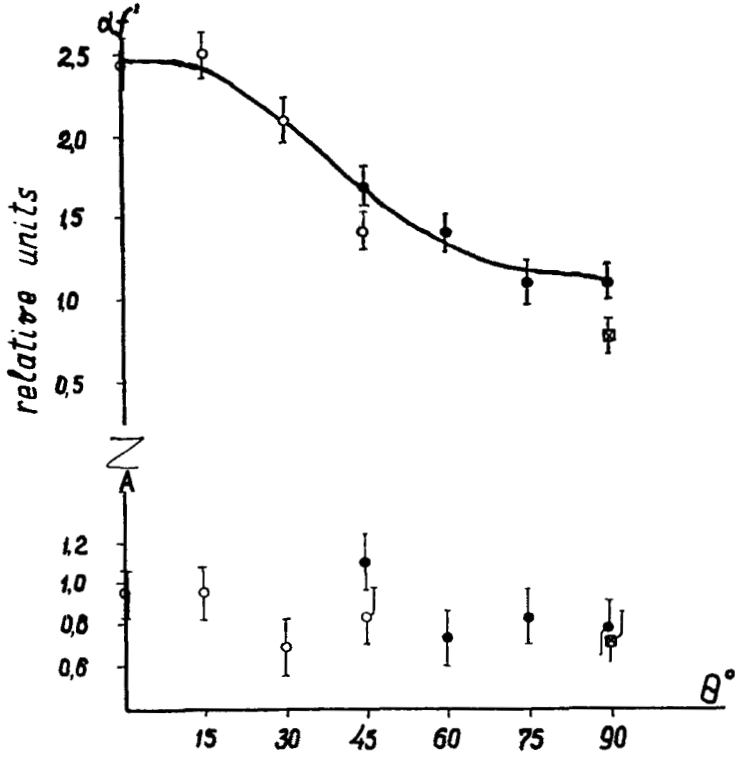

Figure 5. Dependence of $\alpha f'$ and A on the direction of HOAB orientation in DAF + HOAB system (○—magnetic field ⊥ cuvette plane, $T = 30$ °C; ●—magnetic field ∥ cuvette plane, $T = 30$ °C; ×—magnetic field ∥ the cuvette plane, $T = 72$ °C). The solid line is an experimental fitting.

within the limits of accuracy does not change the A values, which are equal to the values obtained in the experiments with the heating and cooling of this system.

Contrary $\alpha f'$ values depend strongly on θ† which is apparently connected to the large difference in the mean squared vibrational

† Observed strong $\alpha f'(\theta)$ dependence also according with the argument that the labelled molecules do not form the separative agglomerations but are distributed in the LC matrix.

In the case of formation of a separate phase by non-oriented subcrystallites of DAF, there would have been no changes of $\alpha f'$ magnitudes with the angle θ, and that was in fact observed for carefully powdered DAF samples (for angles between the plane of the cuvette and the direction of γ-beam $\theta' = 0 - 45°$).

Trying to ascertain the character of $\alpha f'(\theta')$ dependence (which could be in

displacements of the molecules with the Mössbauer label along the smectic planes of the LC and normal to them.

Expressions derived in Ref. 9 describe the dependence of the absolute probabilities of the Mössbauer effect f' on the angle of the LC molecules slope in the smectic layers (Ψ') and on the mean squared vibrational displacements of the molecules of the label along the layer ($\langle r_{\parallel}^2 \rangle$) and normal to it ($\langle r_{\perp}^2 \rangle$)—for the cases of " one rank " (Figs. 4a, b) and " cone of planes " (Fig. 4c) structures of smectic LC oriented by external fields.

