Determination of molecular orientation distribution of a stable paramagnetic probe in oriented 4-cyano-4´-*n*-pentylbiphenyl

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The molecular orientation distribution function of a stable radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl in magnetic-field oriented 4-cyano-4´-*n*-pentylbiphenyl was determined from the angular dependence of the ESR spectra. The preferred molecular orientation of radical species in the liquid-crystal matrix was determined. The temperature evolution of the orientation distribution function was studied.

Key words: species orientation distribution function, ESR, angular dependence of ESR spectra, simulation of ESR spectra, nonlinear least squares method, liquid crystal, paramagnetic probe, 4-cyano-4´-*n*-pentylbiphenyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL).

The orientation distribution function (ODF), $\rho(\alpha,\beta,\gamma)$, is the most accurate measure of the species ordering of a medium. The ODF shows the number (or the fraction) of species oriented in an interval of angles $\alpha + d\alpha$, $\beta + d\beta$, $\gamma + d\gamma$ (α, β, γ are the Euler angles that relate the frame of reference of a separate species to the coordinate system of the sample). A method[1] of determination of the ODF of paramagnetic species from the angular dependence of ESR spectra is based on simulation of the ESR spectra corresponding to different sample orientations with respect to the direction of the magnetic field strength vector. The ODF is represented as an expansion in terms of orthonormal functions. The expansion coefficients are determined by minimizing the deviation of the numerically simulated spectra from the experimental ones.

In the present work we studied the applicability of the method proposed for the analysis of the results obtained in a real experiment. The method was used to study the orientation distribution of paramagnetic probe species in an oriented liquid crystal.

The liquid-crystal matrix used was 4-cyano-4´-*n*-pentylbiphenyl (5CB), which forms a nematic phase in the temperature interval 295—308 K.[2] We also used a stable radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) with the well-known magnetic resonance parameters[3—5] as a paramagnetic probe.

Experimental

Commercially available TEMPOL and 4-cyano-4´-*n*-pentylbiphenyl were used without additional purification. The stable radical was introduced into the liquid crystal by dissolution at 298 K. The liquid crystal was placed in a quartz tube (internal diameter 3 mm; sample height was 10 mm) and oriented by the magnetic field of the ESR spectrometer (field induction was 3000 G) at 298 K. The director of the liquid crystal was aligned normal to the axis of the tube. The oriented sample was rapidly cooled in the magnetic field down to 77 K. Special experiments showed that at this temperature the orientation of paramagnetic species in the sample remains unchanged in the time scale of the experiment (a few hours).

ESR spectra were recorded on a Varian E-3 ESR spectrometer at 77 K. The sample orientation with respect to the magnetic field strength vector was set with an accuracy of $\pm 1°$.

Samples were annealed in nitrogen gas stream of preset temperatures. The temperature was maintained with an accuracy of ± 2 °C.

Results and Discussion

The ESR spectra of a solution of TEMPOL radical in oriented 4-cyano-4´-*n*-pentylbiphenyl are shown in Fig. 1. The spectra were recorded at 77 K with different sample orientations with respect to the magnetic field strength vector. To obtain the angular dependence, the tube with the sample was consecutively turned around its axis. Thus, the axis of the tube was always normal to the plane formed by the director of the sample and the magnetic field strength vector. The angular dependence of the ESR spectra is the indication of the ordering of paramagnetic species in the sample. Apparently, the magnetic-field oriented 4-cyano-4´-*n*-pentylbiphenyl matrix causes partial orientation of the TEMPOL molecules.

