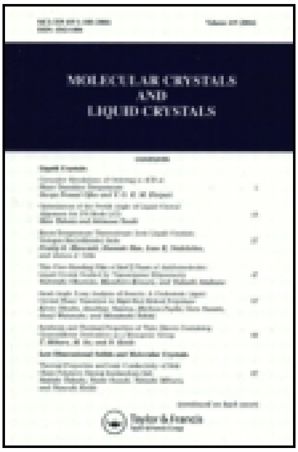

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Temperature Dependence of Field Hysteresis Loop in Nemato-Cholesteric Mixtures

Z. Mikityuk [a] , O. Nevmerzhitska [a] , P. Zaremba [a] & M. Vistak [b]
[a] Lviv Polytecnic Institute, 12 Bandery St., Ukraine
[b] Lviv Medical Institute, 69 Pekarska St., Ukraine

Version of record first published: 24 Sep 2006.

To cite this article: Z. Mikityuk , O. Nevmerzhitska , P. Zaremba & M. Vistak (1996): Temperature Dependence of Field Hysteresis Loop in Nemato-Cholesteric Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 275:1, 3-14

To link to this article: http://dx.doi.org/10.1080/10587259608034057

Mol. Cryst. Liq. Cryst., 1996, Vol. 275, pp. 3–14
Reprints available directly from the publisher
Photocopying permitted by license only

Temperature Dependence of Field Hysteresis Loop in Nemato-Cholesteric Mixtures

Z. MIKITYUK, O. NEVMERZHITSKA, P. ZAREMBA and M. VISTAK*

Lviv Polytecnic Institute, 12 Bandery St., Ukraine
**Lviv Medical Institute, 69 Pekarska St., Ukraine*

(Received July 7, 1994; in final form October 20, 1994)

Temperature dependence of the field hysteresis loop (δU) of the cholesterol-nematic phase transitions in mixtures based on strong and weak polar nematics. The ephires of the cholesterol (0.2...1.6 weight %) were used as optically active dopants. For mixtures, in which fluctuation embryos have a major role at low temperatures, anomalous growth of δU is observed. The influence of temperature dependence of constants of elasticity and *step of induced spiral* on analogical dependence $\delta U = f(T)$ takes place. Magnitude of δU can be changed by changing the percentage of cholesterine in the mixture.

Keywords: Nemato-cholesteric mixtures, the field hysteresis optically active dopants

1. INTRODUCTION

Hysteresis properties of the cholesterol-nematic transformation can be successfully used in liquid crystal displays with the higher information capacity. The main influence on the operation of such displays is temperature, since it causes the disruption of the addressing of the elements.[1]

The important issue is the liquid crystal compositions with stable parameters over wide temperature interval.

2. THEORY

To estimate the hysteresis properties of the cholesterol-nematic phase transitions critical value of δU is used:[2,3]

$$\delta U = \frac{U_{CN} - U_{NC}}{U_{CN}} \tag{1}$$

where U_{CN}, U_{NC} are the threshold tension of the forward and reverse transition. Accounting for the surface free energy, the equation for relative magnitude of the hysteresis loop is:

$$\delta U = 1 - \frac{1}{2\sqrt{2}}\sqrt{\frac{\pi^2 K_{22}\left(\frac{4\gamma^2 d}{P_0} - \frac{1}{\gamma^2 d}\right) + 4F_{SN}}{\frac{\pi^2 K_{22} d}{P_0^2} + \left(F_{SN} - F_{SC}\right)}} \tag{2}$$

where $\gamma = (K_{22}/K_{33})^{1/2}$; F_{SN}, F_{SC} are densities of the surface free energy in different states. Since relative magnitude of the loop depends on d/Po, and also γ and also on the quantity of the surface energies in different states we can calculate the temperature dependence of δU from the temperature dependence of the step end from the Frank constants of elasticity. At this time there is no universal molecular-static theory that describes complex behavior of the temperature dependence of the spiral step. The results of the experimental research on the temperature dependence of the step in nematocholesteric mixtures us to judge, that this, dependence can have either complicated characteristics or can be of linear nature.[4,5] Fig. 1 shows the dependence for mixtures with different compositions. In general,[5,7] the temperature dependence of the twist angle of the spiral $\theta = 2\pi a/P$ is:

$$\theta = \theta_0 + \frac{u_0 t}{s(t)} \tag{3}$$

where

a — the distance between the molecular row;
θ_0 — the twist angle of the spiral, which corresponds to the potential minimum;
U_0 — the parameter of the anharmonicity of the rotation fluctuation of the molecules;
$t = T/T_i$, where T_i–temperature transition to the isotrope liquid.
$s(t)$ — the parameter of the orientation ordering.

