DETERMINATION OF THE DYNAMICAL AND STRUCTURAL CHARACTERISTICS OF LIQUID CRYSTALS FROM MÖSSBAUER SPECTRA

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Equations are obtained for the angular dependence of the absolute probability f′ of the Mössbauer effect, corresponding to different (one-row and herring-bone) structures of smectic and nematic liquid crystals oriented by an external field. An equation is also obtained for the probability f′ of the Mössbauer effect in polycrystals for the case of large mean-square vibration amplitudes $\langle r_{\parallel}^2 \rangle$ and $\langle r_{\perp}^2 \rangle$ of the Mössbauer nuclei. Under the assumption that a herring-bone structure is formed on orientation of the smectic phase of the system diacetyl ferrocene + 4,4′-di-n-heptyloxyazoxybenzene, the equations obtained and the experimental values of f′ are used to calculate the mean-square vibration amplitudes of the marker molecules in the liquid-crystal matrix (these amplitudes characterize the anisotropy of the vibrations of the molecules of oriented liquid crystals) and the angle of inclination of the layers of the smectic phase relative to the direction of the orienting field.

Up to the present time, many interesting and original data on the structure and properties of different substances (cf., e.g.,[1]) have been obtained by the method of Mössbauer spectroscopy. One can hope that this will be found to be a promising method for the study of liquid crystals (LC) and, in particular, for the investigation of their structural features and their dynamical and orientational properties. Unfortunately, as yet, there are no known LC systems containing Mössbauer nuclei directly; however, it is possible to investigate liquid crystals by the method of Mössbauer spectroscopy by introducing "markers" in the form of compounds containing Mössbauer nuclei.

The first experiments on the Mössbauer study of a LC system (4,4′-di-n-heptyloxyazoxybenzene (HOAOB)) are described in a paper by Uhrich, Wilson and Resch[2]. These authors observed the Mössbauer effect on introducing a marker (diacetyl ferrocene (DAF)) into the most ordered (smectic) LC phase. In[3], the area af′ under the absorption curve (which is proportional to the probability of the Mössbauer effect) in the Mössbauer spectra of DAF dissolved in HOAOB oriented by a magnetic field[1)] was found as a function of the angle between the directions of the orienting field and the γ-ray beam. From this dependence, in addition to data on the dynamical properties of the marker molecules, one can obtain data characterizing the properties of the LC matrix. In the case when strong (e.g., chemical) bonds are formed between the marker molecules and the LC matrix, the anisotropy of the vibrations of the marker molecules dissolved in the oriented LC matrix will be directly related to the anisotropy of the vibrations of the molecules of the complexes formed. When weak bonds are formed between the marker molecules and the matrix (as is the case when DAF is dis-

solved in HOAOB), the orientation of the matrix will lead only to partial ordering of the directions of motion of the marker molecules as a result of steric effects; however, in this case too, one can obtain certain information on the macrostructure of the LC matrix from the angular dependence of af′, e.g., data on the effective angle of inclination of the smectic layers of the LC matrix relative to the direction of the orienting field.

In the case when the orientation of the LC matrix is accompanied by orientation of the marker molecules (i.e., of the axes of the electric field gradient), additional information on the LC structure can be obtained from the angular dependence of the asymmetry of the quadrupole doublets of the Mössbauer spectra[6].

It may be assumed that in the "marker + LC" system, as in molecular crystals, the vibrations of the Mössbauer nuclei are a superposition of two types of vibrations, lying in different frequency ranges: the high-frequency vibrations of the atoms in the molecules and the low-frequency vibrations of the molecules as a whole[1]. In this case,

$$ f' = \exp\left\{-\frac{1}{\lambdabar^2}\langle(\mathbf{1r})^2\rangle\right\} = \exp\left\{-\frac{1}{\lambdabar^2}\langle[\mathbf{1}(\mathbf{r_a}+\mathbf{r_m})]^2\rangle\right\} \approx f'_a f'_m, \quad (1) $$