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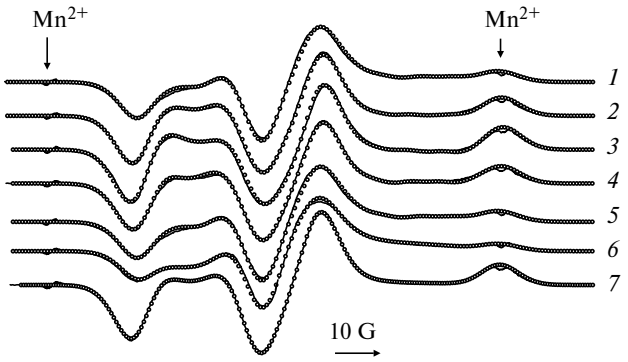

Fig. 1. ESR spectra of TEMPOL radical in oriented 4-cyano-4´-*n*-pentylbiphenyl recorded at 77 K; 0° (*1*), 30° (*2*), 60° (*3*), 90° (*4*), 120° (*5*), 150° (*6*), and spectrum of isotropic sample (*7*). Solid lines are experimental data and points denote the results of simulation.

Determination of magnetic parameters of TEMPOL radical in 4-cyano-4´-*n*-pentylbiphenyl

To determine the orientation of paramagnetic species from the angular dependence of ESR spectra, one must know the magnetic resonance parameters of the species. The magnetic parameters of TEMPOL in 4-cyano-4´-*n*-pentylbiphenyl (components of the [*g*]-tensor and HFS tensor) and the individual lineshape parameters were determined from the experimental ESR spectrum of an isotropic sample recorded at 77 K. To this end, we simulated the spectrum of an isotropic sample and fitted the desired parameters in such a way that the sum of the squares of the deviations of the simulated spectrum from the experimental one be minimum.[6] The results of simulation of the spectrum of the isotropic sample are shown in Fig. 1 (curve *7*).

The optimum magnetic parameters of TEMPOL were found to be g_{xx} = 2.0096±0.0001, g_{yy} = 2.0067±0.0004, g_{zz} = 2.0028±0.0001; a_{xx} = 8.4±0.4 G, a_{yy} = 3.6±1 G, and a_{zz} = 35.2±0.2 G. The principal values of the [*g*]-tensor coincide with the published data[5] within the limits of experimental error. The principal values of the HFS tensor determined in our experiments differ from the values typical of TEMPOL radical. Usually,[3–5] the parameter a_{xx} is nearly equal or slightly smaller than a_{yy}. The results obtained in our experiments, $a_{xx} \gg a_{yy}$, can be due to complexation in the system TEMPOL—4-cyano-4´-*n*-pentylbiphenyl. Nitroxyl radicals are known to form complexes with aromatic compounds; often, this leads to changes in their HFS constants.[7]

The shape of an individual line is described by a Gaussian curve with the half-width specified as a second-rank tensor. The isotropic spectrum was best described with the following principal values of the half-width tensor: Δh_{xx} = 7.6±0.5 G, Δh_{yy} = 12.1±0.5 G, and Δh_{zz} = 4.6±0.5 G; the orientation of this tensor with respect to the principal axes of the [*g*]-tensor is specified by the Euler angles $\alpha = 99°\pm1°$, $\beta = 46°\pm1°$, and $\gamma = -63°\pm1°$. Therefore, in our experimental system the linewidth depends on the species orientation relative to the external magnetic field direction. This dependence and the large half-widths seem to be a consequence of line broadening due to unresolved anisotropic HFS between the unpaired electron and methyl protons of the TEMPOL molecule. Probably, hyperfine coupling between 4-cyano-4´-*n*-pentylbiphenyl protons also manifests itself in the case of complexation.

Details of the ODF determination procedure

The procedure for determination of the ODF of paramagnetic species from the angular dependence of ESR spectra was reported earlier.[1] However, our experimental conditions allow simplification of this procedure. The liquid-crystal matrix containing stable radicals was oriented by the magnetic field of the ESR spectrometer; therefore, the samples possessed axial symmetry. The symmetry axis of such a sample coincides with the direction of the orienting magnetic field strength vector. During registration of the angular dependence of the ESR spectra, the magnetic field strength vector in the sample coordinate system was turned in the plane containing the anisotropy axis of the sample. In this case, the ODF of the species[1] can be determined unambiguously. Knowing the angle between the anisotropy axis of the sample and the magnetic field strength vector, it is possible to unambiguously determine the orientations of the ODF symmetry axes in the coordinate system related to the sample. The program used in our study determines this angle automatically.