The magnitude θ_0 depends on the energy of the intermolecular reciprocal action. The temperature dependence of the step of the spiral is described by the second term of equation (3).

The presence of the anharmonic source of the rotating fluctuation in the molecular structure can lead to the increase of dP/dT until the change of the sign (the characteristic curve is shown in Figure 1).

The temperature dependence of the constants of Frank's elasticity, K_{22} and K_{33}, is shown in publications.[8,9] If the anomaly of this dependence in pre-transition fields is taken in account, dependence of K_{22} and K_{33} on the temperature has a linear character. Obviously the anomalous temperature dependence of the constants of the elasticity near the phase transformation of the cholesteric-smectic are caused by the increase in the role of the fluctuations of the smectic ordering parameter near the point of phase transition. In general, K_{22} and K_{33}, which contain their own nematic member, K^n_{22}, also have an additional term K^s_{22}, resulting from the smectic fluctuations, so that

$$K_{22} = K^n_{22} + K^s_{22}$$

$$K_{33} = K^n_{33} + K^s_{33}.$$

The magnitudes, K^s_{22} and K^s_{33} are proportional to the longitudinal correlational lengths $K_{22} \sim \xi_{\|}$; $K_{33} \sim \xi_{\|}$. In this manner, the growth of the smectic fluctuations cause the abnormal behavior of constants of elasticity K_{22} and K_{33} near the point of phase transition.

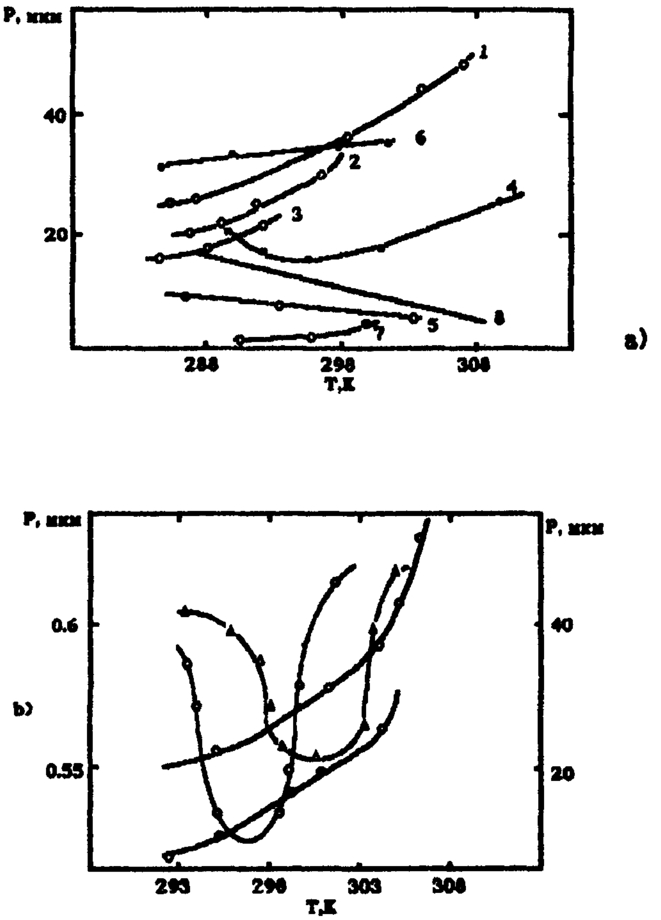

FIGURE 1 Temperature-concentration dependences of the spiral step of mixtures MBBA with dioxalanes: a-dioxalan 1 (1-0.65, 2-1, 3-1.5%), dioxalan 2 (4-1%), dioxalan 3 (5-1%), dioxalan 4 (6-1%), dioxalan 10 (7-1%), dioxalan 11 (8-1%); b-dioxalan 11 (1-1.2, 2-5, 3-5.6, 4-6%).

