X-RAY ANALYSIS OF THE STRUCTURE OF NEMATIC LIQUID CRYSTALS IN ELECTRIC AND MAGNETIC FIELDS BY MEANS OF DISTRIBUTION FUNCTIONS

CRYSTALLOGRAPHY

1967

SovietRxiv

Abstract

Full Text

UDC 548.783

CRYSTALLOGRAPHY

Corresponding Member of the USSR Academy of Sciences B. K. VAINSTEIN,
I. G. CHISTYAKOV,
E. A. KOSTERIN, V. M. CHAIKOVSKII

X-RAY ANALYSIS OF THE STRUCTURE OF NEMATIC LIQUID CRYSTALS IN ELECTRIC AND MAGNETIC FIELDS BY MEANS OF DISTRIBUTION FUNCTIONS

For the liquid-crystalline state, both nematic and smectic, an approximately parallel arrangement of molecules within certain regions (domains) is characteristic. As was shown earlier ([1–6]), to study the packing of molecules in liquid crystals one can use distribution functions derived from X-ray experimental data by the method of Fourier transformation.

As an object for investigating the influence of electric and magnetic fields on the structure of liquid crystals, *n*-azoxyanisole (PAA) was chosen

[[chemical structural formula of *n*-azoxyanisole (PAA)]]

This substance forms a nematic mesophase in the temperature interval 116–134°. The presence of the lateral grouping N = O leads to the presence of a dipole moment of the molecule $\mu = 2.48 \cdot 10^{-18}$, forming an angle of 57°31′ with its long axis ([11]). Unlike an isotropic liquid, the nematic phase is readily oriented in external electric and magnetic fields. In magnetic fields, PAA molecules align with their long axes parallel to the lines of force ([7–10]).

The orientation in a magnetic field is caused by the diamagnetic anisotropy of the substance. The particles tend to arrange themselves so that the direction of their maximum magnetic susceptibility coincides with the direction of the magnetic field. Apparently, the effect is mainly reduced to the orientation of domains, although the perfection of the molecular packing within domains should also improve. To separate these contributions to the total angular distribution function in an oriented liquid-crystalline specimen from X-ray data is at present difficult, and we shall operate with the term "orientation of molecules." The tendency toward saturation of the orientational effect is already clearly noticeable in fields of the order of 500 Oe. Magnetic orientation is more perfect than electric orientation, and in the X-ray diagrams it is possible to reveal

Fig. 1. Scheme of the arrangement of reflections on the X-ray diagram of nematic *n*-azoxyanisole oriented by a magnetic field

Figure 1: Fig. 1. Scheme of the arrangement of reflections on the X-ray diagram of nematic *n*-azoxyanisole oriented by a magnetic field

more interference maxima both along the equator and along the meridian of the photograph. The scheme of the X-ray diagram

Fig. 1. Scheme of the arrangement of reflections on the X-ray diagram of nematic *n*-azoxyanisole oriented by a magnetic field.

shown in Fig. 1, and the values of the angles ϑ and interplanar spacings d are summarized in Table 1.

Apparently, all meridional reflections, with the exception of 1M, are due to intramolecular interference. The strongest equatorial reflections 1E and 2E are due mainly to intermolecular interference, although some insignificant part of their intensity is, possibly, also contributed by intramolecular interference. This is connected with the fact that covalent bonds between atoms are present not only in the direction of the long axis, but also in the direction of the short molecular axis—across the width of the molecule. The very weak equatorial reflections 3E–6E are also caused by intramolecular scattering.

Table 1

Angles ϑ and interplanar spacings d for PAA in a field of 8000 G, $t = 122.3^\circ$

	Equatorial reflections	Equatorial reflections	Equatorial reflections	Equatorial reflections	Equatorial reflections	Equatorial reflections	Meridional reflections	Meridional reflections	Meridional reflections	Meridional reflections	Meridional reflections	Meridional reflections
	CuK_α 1E	CuK_α 2E	MoK_α 3E	MoK_α 4E	MoK_α 5E	MoK_α 6E	CuK_α 1M	CuK_α 2M	CuK_α 3M	MoK_α 4M	MoK_α 5M	MoK_α 6M
ϑ, deg.	5.7	10	16	19.5	24.5	41	2.8	6.2	8.8	14.3	25	42
d, Å	7.82	4.4	2.8	2.31	1.88	1.18	16.25	7.18	5.07	3.13	1.83	1.15
Intensity	s.	v. s.	v. wk.	v. wk.	v. wk.	v. wk.	s.	s.	med.	wk.	v. wk.	v. wk.

In weak constant electric fields (up to 50 V/cm at $t = 123^\circ$), PAA molecules are arranged with their long axes across the lines of force. This agrees with electrophoretic studies of dilute PAA solutions (11). However, at higher field strengths the character of the orientation changes and the long axes of the molecules become parallel to the lines of force. This is explained by the arising

Fig. 2

Figure 2: Fig. 2

motion of the substance in the direction of the field, if the latter is sufficiently intense.

In low-frequency electric fields of sufficient strength, an orientation of the molecules parallel to the field is also observed. With increasing frequency, the direction of orientation changes to the perpendicular one. The change in molecular orientation does not occur at a definite "critical" frequency, as Kast indicated (12), but over a rather broad frequency range. This range increases considerably with increasing temperature. Of course, one may operate with the mean values of this frequency range, which, in Kast' s terminology, may be called critical frequencies. In this case, Kast' s conclusion that the critical frequency decreases with decreasing temperature agrees with our data. However, the numerical values of the critical frequencies, as well as of the entire range, in our experiments proved to be smaller than those indicated by Kast. Most likely, this difference is caused by different degrees of purity of the substance (13).