The ODF of paramagnetic species characterized by three different principal values of the [*g*]-tensor in an axially symmetric sample is a function of two angles that describe the position of the symmetry axis of the sample in the coordinate system related to a separate paramagnetic species. In this case, the ODF can be represented as an expansion in terms of spherical harmonics:

$$\rho(\beta,\gamma) = \sum_{j=0}^{\infty}\left\{\frac{1}{2}a_{j0}P_j(\cos\beta) + \sum_{k=1}^{j}P_j^k(\cos\beta)[a_{jk}\cos(k\gamma) + b_{jk}\sin(k\gamma)]\right\}, \quad (1)$$

where P_j are the *j*th-power Legendre polynomials and P_j^k are the *j*th-power added Legendre functions of the first kind and the *k*th order.

In the coordinate system related to the paramagnetic species, any ODF possesses a certain symmetry because the effective magnetic resonance parameters of the spe-

cies are determined by the squared direction cosines of the magnetic field strength vector in the coordinate system related to the paramagnetic species. In this connection only the coefficients a_j and a_{jk} with even j and k subscripts will differ from zero in the expansion (1).

Molecular orientation distribution of TEMPOL in the oriented liquid crystal

The ESR spectra of TEMPOL radical in oriented 4-cyano-4′-*n*-pentylbiphenyl recorded at different orientations of the sample with respect to the magnetic field strength vector and the results of simulation of these spectra using the method[1] are shown in Fig. 1. In simulating the spectra the expansion for the ODF included the second- and fourth-order terms. In this case a total of six expansion coefficients, namely, a_{00}, a_{20}, a_{40}, a_{22}, a_{42}, and a_{44} differ from zero. The sum of squared deviations of the simulated ESR spectra from experimental ones was $\Lambda = 5.24 \cdot 10^{-9}$ per spectrum point (experimental spectra were preliminarily normalized to their double integrals). This value is comparable with the error of our experiments. As the number of expansion coefficients increases, the Λ value decreases by less than 5%.

Joint simulation of the spectra shown in Fig. 1 gave the following ODF expansion coefficients in terms of spherical harmonics: $a_{00} = 1.0$, $a_{20} = -0.87$, $a_{40} = 0.25$, $a_{22} = 0.082$, $a_{42} = -0.00045$, and $a_{44} = -0.0048$. A typical error in determination of the coefficients a_{00}, a_{20}, a_{40}, and a_{22} in these experiments was at most 5% (*cf.* the accuracy of nearly 15% in determining a_{42} and a_{44} values). Thus, the expansion coefficients reflecting different features of the ODF are determined with different accuracy.

Special experiments showed that the ODF determination procedure is stable to the changes in the magnetic resonance parameters of the probe within the limits of error in determination of these parameters.

The ODF of the TEMPOL molecules in oriented 4-cyano-4′-*n*-pentylbiphenyl plotted using the order parameters found (Fig. 2, *a*) demonstrates the position of the anisotropy axis of the sample in the coordinate system related to the TEMPOL molecule. Three principal axes of the [*g*]-tensor (see Fig. 2, *b*) were chosen to be the coordinate axes of the species. As mentioned above, in the coordinate system related to the species any ODF possesses a certain symmetry, which complicates the interpretation of the ODF. Let us represent the results obtained in more illustrative form. Consider separately the ODFs of the *X*, *Y*, and *Z* axes of the probe molecules in the sample coordinate system (Fig. 3). Since the sample is axially symmetric, each of these distribution functions depends on one angle, that is, $\rho_x = f(\eta_x)$, $\rho_y = f(\eta_y)$, and $\rho_z = f(\eta_z)$, where η_x, η_y, and η_z are the angles between the direction of the director of the liquid crystal matrix and

