On the optical activity in mixtures of liquid crystals

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Possible dependences of the cholesteric pitch in mixtures on the composition and temperature of the latter are considered for simple models. The available experimental data are explained qualitatively.

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1. INTRODUCTION

Studies of optical phenomena comprise the simplest and most effective method of investigation of liquid crystals. Therefore a broad literature is devoted to these questions. A special place is occupied by cholesteric liquid crystals (CLC). Their surprising optical properties (selective reflection of light of a certain polarization and wavelength, large value of the rotation of the plane of polarization, and so on) are connected with the structure of the ordering of the molecules. Everything is determined essentially by the magnitude and sign of the pitch of the CLC helix. The pitch of the helix changes under the action of small electric, magnetic and other influences, thus changing the optical properties of the CLC. The pitch reacts even more sensitively to impurities. However, much less progress in understanding the phenomena in mixtures has been made than in pure CLC. This relates particularly to the case in which the components of the mixture have different signs of the intrinsic optical activity (see below) or in which one of the components is a nematic liquid crystal (NLC). At the same time, it is precisely these mixtures that are promising for applications, since a wide variation in their structure characteristics (for example, the pitch of the CLC) is possible. It must also be noted that a great deal of experimental data has been accumulated in this region (see, for example, the anthology, Ref. 1).

Of course, a detailed quantitative interpretation of these data is possible only on the basis of a corresponding microscopic (quantum-chemical) calculation. This does not enter into the problem of the present paper (and at any rate can be carried out only numerically). However, some general qualitative laws can be established even on the "macroscopic" level. The present paper is devoted to a consideration of such regularities.

In Sec. 2 a simple model is proposed, which describes the dependence of the helix pitch of a mixture of CLC and NLC on the concentration of the CLC. Van der Waals forces acting between anistropic and gyrotropic systems are taken into account. It is shown that, when account is taken of non-additive triplet forces, an induced optical activity of the NLC appears (for a particular position of the mass centers of the molecules), with a sign opposite that of the optical activity of the CLC molecules.

In Sec. 3, the properties of mixtures of CLC and NLC are studied phenomenologically in the case of small concentrations of the CLC. When such mixtures (and also of pure CLC) are considered on the basis of the Frank,[1] expansion of the free energy the pitch of the CLC helix turns out to be independent of the temperature. This conclusion so strongly contradicts all the experimental facts that the validity of the Landau theory in CLC is called into question.[1] However, the critical scattering and other phenomena in the CLC are excellently described by the Landau theory. The contradiction can be avoided if terms in the elastic energy proportional to higher powers of the order parameter (up to s^4) are taken into account. Such an expansion is not an exaggeration of the accuracy, since transitions in liquid crystals are phase transitions of first order and the order parameter at the transition point is not very small ($s_c \sim 0.4$). Therefore, terms of the same order in s ought to be taken into account in the gradient part of the free energy as well as in the homogeneous part. In the same section, similar phenomena are considered in the vicinity of the racemic point in the mixture of CLC with opposing signs of rotation (of the optical activity). It is shown from symmetry considerations that when electric and magnetic fields (of sufficient magnitude) perpendicular to the director of the NLC (in the racemic mixture) are applied, an NLC–CLC transition is possible.

In Sec. 4, the possibility is discussed, in the case of the NLC–CLC transition, of the phase transition predicted in an isotropic liquid by Zel'dovich[2] and connected with the disappearance of the center of inversion in NLC. It is shown in self-consistent fashion how the requirements for such a transition are satisfied in the given case. It is noted that the pitch of the helix in the CLC obtained in such fashion, would be decreased upon decrease in temperature (while the pitch of the helix in pure CLC usually increaes with decrease in temperature). In conclusion (Sec. 5), possible new experimental effects connected with the presence of additional degrees of freedom in the CLC mixtures (in ultrasound absorption and light scattering) are investigated briefly.

2. CONCENTRATION DEPENDENCE OF THE HELIX IN MIXTURES OF CLC AND NLC

In order to describe the dependence of the helix pitch (or, what is more convenient, the reciprocal of the quantity q_m) on the composition in a self-consistent manner it is necessary to have an expression for the interaction energy between the anisotropic and gyrotropic molecules. The corresponding formulas can be obtained

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by simple generalization of the results which are known for the interaction between neutral atoms.[3]

As is well known, the potential energy of the interaction is expressed in terms of the corresponding average of the S matrix:

$$\langle S(\mathbf{r})\rangle=-itU(\mathbf{r}). \tag{1}$$

The field components of importance in the interaction of molecules are those with frequencies that do not exceed the atomic; therefore the operator of electromagnetic interaction can be written in the form:

$$V=-E_\alpha(\mathbf{r}_1)d_{1\alpha}-E_\alpha(\mathbf{r}_2)d_{2\alpha}-\frac{1}{6}Q_{\alpha\beta 1}\frac{\partial E_\beta(\mathbf{r}_1)}{\partial x_\alpha}-\frac{1}{6}Q_{\alpha\beta 2}\frac{\partial E_\beta(\mathbf{r}_2)}{\partial x_\alpha}, \tag{2}$$

where d_α and $Q_{\alpha\beta}$ are the components of the operators of the dipole and quadrupole moments of the molecules, and $\mathbf{E}(\mathbf{r})$ is the electric-field operator.