This very general behavior in the change of constants of elasticity and in the step of the induced spiral with temperature are the basis for the calculation of the temperature dependence of the relative magnitudes of the hysteresis loop. We now analyze the results. In Figure 2 it is shown the dependence $\delta U = \delta(T)$ for the case, when Frank's constants K_{22} and K_{33} lineary are demanding with the temperature and step of the induced spiral changes with the temperature by the exponent (1, 2) or else constant in given temperature interval. The relative magnitude of the loop of the hysteresis in this case changes with the increase (1, 2) or else does not depend on the temperature (3). From the point of practical use of the hysteresis of the cholesterol-nematic transmovement the dependence is more preferable.

In Figure 3 is shown the dependence $\delta U = f(T)$ for the case when the registration of the pretransformal appearance leads to the exponential dependence of constants of the

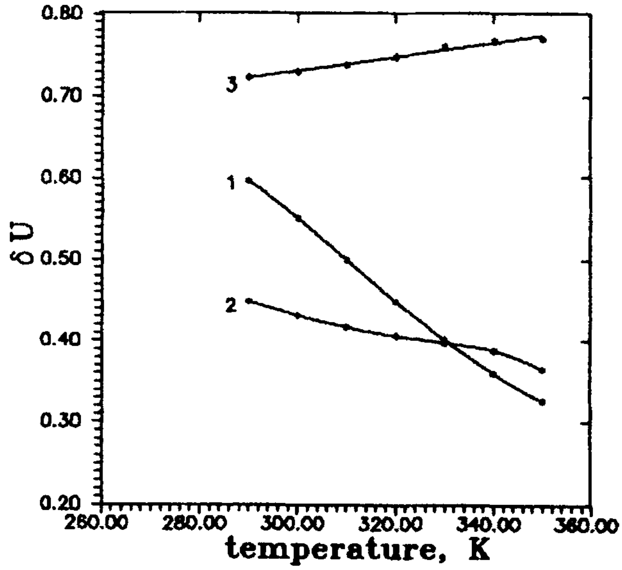

FIGURE 2 Dependence of the relative value of the hysteresis loop of the cholesteric-nematic phase transition on the temperature.

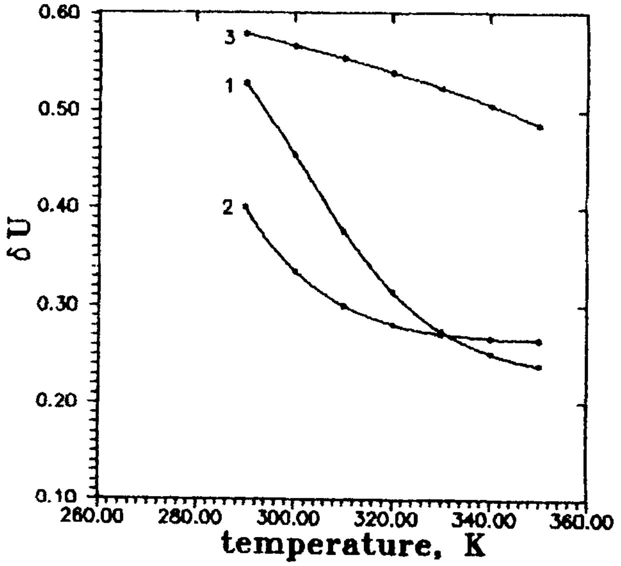

FIGURE 3 Dependence of the relative value of the hysteresis loop of the cholesteric-nematic phase transition on temperature.

elasticity K_{22} and K_{33}. The dependence of the step with the temperature is analogical to the case before. In this case, when the step of the induced spiral is decreasing (1) or else increasing (2) with the temperature by the exponent in curves of the dependence $\delta U = f(T)$ the decrease is observed and the matter of it is that with the decrease of the temperature the normal growth of δU is taking place so that the registration of the pretrans movement appearances and anomalies in dependencies of constants of the elasticity within the low temperatures leads to the big change of δU (within the low temperatures).

3. THE EXPERIMENT

Liquid crystal material for the experiment is the nemato-cholesterol mixture, based on nematic matrix, doped with ephires of the cholesterol. NCM matrices are the mixture of cianobipheniles with nitrooxycompounds.

The dopants are the cholesterol ephires of the one base carbonate acids-propionate and palmitate with the concentration of 0.2 to 1.2 weight %.

Mixture *N*-1 — 22.3 weight % *p*-octil cianobiphenile, mezophase interval-291...357 *K*, $\Delta\varepsilon = 3.83$.