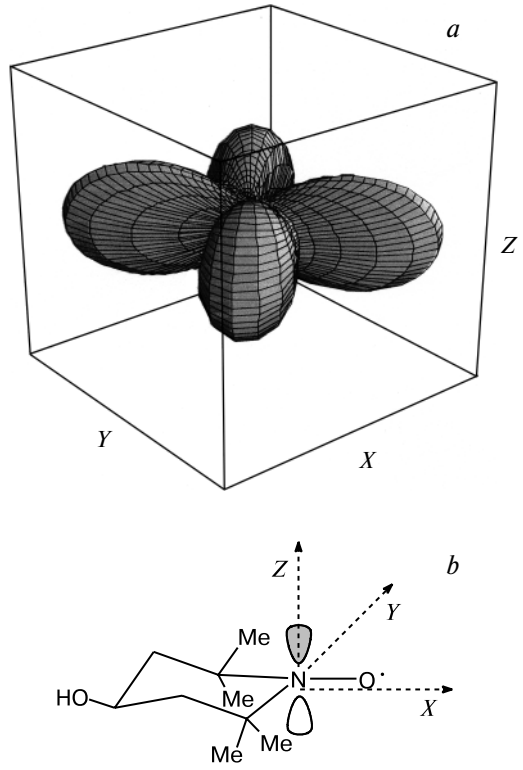

Fig. 2. *a*. The orientation distribution function of TEMPOL molecules in oriented 4-cyano-4′-*n*-pentylbiphenyl. *b*. Coordinate system related to TEMPOL molecule; the coordinate axes coincide with the principal axes of the [*g*]-tensor.

the *X*, *Y*, and *Z* axes of the probe molecule, respectively. The *Z* axes of the majority of radicals are normal to the anisotropy axis of the sample (see Fig. 3). A possible explanation is as follows. An electron cloud formed by the lone electron pairs of the nitrogen and oxygen atoms interacts with the benzene ring π-system of the 4-cyano-4′-*n*-pentylbiphenyl molecule. The *X* and *Y* axes of most TEMPOL molecules make angles of 50° and 40°, respectively, with the anisotropy axis of the sample. Two possible positions of the probe molecules with respect to the liquid crystal molecules are shown in Fig. 4. It is impossible to determine the probability of realization of each orientation using the method employed.

Usually, the degree of ordering in liquid crystals is characterized by the so-called order parameter[8–10]

$$S = 0.5(\langle 3\cos^2\theta \rangle - 1),$$

where θ is the angle of deviation of the specified axis of the molecule from the director of the sample and the angle brackets denote the averaging over all molecules. The parameter *S* varies between −1/2 and 1; a completely isotropic sample corresponds to $S = 0$. The degree of ordering can be calculated from the coefficients of ODF