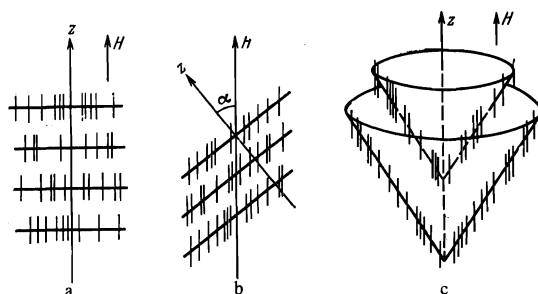where $\mathbf{1}$ is the unit vector in the direction of the γ-ray

FIG. 1. Possible structures of smectic LC's oriented by a magnetic field: a) and b) one-row structures (α is the angle of inclination of the normal to the smectic planes relative to the direction of the orienting field; c) herring-bone structure.

[1)] In external magnetic fields, the long axes of the molecules of nematic and smectic LC's are aligned along the field lines, and LC structures of the one-row type (see Figs. 1a, b) or herring-bone type (a cone of planes) (see Fig. 1c) are formed.

beam; the parameters f_a' and f_m' are respectively associated with the intramolecular and inter-molecular vibrations (of the marker molecules in the case when weak bonds are formed, or of the "marker + LC" complex in the case when strong bonds are formed); r_a and r_m are the corresponding vibration amplitudes; the averaging is performed over a time interval equal to the life-time of the excited nucleus.

For molecular crystals, f_a' is usually close to unity at low temperatures and depends weakly on the temperature[1]. Thus, for ferrocene, the values of f_a' calculated using the Einstein model of a solid vary from 0.79 to 0.60 when the temperature changes from 80 to 300°K. Since the values of f_a' should be close for related compounds[7], it may be assumed that the value of f_a' is about 0.6 for DAF at 300°K. Therefore, for the system DAF + oriented HOAOB, we can write

$$f' = 0.6f_m' = 0.6 \exp\left\{-\frac{1}{\lambda^2}\langle(ir_m)^2\rangle\right\} \qquad (2)$$

and assume that the angular dependence of af' obtained in[3] is determined mainly by the change of f_m'.

The sharp anisotropy of the structure of smectic LC's can have the result that motion of the marker molecules occurs with differing facility along the layers and along the normals to the layers, and this leads to the observed anisotropy of af' in the Mössbauer spectra of such systems[3].

In the laboratory coordinate frame xOyz (the magnetic-field direction coincides with the z-axis), the position of the generating line Oy' of the cone of smectic planes is defined by the azimuthal angle ψ and the polar angle ξ, while the position of the vector i is defined by the azimuthal angle θ and the polar angle φ (Fig. 2). The coordinate system x'Ay'z' is associated with a marker molecule positioned at the point A on the generating line; $(r_{x'}, r_{y'}, r_{z'})$ are the Cartesian coordinates of the vector r_m in this frame.

If we assume that the mean-square displacements of the marker molecules are the same in different directions along a smectic layer, i.e., if we consider the axially symmetric case, then

$$\langle r_{x'}^2\rangle = \langle r_{y'}^2\rangle = \langle r_{\|}^2\rangle,$$
$$\langle r_{z'}^2\rangle = \langle r_{\perp}^2\rangle, \qquad (3)$$

where $\langle r_{\|}^2\rangle$ and $\langle r_{\perp}^2\rangle$ are the mean-square displacements of the Mössbauer marker molecule in the plane of the layer and along the normal to the layer respectively. We then have

$$\langle(ir_m)^2\rangle = \langle r_{\|}^2\rangle[\,(\sin\theta\sin\varphi\cos\xi - \sin\theta\cos\varphi\sin\xi)^2 \qquad (4)$$
$$+ (\sin\theta\sin\varphi\sin\psi\sin\xi + \sin\theta\cos\varphi\sin\psi\cos\xi + \cos\theta\cos\psi)^2]$$
$$+ \langle r_{\perp}^2\rangle(\cos\theta\sin\psi - \sin\theta\sin\varphi\cos\psi\sin\xi$$
$$- \sin\theta\cos\varphi\cos\psi\cos\xi)^2.$$

By substituting the expression for $\langle(i\cdot r_m)^2\rangle$ given by Eq. (4) into formula (2), we obtain f_m' corresponding to marker molecules positioned along the generating line of the cone of planes (f_{gen}').