Mixture *N*-2 — 30.5 weight % *p*-octil cianobiphenile, mezophase interval-291...357 K, $\Delta\varepsilon = 5.07$.

Sandwich type chambers were filled with resulting mixtures. The translucent membranes from SnO_2 were rubbed in order to induce planar orientation in the conducting covers. Their thickness is 25 µm. The electrooptic measurements were performed using standard methods. After fabrication of the volt-contrasting characteristic values of K_{22} and K_{33}[10] were obtained.

The step of the induced spiral was measured using the Kano's wedge method by the diffraction of the laser radiation on the texture of the "finger prints".

Figures 4–7 shows the temperature dependence of constants of elasticity K_{22} and K_{33} for different mixtures. For mixtures *N*-1 doped with ephires of the cholesterol, a typical linear dependence in the change of the constant of the elasticity K_{22} and K_{33} with the temperature is obtained, so that mixtures with a compound of lower homologous have lower values of K_{22} and K_{33} than mixtures doped with higher homologous.

Thus, mixtures doped with cholesterolpropionate have lower values of K_{22} and K_{33} than mixtures doped with cholesterolpalmitate in the range of temperatures investigated.

Figure 4 and figure 6 give the temperature dependence K_{22} and K_{33} for mixture *N*-2 doped with ephires of the cholesterol. Their main characteristic is the fact that with the decrease temperature the anomalous growth of constants of elasticity is observed in the pre-transition phase, caused by the appearance of the fluctuation embryos of the smectic phase. This growth is largest for mixtures doped with cholesterolpropionate. Thus, the magnitude of the constants of elasticity K_{22} and K_{33} depend on longitudinal correlation lengths, that is on the degrees of perfection of the liquid crystal structure. Thus the conclusion is that mixtures *N*-2 with cholesterolpropionate have a better structure than mixtures doped with cholesterol palmitate. In mixtures based on *N*-1 the

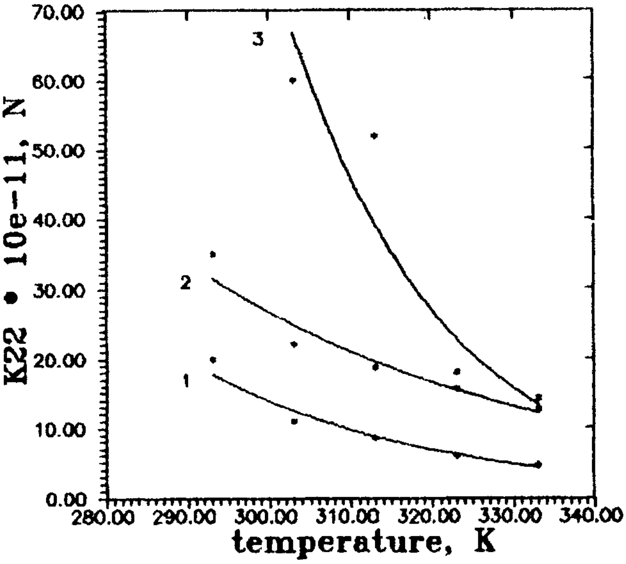

FIGURE 4 Temperature dependence of the elastic constant K_{22} for NCM on the basis of the matrix *N*-2 with the dopant of the cholesteric esters:1-palmitate, 2-undecilate, 3-propionate.

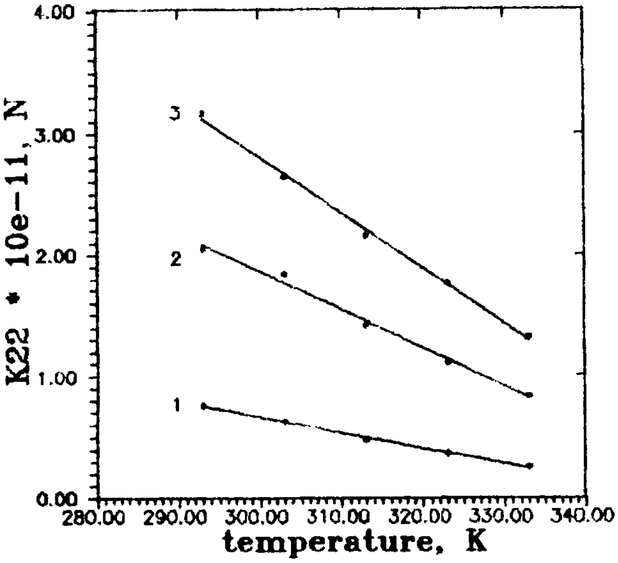

FIGURE 5 Temperature dependence of the elastic constant K_{22} for NCM on the basis of the matrix *N*-1 with the dopant of the cholesteric esters:1-propionate, 2-palmitate, 3-undecilate.