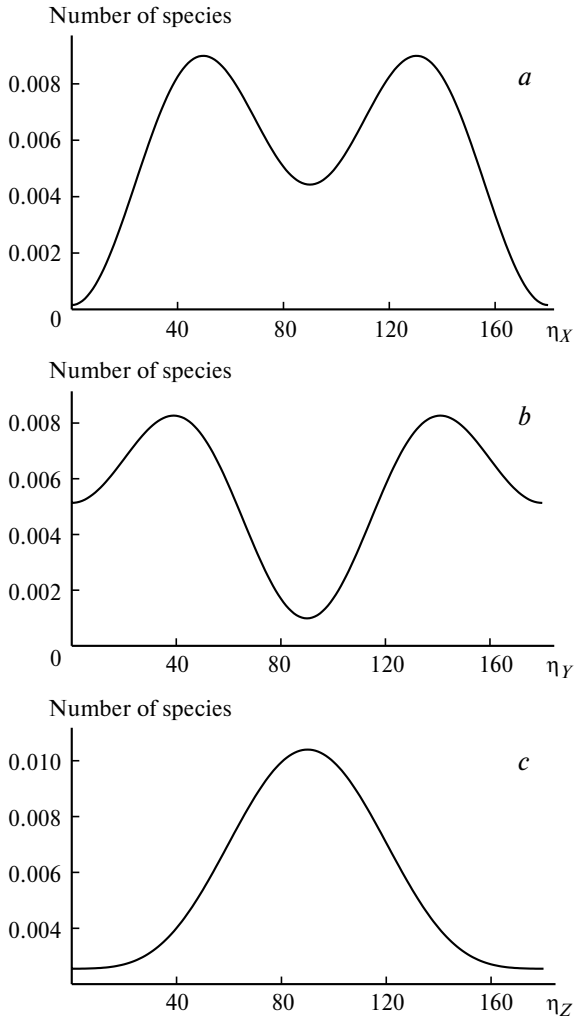

Fig. 3. Orientation of the X (*a*), Y (*b*), and Z (*c*) axes of the probe molecules in oriented 4-cyano-4´-*n*-pentylbiphenyl.

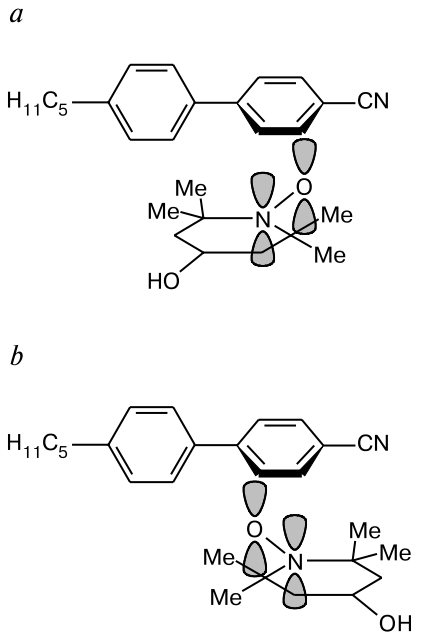

Fig. 4. Possible positions of TEMPOL molecules with respect to 4-cyano-4´-*n*-pentylbiphenyl molecules.

expansion in terms of spherical harmonics. The degree of ordering of the Z axes of molecules is given by

$$S_z = a_{20}/(5a_{00}).$$

In our experiments, $S_z = -0.17 \pm 0.01$. It is known that the degree of orientational order of nematic liquid crystals oriented by a magnetic field of 3000 G at room temperature reaches saturation. In particular, it was shown[10] that the degree of orientational order of the molecules of an azoxyanisole nematic liquid crystal at room temperature reaches saturation at 500 G. Therefore, we can assume that the degree of ordering of 4-cyano-4´-*n*-pentylbiphenyl in our system approaches unity. In this case, the degree of ordering, S, of the molecules oriented normal to the director must be $-1/2$. The experimentally determined S_z value is appreciably different from the ideal value. This is probably due to the fact that the radical species represent structural defects in the liquid-crystal matrix owing to different molecular geometries of TEMPOL and 4-cyano-4´-*n*-pentylbiphenyl. In this case the degree of ordering of the matrix molecules bound to the probe molecules must be lower than the average degree of ordering of the liquid crystal.

Temperature evolution of the distribution function

The degrees of orientational order of the Z axes of TEMPOL molecules were calculated using the ESR spectra recorded at 77 K after annealing of the oriented samples at different temperatures (Table 1). The ODFs calculated for 77, 195, 226, and 236 K are presented in Fig. 5. Successive changes in the ODF of the paramagnetic probe with an increase in the annealing temperature seemingly indicate that 4-cyano-4´-*n*-pentylbiphenyl loses orientational order on heating.