These equations were obtained assuming the equality of mean-squared amplitudes of vibrations of labelled molecules in the plane of drawing and in the normal direction. For the most general case of Fig. 4c one obtains:

$$f'(\theta) = \exp\left\{-\frac{1}{\lambda^2}\left[\langle r_{\parallel}^2\rangle(\sin^2\theta + \cos^2\theta\cos^2\Psi) + \langle r_{\perp}^2\rangle\cos^2\theta\sin^2\Psi + \frac{\langle r_{\perp}^2\rangle - \langle r_{\parallel}^2\rangle}{2}\sin^2\theta\cos^2\Psi\right]\right\}$$
$$\cdot\sum_{n=-\infty}^{\infty} I_n\left(\frac{\langle r_{\perp}^2\rangle - \langle r_{\parallel}^2\rangle}{2\lambda^2}\sin 2\theta\sin 2\Psi\right)$$
$$\cdot I_{-(n/2)}\left(\frac{\langle r_{\parallel}^2\rangle - \langle r_{\perp}^2\rangle}{2\lambda^2}\sin^2\theta\cos^2\Psi\right)$$

where θ is the angle between the directions of magnetic field H and γ-beam, Ψ—the angle of the slope of smectic planes to the direction of orienting field H ($\Psi' = \pi/2 - \Psi$), λ—wave length of γ-ray, $I_\nu(x)$—Bessel function of imaginary argument.

$\langle r_{\perp}^2\rangle$ and $\langle r_{\parallel}^2\rangle$ parameters defining the anisotropy of the dynamical properties of the solute molecules which were labelled and Ψ' parameter defining the LC matrix structure can be determined from the experimental f' values for $\theta = 0°$, $\theta = 90°$ and for polycrystalline LC sample (isotropic melt of DAF in HOAB, carefully powdered after the cooling down to the room temperature).

In the general case, the f' dependence on $\langle r_{\perp}^2\rangle$ and $\langle r_{\parallel}^2\rangle$ for the

principle created by possible ordering of DAF subcrystallites, caused by orienting of the LC matrix), we have studied such dependence also for mosaics of needle-shaped crystals of DAF, imitating the " cone of planes " structure of oriented HOAB. The ratios $\alpha f'_0/\alpha f'_{45}$ for such mosaics, corresponding to $\Psi = 35 - 65°$ (vide infra) are not more than 1.1 and so considerably lower than those corresponding to θ changes of 45° which are equal to 1.3 – 1.4 (see Fig. 5).

polycrystalline sample (when $[\langle r_{\parallel}^2\rangle - \langle r_{\perp}^2\rangle] > 0$) can be expressed as (Ref. 9):

$$f' = \sqrt{\frac{\pi\lambda^2}{4(\langle r_{\parallel}^2\rangle - \langle r_{\perp}^2\rangle)}} \exp\left\{-\frac{\langle r_{\parallel}^2\rangle}{\lambda^2}\right\} \Phi\left(\sqrt{\frac{\langle r_{\parallel}^2\rangle - \langle r_{\perp}^2\rangle}{\lambda^2}}\right),$$

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{t^2}\,dt$$

The absolute values of $f'_{0°}, f'_{90°}$ and $f'_{\text{polycryst}}$ have been defined by the " black absorber " method. At room temperature for the DAF + HOAB system oriented by the magnetic field: $f'_{0°} = 0.22 \pm 0.01$; $f'_{90°} = 0.11 \pm 0.01$; $f'_{\text{polycryst}} = 0.17 \pm 0.01$.

In the case of " cone of planes " structure of oriented smectic LC phase the mean squared displacement of the labels is equal to $\langle r_{\perp}^2\rangle = (0.1 \pm 0.05)\cdot 10^{-17}$ cm^2 and $\langle r_{\parallel}^2\rangle = (0.5 \pm 0.2)\cdot 10^{-17}$cm^2, and the angle of the LC molecules slope in the layer (tilt angle) is: $\Psi' = (40 \pm 15)°$.

This value of Ψ' is in good agreement with the published data: $\Psi = 30°$(ESR[10] and X-ray diffraction analysis[11]), $\Psi' = 45°$ (optical investigations[12]).

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