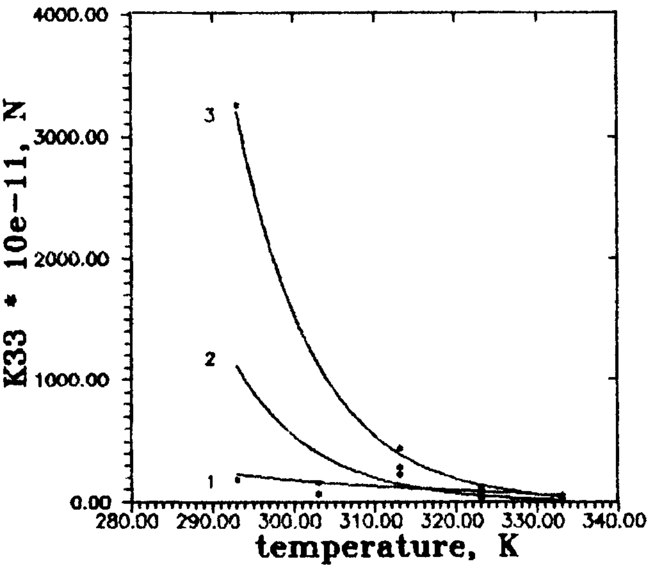

FIGURE 6 Temperature dependence of the elastic constant K_{33} for NCM on the basis of the matrix *N*-2 with the dopant of the cholesteric esters:1-palmistate, 2-undecilate, 3-propionate.

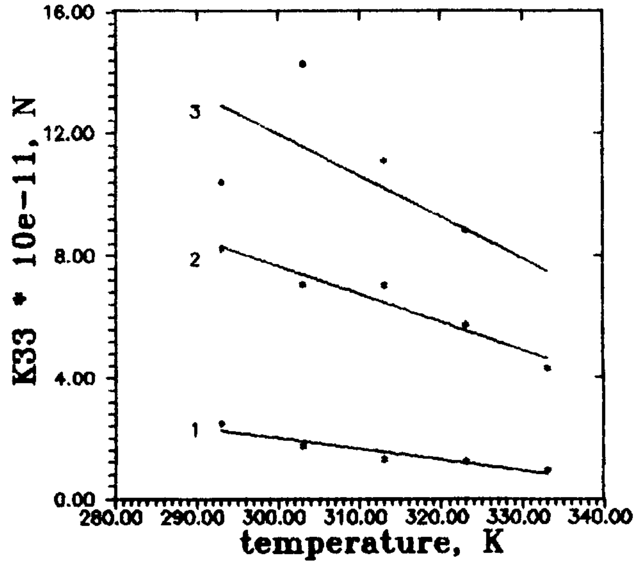

FIGURE 7 Temperature dependence of the elastic constant K_{33} for NCM on the basis of the matrix *N*-1 with the dopant of the cholesteric esters:1-propionate, 2-undecilate, 3-palmistate.

opposite picture is observed; the mixture *N*-1 doped with cholesterolpropionate in the whole temperature interval has lower value of K_{22} and K_{33}. Therefore, the formation of the structure in mixtures based on *N*-1 and *N*-2 with the same dopant has many different properties.

Figure 8 shows a typical dependence of the step-induced spiral on temperature for two nematic matrices, doped with ephires of the propionate. Small change in the step with change in temperature is observed.

Figure 9 shows the change of the relative magnitude of the loop of the hysteresis with temperature for different mixtures doped with palmitate and propionate. These changes in now analyzed. Experimental results are satisfactorily described by the theory in the framework of the accepted mathematical model.

In mixtures based on *N*-1 doped with ephires propionate or palmitate (Figure 9(1) and 10(1)) the linear change of the relative magnitude of the loop of the hysteresis with temperature is observed, typical peculiarity of these dependencies is that the increase of the concentration of the ephire in the mixture leads to a change of δU. The dependence of the relative magnitude of the hysteresis loop on the number of the homologous should be mentioned, and with increase of the latter it is also increasing, so that mixtures doped with propionate, in case of the fixated concentration of the ephire, give lower magnitude of δU, than mixtures doped with palmitate. The anomalies in the temperature dependence of δU are shown in mixtures based on nematic matrix *N*-2 (Figure 11). In case of low temperatures, the increase of δU is taking place.