Table 1. Degree of ordering of the Z axes of TEMPOL molecules in oriented 4-cyano-4´-*n*-pentylbiphenyl as function of the sample annealing temperature

T/K	$S_z \pm 0.01$	T/K	$S_z \pm 0.01$
77	−0.17	236	−0.05
156	−0.18	245	−0.05
195	−0.19	258	−0.05
226	−0.13	267	−0.02

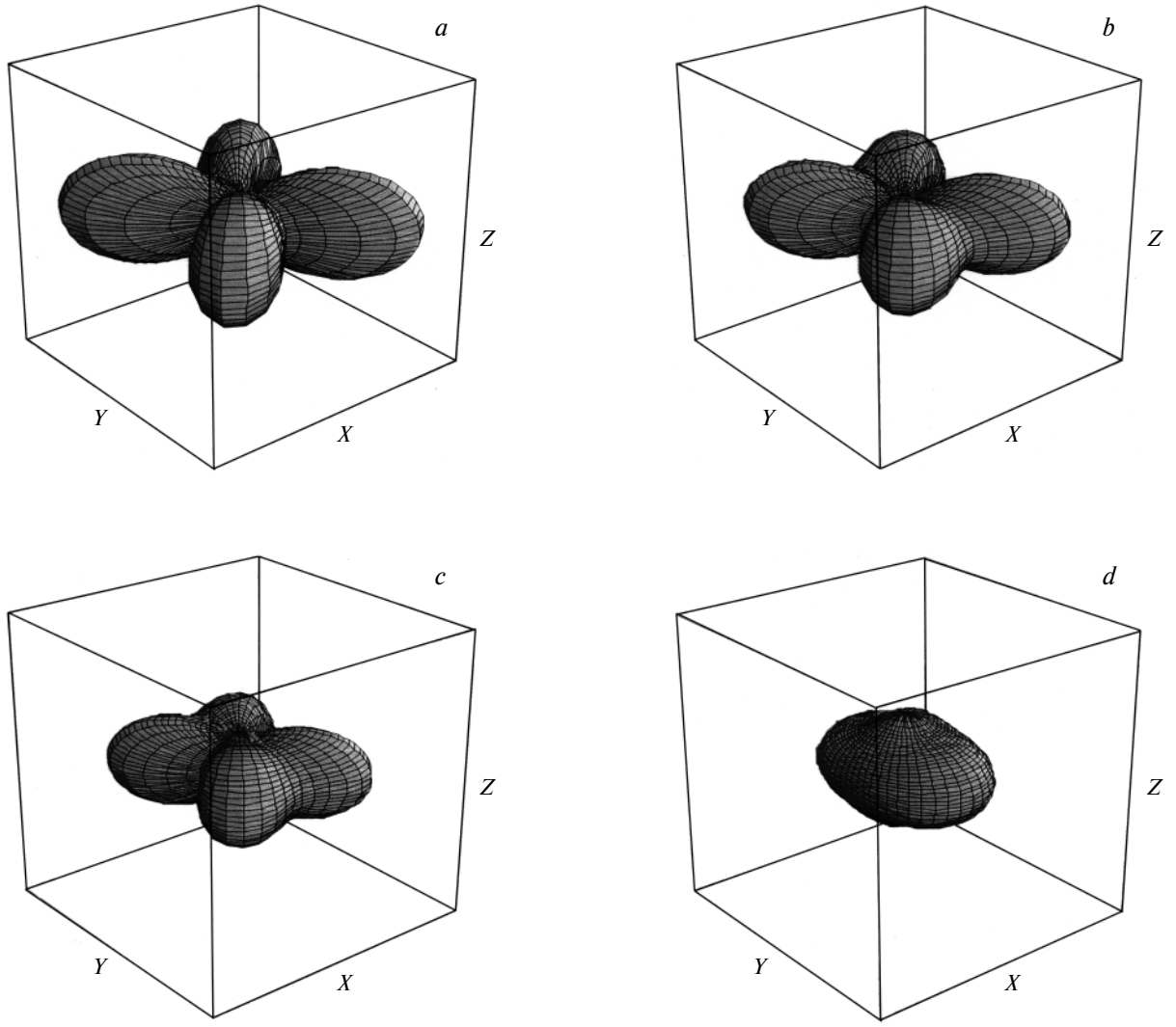

Fig. 5. Temperature dependence of the ODF of TEMPOL in oriented 4-cyano-4′-*n*-pentylbiphenyl at 77 (*a*), 195 (*b*), 226 (*c*), and 236 K (*d*).