To obtain the corresponding expression for f' of the cone, we must average the expression for f_{gen}' over the polar angle ξ. Because of the axial symmetry, we can rotate the coordinate frame xOyz about the z-axis such
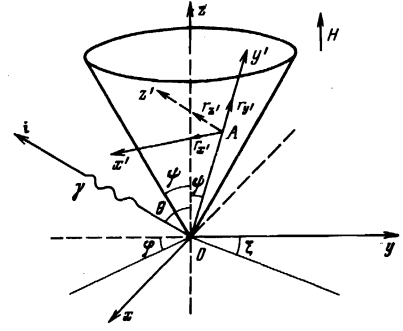

FIG. 2. Positions of the generating line of the cone of smectic planes and of the vector i in the laboratory coordinate frame.

that $\varphi = 0$; then ξ becomes ξ', where $\xi' = \xi - \varphi$. In this case,

$$f_{cone}' = \int_0^{2\pi} f_{gen}'(\xi')\,d\xi' \Big/ \int_0^{2\pi} d\xi'. \qquad (5)$$

Using the notation $p = \langle r_{\|}^2\rangle/\lambda^2$, $q = \langle r_{\perp}^2\rangle/\lambda^2$, and

$$a_1 = p(\sin^2\theta + \cos^2\theta\cos^2\psi) + q\cos^2\theta\sin^2\psi,$$
$$a_2 = \frac{1}{2}(q - p)\sin 2\theta\sin 2\psi, \qquad (6)$$
$$a_3 = (p - q)\sin^2\theta\cos^2\psi,$$

we obtain

$$f_{gen}' = \exp\{-a_1 + a_2\cos\xi' + a_3\cos^2\xi'\},$$
$$f_{cone}' = \int_0^{2\pi}\exp\{-a_1 + a_2\cos\xi' + a_3\cos^2\xi'\}\,d\xi' \Big/ \int_0^{2\pi} d\xi'. \qquad (7)$$

Since

$$\int_0^{2\pi}\exp\{a_2\cos\xi' + a_3\cos^2\xi'\}\,d\xi' = 2\pi\exp\left\{\frac{a_3}{2}\right\}\sum_{n=-\infty}^{\infty} I_n(a_2)I_{-n/2}\left(\frac{a_3}{2}\right),$$

where $I_\nu(x)$ is a Bessel function of imaginary argument, we have

$$f_{cone}' = \exp\{-[p(\sin^2\theta + \cos^2\theta\cos^2\psi)$$
$$+ q\cos^2\theta\sin^2\psi + \frac{1}{2}(q - p)\sin^2\theta\cos^2\psi]\}\sum_{n=-\infty}^{\infty} I_n(\frac{1}{2}(q - p)\sin 2\theta\sin 2\psi)$$
$$\times I_{-n/2}(\frac{1}{2}(p - q)\sin^2\theta\cos^2\psi). \qquad (8)$$

From (8) we can easily obtain expressions corresponding to the different one-row LC structures:

a) The layers are parallel to each other and the normal to the layer is at an angle α to the magnetic-field direction. In this case, $\psi = \pi/2$ and

$$f_{one\,row}' = \exp\{-[p\sin^2(\theta - \alpha) + q\cos^2(\theta - \alpha)]\}; \qquad (9)$$

b) For $\alpha = 0$, the formula obtained naturally coincides with the angular dependence of f' for axial monocrystals:

$$f' = \exp\{-[p\sin^2\theta + q\cos^2\theta]\}. \qquad (9a)$$

Thus, in the general case, to determine the mean-square displacements of the marker molecules and also the angle of inclination of the smectic planes to the direction of the orienting field, it is sufficient to know values of f' corresponding to three different θ. However, as can be seen from (8), the expressions for f' are sufficiently simple only when $\theta = 0$ or 90°. For $\theta = 0$ (the directions of the γ-rays and of the orienting field coincide),

$$\sum_{n=-\infty}^{\infty} I_n(0)I_{-n/2}(0) = 1,$$
$$f_{cone}' = \exp\{-[q + (p - q)\cos^2\psi]\}, \qquad (10)$$

while for $\theta = 90°$ (the direction of the γ-rays is perpendicular to H),

$$\sum_{n=-\infty}^{\infty} I_n(0)I_{-n/2}(\tfrac{1}{2}(p-q)\cos^2\psi) = I_0(\tfrac{1}{2}(p-q)\cos^2\psi),$$

$$f'_{cone} = \exp\{-p + \tfrac{1}{2}(p-q)\cos^2\psi\}I_0(\tfrac{1}{2}(p-q)\cos^2\psi). \quad (11)$$