In such a manner, the anomalies in the temperature dependence of K_{22} and K_{33} lead to the anomaly in the temperature dependence of δU.

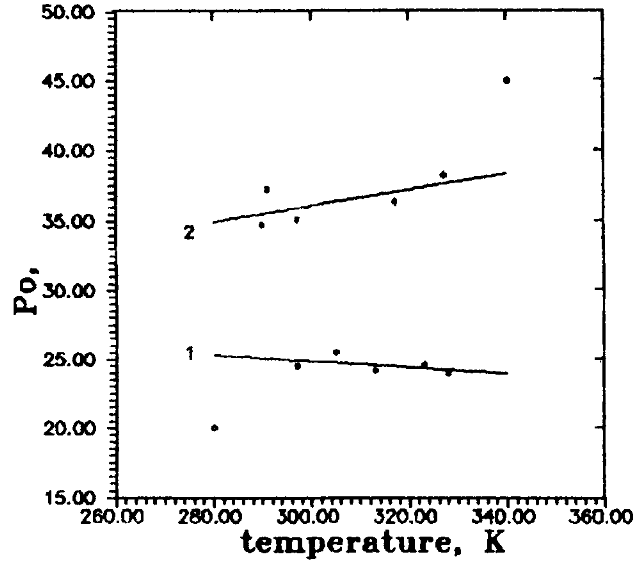

FIGURE 8 Typical experimental dependence of the induced spiral step on temperature; 1–N1 + 0.32% cholesterylpropionate, 2–N2 + 1% cholesterylundecilate.

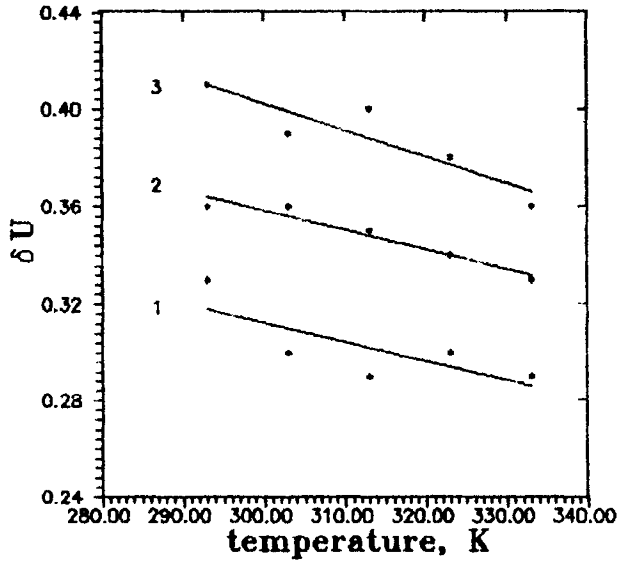

FIGURE 9 Temperature dependence of the relative value of the hysteresis loop δU for NCM on the basic matrix N-1 with dopant cholesterolpropionate with the concentrations: 1–1.2%, 2–0.8%. 3–0.6%.

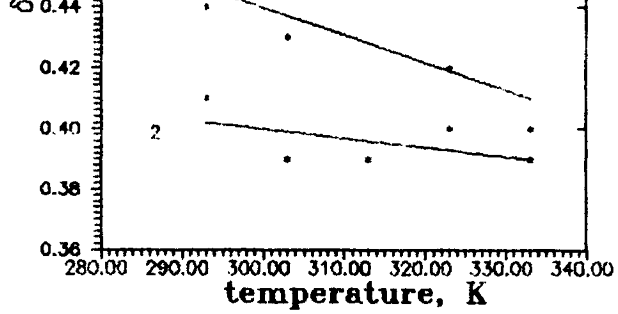

FIGURE 10 Temperature dependence of the relative value of the hysteresis loop δU for NCM on the basic matrix N-1 with dopant cholesterolpalmitate with the concentrations: 1–1.2%, 2–0.8%,