The occurrence of molecular orientation parallel to the field at low frequencies as a result of the motion of the liquid crystal explains the increase in the averaged "critical" frequency with increasing temperature. The viscosity of the liquid crystal decreases and the motion becomes more intense. The broadening of the critical frequency range, for which a chaotic arrangement of molecules is characteristic, with increasing temperature is caused by the disorienting action of thermal motion. On approaching the clearing point (134°), this range increases rapidly, since thermal disturbances exert a predominant effect.

To characterize the oriented texture of PAA, cylindrical distribution functions of the molecular axes on the basal plane were constructed:

$$2\pi r z_{\mathrm{M}}(r) = 2\pi r z_0 + 4\pi^2 r \int_0^{S_{\max}} I(R) I_0(2\pi r R) R\, dR.$$

It turned out that these functions change little with variation in the intensity of the electric and magnetic fields. This is explained by the rapid saturation of the orienting effect. Figure 2 shows the functions $2\pi r z_M(r)$ for maximally oriented samples in constant and alternating electric fields and in a magnetic field. These functions differ little from one another.

Fig. 2. Functions of the cylindrical distribution of projections of molecular axes onto the basal plane:
a–$H = 16\,000$ G, $t = 122.3°$; b–$E_{\mathrm{const}} = 400$ V/cm, $t = 123°$; v–$E_{\mathrm{altern}} = 7000$ V/cm, $t = 120°$

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Only a certain shift of the principal peaks toward smaller values for magnetic fields is noticeable, which is apparently explained by the denser packing of molecules inside domains in comparison with the packing in electric fields.

Proceeding from the known values of covalent and intermolecular radii, one can construct a model of the PAA molecule and of the packing (Fig. 3), for which the characteristic distances were found from consideration of the distribution functions (Fig. 2). From comparison of Figs. 2 and 3a, c it is seen that the values of the peaks on the curves find a satisfactory explanation in modeling the structure of the liquid crystal.

Fig. 3. Model representations of the arrangement of molecules inside domains of liquid-crystalline *p*-azoxyanisole oriented by electric and magnetic fields: *a*—in a strong constant electric field; *b*—in a high-frequency alternating electric field; *v*—in a magnetic field

The position of the reflections on the roentgenogram and the form of the functions of the cylindrical distribution of molecular axes $2\pi r z_M(r)$ depend on temperature (Fig. 4a, b). From roentgenograms in magnetic fields this regularity can be traced for the sharper reflections 1E, 2E, 2M-4M. The remaining maxima are more diffuse, which does not allow one to go beyond the limits of experimental error. As is seen in Fig. 4a, the angle ϑ for equatorial reflections decreases with increasing temperature. The interplanar distances correspondingly increase, which indicates that thermal fluctuations destroy the orientation of molecules caused by the magnetic field. The angular deviation of the long molecular axes becomes increasingly more···

significant as the temperature increases, and the structure of the liquid crystal becomes looser.

For meridional reflections the dependence of ϑ on temperature is opposite. As the temperature rises, ϑ increases. This is understandable, since with an increase in the angle between the long molecular axis and the direction of the field, which coincides with the meridional direction in the photograph, the projections of the interatomic distances onto this direction decrease.

Fig. 4. *a*—dependence of ϑ on temperature for various reflections; *b*—cylindrical distribution functions of the projections of the molecular axes of an oriented texture at various melt temperatures

It should also be noted that the angles ϑ for the reflections ($1E, 1M$ and $2E, 3M$)

tend, as the temperature increases, to converge to the values 5°10′ and 9°24′, respectively, which are characteristic of the diffuse rings of amorphous PAA at 134°.

The change in intermolecular distances with increasing temperature shifts the peaks on the $2\pi r z_m(r)$ curves toward larger values (Fig. 4*b*). This also indicates the emergence of a looser packing of the molecules as the temperature approaches the transition point to the isotropic liquid.

Institute of Crystallography
Academy of Sciences of the USSR
Institute of Crystallography

Received
25 I 1966
Received

REFERENCES

1. B. K. Vainshtein, *Diffraction of X-rays by Chain Molecules*, Publishing House of the Academy of Sciences of the USSR, 1963.
2. I. G. Chistyakov, B. K. Vainshtein, *Kristallografiya*, **8**, 570 (1963).
3. I. G. Chistyakov, *Kristallografiya*, **8**, 859 (1963).
4. B. K. Vainshtein, I. G. Chistyakov, *Dokl. Akad. Nauk SSSR*, **153**, No. 2, 326 (1963).
5. I. G. Chistyakov, *Zh. Strukt. Khim.*, **5**, No. 4, 555 (1964).
6. B. K. Vainshtein and I. G. Chistyakov, *Collection: Growth of Crystals*, **5**, 1965, p. 163.
7. W. Kast, *Ann. Phys.*, **4**, 83, 418 (1927).
8. P. W. Glamann, K. Herrmann, A. H. Krummacher, *Zs. Kristallogr.*, **74**, 73 (1930).
9. G. W. Stewart, *Phys. Rev.*, **38**, 931 (1931).
10. J. Falgu irettes, *C. R.*, **241**, 71 (1955).
11. V. Tsvetkov, V. M. Marinin, *ZhETF*, **18**, No. 7, 641 (1948).
12. W. Kast, *Zs. Phys.*, **71**, 39 (1931).

13. W. Kast, *Zs. Phys.*, **76**, 19 (1932).

Note: Figure translations are in progress. See original paper for figures.