As the third equation, it is convenient to use the dependence of f' on the mean-square amplitudes of vibration of the marker nuclei in an unoriented LC matrix (polycrystalline sample).

However, in the case of a LC system, when $\langle r_\parallel^2 \rangle$ and $\langle r_\perp^2 \rangle$ are substantially different ($q \ll p$) and f' is much smaller than for ordinary polycrystals, we cannot use the well known formula[1]

$$f'_{polyer} = \exp\{-(\langle r_z^2 \rangle + 2\langle r_x^2 \rangle)/3\lambda^2\} \quad (12)$$

(where z and x are the principal axes of the electric field gradient), which is valid only for small $\langle r^2 \rangle$ and values of f' close to unity, or when $\langle r_x^2 \rangle$ and $\langle r_z^2 \rangle$ differ little.

An equation for f_{polycr} of marker molecules dissolved in a LC matrix can be obtained by averaging the expression (9a) over θ:

$$f'_{LC\text{-}polyer} = \int_0^\pi f'_{one\ row} \sin\theta\, d\theta \bigg/ \int_0^\pi \sin\theta\, d\theta. \quad (13)$$

As a result of the averaging, we obtain:
a) for $q - p > 0$,

$$f'_{LC\text{-}polyer} = \left[\frac{\pi}{4(q-p)}\right]^{1/2} e^{-p}\Phi_1(\sqrt{q-p}); \quad (14)$$

b) for $q - p < 0$

$$f'_{LC\text{-}polyer} = \left[\frac{\pi}{4(p-q)}\right]^{1/2} e^{-p}\Phi_2(\sqrt{p-q}), \quad (15)$$

where

$$\Phi_1(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)\,dt, \qquad \Phi_2(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(t^2)\,dt.$$

The experimental values of f' given previously[3], together with Eqs. (10), (11) and (15), have been used to determine the mean-square displacements $\langle r_\perp^2 \rangle$ and $\langle r_\parallel^2 \rangle$ of molecules of the Mössbauer marker DAF in the smectic phase of HOAOB oriented by a magnetic field, and the angle of inclination ψ' of the long axes of the HOAOB molecules in the smectic layer, which is usually defined relative to the normal to the smectic plane of the LC, i.e., $\psi' = 90° - \psi$.

In the case when a herring-bone structure (Fig. 1c) is formed on orientation of the smectic phase of HOAOB, a calculation from the experimental data using formula (8) gives

$$\langle r_\perp^2 \rangle = (0.08\pm0.04)\cdot10^{-18}\ cm^2,\ \langle r_\parallel^2 \rangle = (0.7\pm0.2)\cdot10^{-18}\ cm^2,$$

$$\psi' = (40\pm15)°.$$

The value of ψ' obtained is in good agreement with the data in the literature: $\psi' = 30°$ [8,9] and $\psi' = 45°$ [10].

On the basis of Eq. (9a) and the experimental values of f', we have also calculated $\langle r_\parallel^2 \rangle$ and $\langle r_\perp^2 \rangle$ (and also the angle α) corresponding to the formation of the one-row structure of Fig. 1b on orientation of the smectic phase of HOAOB. The results obtained ($\alpha \approx 90°$; $\langle r_\parallel^2 \rangle < \langle r_\perp^2 \rangle$) show that this structure is apparently not realized on orientation of HOAOB by a magnetic field.

Thus, the method proposed in this paper for determining the angles of inclination of the long axes of LC molecules in smectic layers enables us to make a choice between the different possible structures of smectic LC's oriented in external magnetic fields.

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