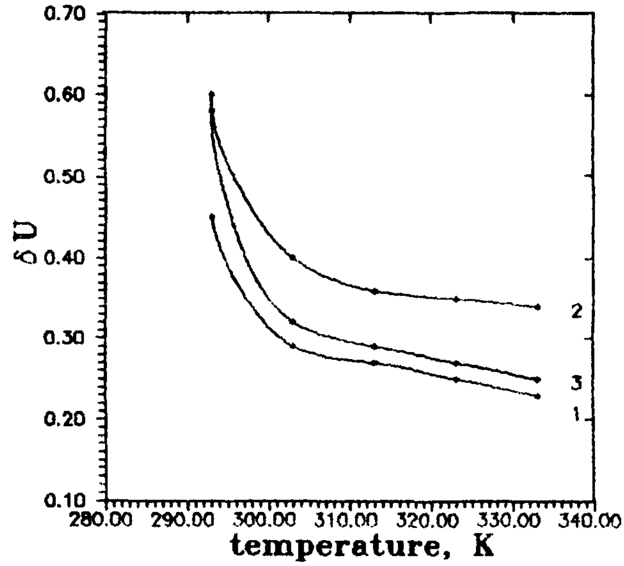

FIGURE 11 Temperature dependence of the relative value of the hysteresis loop δU for NCM on the basic matrix N-2 with dopant cholesterolpropionate with the concentrations: 1–1.2%, 2–0.8%. 3–0.6%.

Accounting for the fact, that the step of the induced spiral depends weakly on the temperature, we assume that the physical nature of the anomalous behavior of δU with temperature is associated with the increasing role of the fluctuation of the smectics ordering parameter with the decrease in temperatures; thus the temperature dependence of constants of the elasticity that determines the temperature dependence of δU. To provide a more accurate clarification of the physical nature of the temperature dependence of δU it's necessary to turn to the issue of temperature dependence of K_{22}; i.e., to the fact that in the matrix N-1 the magnitude of K_{22} increases as one goes from mixtures with propionate to mixtures with palmitate and in matrix N-2 the increase goes from mixtures with palmitate to mixtures with propionate. Magnitudes of K_{22} have large differences in the induced cholesteric phases based on nematic matrices N-1 and N-2.

Nematic matrices N-1 and N-2 are mixtures of weakly-polar molecules 4-butil-4-metoxynitricbenzol and highly polar molecules of n-oktilcyanobyphenil, where concentration of highly-polar components is higher in N-2 because the smectic phase appears in the matrix. Polar nematic liquid crystals are made up from dimers. The dilution of dimers with weakly-polar nemat moves the equilibrium of the system (dimer-monomer) towards the monomers. In such a manner, the mixture contains both monomers and dimers of polar components of molecules and of weakly-polar components. A more complicated case can also take place, where the associates of monomer-weakly-polar molecule- type are present.

The molecule 8CB has a large dipole moment. Its length is 21,85 approximately equal to the length of the molecule of the cholesterolpropionate (23.9 A) which also has a dipole moment so that a specific interaction is possible. In the matrix *N*-2 the strong polar component has a bigger concentration. Here the major part of dimers of strong-polar components, with the size of the dimers coinciding with the size of cholesterolpalmitate (40, 1 A), so the reciprocity can take place.

Thus, a small addition of cholesterolpalmitate to the *N*-1 matrix effectively "stabilizes" the dimers. Additions of cholesterolpropionate binds the monomers. The result of these interactions has a more perfect structure of the liquid crystals. In case of the *N*-2 matrix small or large amount of monomers binds the propionate molecules. As a result, the *N*-2 structure with the propionate is more perfect. Corresponding to various types of association of derivative molecules of cholesterine with matrix molecules are different structural organizations, resulting in different characteristics of each combination. Obviously, only experimental X-ray analysis can provide the proof of the model's validity.

The magnitude δU depends on the concentration of the ephire of the cholesterol in the mixture. Figure 12 shows the temperature on dependence for different concentrations of cholesterolpalmitate. Increasing the concentration of the palmitate increases the magnitude of δU in the entire temperature interval. Constants of elasticity, as well as γ do not depend on the concentration (in the given interval).[12] With an increase of concentration of the ephire, the magnitude of the step of the induced spiral decreases. The decrease of the magnitude of the step lead to the increase of δU. This theory describes the experiment satisfactorily. For mixtures with cholesterolpropionate this regularity is not shown clearly.