A single numerical parameter cannot reflect the whole picture of orientational ordering in this system (see Table 1 and Fig. 5). For instance, $S_z(77\ \text{K}) \approx S_z(195\ \text{K})$, whereas the ODF corresponding to the annealing temperature of 195 K is much less anisotropic compared to the ODF of the radical species in the unannealed sample. In addition, in the temperature range 77—226 K the TEMPOL molecules in the sample gradually lose their orientations, which probably reflects relaxation of mechanical strain and structural nonequilibrium in the supercooled 4-cyano-4′-*n*-pentylbiphenyl glass. In the temperature range 226—236 K the paramagnetic probes rapidly lose orientational order, which can indicate a phase transition of 4-cyano-4′-*n*-pentylbiphenyl in this temperature interval. Indeed, calorimetric measurements[11] revealed a phase transition of glassy 4-cyano-4′-*n*-pentylbiphenyl to the crystalline phase at 231 K. Likely, crystalline 4-cyano-4′-*n*-pentylbiphenyl is a polycrystal possessing no macroscopic ordering.

By and large, we can conclude that the method[1] of determination of the spatial orientation of paramagnetic species from the angular dependence of ESR spectra is appropriate for analyzing the results of real experiments. The method allows fine details of the ODF of species to be established, being sufficiently sensitive for studying the temperature evolution of the ODF.

References

1. A. Kh. Vorob′ev and N. A. Chumakova, *Izv. Akad. Nauk. Ser. Khim.*, 2004, 2595 [*Russ. Chem. Bull., Int. Ed.*, 2004, **53**, 2706].

2. K. Skarp, S. T. Lagewall, and B. Stebler, *Mol. Cryst. Liq. Cryst.*, 1980, **60**, 215.
3. A. N. Kuznetsov, *Metod spinovogo zonda* [*The Spin Probe Technique*] Nauka, Moscow, 1976, 210 pp. (in Russian).
4. Ya. S. Lebedev, O. Ya. Grinberg and A. A. Dubinskii, in *Nitroksil´nye radikaly. Sintez, khimiya, prilozheniya* [*Nitroxyl Radicals. Synthesis, Chemistry, and Applications*], Nauka, Moscow, 1987, 266 pp. (in Russian).
5. L. J. Berliner and J. Reuben, *Spin Labeling. Theory and Applications*, Plenum Press, New York—London, 1989.
6. A. Kh. Vorob´ev, V. S. Gurman, and T. A. Klimenko, *Izv. Akad. Nauk. Ser. Khim.*, 2000, 1065 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1059].
7. A. L. Buchachenko, *Kompleksy radikalov i molekulyarnogo kisloroda s organicheskimi molekulami* [*Complexes of Radicals and Molecular Oxygen with Organic Molecules*], Nauka, Moscow, 1984, 157 (in Russian).
8. L. M. Blinov, *Elektro- and magnitooptika zhidkikh kristallov* [*Electro-Optics and Magneto-Optics of Liquid Crystals*], Nauka, Moscow, 1978, 360 (in Russian).
9. V. A. Belyakov, *Zhidkie kristally* [*Liquid Crystals*], Znanie, Moscow, 1986, 159 (in Russian).
10. Z. Yu. Gotra, M. V. Kurik, and Z. M. Mikityuk, *Struktura zhidkikh kristallov* [*The Structure of Liquid Crystals*], Naukova Dumka, Kiev, 1989, 110 (in Russian).
11. T. I. Shabatina, Yu. N. Morosov, A. I. Konstantinov, V. A. Batyuk, and G. B. Sergeev, *Mol. Cryst. Liq. Cryst.*, 1994, **248**, 103.

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