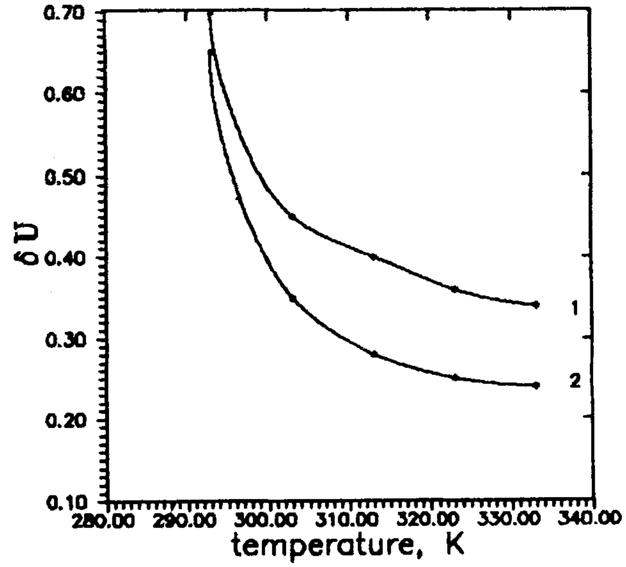

FIGURE 12 Temperature dependence of the relative value of the hysteresis loop δU for NCM on the basic matrix N-2 with dopant cholesterolpalmitate with the concentrations: 1–1.2%, 2–0.8%.

CONCLUSIONS

The analysis of the experimental data describing the temperature dependence of the relative magnitude of the hysteresis for nematic-cholesteric mixtures based on strong and weakly polar nemats doped with ephires of cholesterol makes it possible to draw the following conclusions:

- for mixtures with different amounts of strong polar components various modes of behavior of the magnitude of the hysteresis loop are observed;
- for mixtures with matrices which have a smectic phase the abnormal growth of δU is observed at low temperatures;
- for mixtures with no smectic phase the monotonic growth of δU takes place as temperature decreases;
- K_{22} and K_{33} have the same behavior;
- the abnormal growth of δU, K_{22} and K_{33}, is associated with the appearance of smectics fluctuation embryos in cholesteric phase;
- changing the percentage of the cholesteric in the mixtures over the range of 0.2 to 1.6%, the magnitude of step can be changed, so that K_{22} and K_{33} remain constant, but the magnitude of δU is changed also;
- to ensure the stability of δU over the wide temperature interval, it is necessary to use nematic matrix with weakly ordered structure in which no major smectic fluctuations occur especially at low temperatures.

References

1. Y. Koire, A. Mochizuki and K. Yohikava, *Fujitsu Sci Tech. J.*, **23**, 146 (1987).
2. Z. Gotra, L. Gresko, Z. Mikityuk and M. Vistak, *Liquid Crystal Materials, Devices and Applications*, SPIE, Vol., 1665, 240 (1992).
3. Z. Gotra, Z. Mikityuk, D. Megei and P. E. Zaremba, *Liquid Crystals*, **9**, 6, 893–898 (1991).
4. N. V. Vladimirskij, R. V. Kondratjeva, B. L. Kramarenko and N. M. Shkabara, *Crystallography*, **33**, 3, 701 (1988).
5. A. V. Tolmachev and L. I. Lisezkij, General information NIITEXIM Monocrystals and peculiar clean materials, Moskow, 1–63 (1987).
6. G. S. Chilaya and L. I. Lisezkij, *Progress Physics Sciences*, (1981).
7. A. I. Galatina, L. G. Derkach and N. L. Kramarenko, *Crystallography*, **29**, 6, 1114 (1984).
8. W. H. de Jen and W. A. P. Classen, *J. Chemical Phys.*, **67**, 8, 3705 (1977).
9. E. P. Raynes, R. J. A. Tough and K. A. Deries, *Mol. Cryst. and Liq. Cryst.*, **56**, 63–68 (1979).
10. Z. Gotra, P. Zaremba and L. Gresko, Proceeding All-Union Conference "*Liquid Crystals and its Application*", Baku, 33 (1990).
11. L. M. Blinov, M. F. Grebenkin and R. A. Zejnalov, *Crystallography*, **34**, 2, 398 (1989).
12. Z. Yu. Gotra, M. V. Kuryk and Z. Mikityk, "*Structure of the Liquid Crystals*", Kiev, p. 110 (1989).