In formula (2), in contrast with the well-known results of Ref. 3, the next (quadrupole) components of the multipole expansion are taken into account, which is specially important for the interaction of gyrotropic molecules. We shall further assume (as in Ref. 3) that the mean values of the multipole moments (in stationary states of the molecule) are equal to zero. Therefore, a non-zero scattering amplitude appears only in the fourth-order approximation of perturbation theory:

$$S=\frac{(-i)^4}{4!}\int dt_1\,dt_2\,dt_3\,dt_4 T\{V(t_1)V(t_2)V(t_3)V(t_4)\}. \tag{3}$$

Diagrams corresponding to the averaging of Eq. (3) over the photon vacuum are shown in Fig. 1. The dashed lines represent the Green's function of the electric field:

$$D_{ik}{}^E(x_1-x_2)=\langle T(E_i(x_1)E_k(x_2))\rangle, \quad x_i\equiv(\mathbf{r}_i, t_i). \tag{4}$$

The solid lines correspond to the functions

$$D_{ik,j}(x_1-x_2)=\left\langle T\left(E_i(x_i)\frac{\partial E_k(x_2)}{\partial x_{2j}}\right)\right\rangle, \tag{5}$$

which can be expressed in terms of the derivations of D^E_{ik} and the magnetic field Green's function D^H_{ik}.

At the accuracy of interest to us, there are 12 diagrams containing only dashed lines and 36 diagrams with single continuous lines. The corresponding contributions to the S matrix are:

$$\begin{gathered}\langle S_{12}\rangle=\frac{1}{2}\int dt_1\,dt_2\,dt_3\,dt_4\{D^E_{ik}(x_1-x_2)D^E_{lm}(x_3-x_4)\\ \times\langle T[d_{1i}(t_1)d_{1m}(t_4)]\rangle\langle T[d_{2k}(t_2)d_{2l}(t_3)]\rangle+{}^1/{}_3D_{ik}{}^E(x_1-x_2)D_{lm,j}(x_3-x_4)\\ \times\langle T[d_{1i}(t_1)d_{1m}(t_4)]\rangle\langle T[d_{2k}(t_2)Q_{lj2}(t_3)]\rangle\}.\end{gathered} \tag{6}$$

As usual, we transform in (6) to the Fourier components in time. Moreover, in further transformations we shall retain in (6) only components that depend on the orientation of the molecules. We assume axial symmetry and denote the unit vector directed along the long axis of the i-the molecule by $\mathbf{c}_i$. We then have from (6) and (1):

$$U_{12}(r)=J_{12}(r)(\mathbf{c}_1\mathbf{c}_2)^2+I_{12}(r)(\mathbf{c}_1\mathbf{c}_2)([\mathbf{c}_1\times\mathbf{c}_2]\mathbf{e}_{12}). \tag{7}$$

Here $\mathbf{e}_{12}$ is a unit vector connecting the centers of the masses of the interacting molecules 1 and 2, and $J_{12}(r)$ and $I_{12}(r)$ are obtained by the corresponding integration in (6). The general expressions for $J_{12}(r)$ and $I_{12}(r)$ are rather cumbersome and we shall not write them out.

We shall consider in more detail only the important special case in which we can neglect the retardation of the interaction. Then the Green's functions D^E_{ik} and $D_{ik,j}$ depend only on the "three-dimensional" coordinates $\mathbf{r}$, and the corresponding expressions can easily be obtained[3]:

$$D_{ik}{}^E=\frac{3r_ir_k-r^2\delta_{ik}}{r^5}, \quad D_{ik,j}=\frac{\partial}{\partial r_j}D_{ik}{}^E, \tag{8}$$

where $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$. In this approximation,

$$\begin{gathered}J_{12}(r)=\frac{9}{r^6}\int d\omega\,\delta_1(i\omega)\delta_2(i\omega,)\\ I_{12}(r)=\frac{3}{r^7}\int d\omega[\delta_1(i\omega)\sigma_2(i\omega)+\delta_2(i\omega)\sigma_1(i\omega)].\end{gathered} \tag{9}$$

Here $\delta_{1,2}(i\omega)$ is the anisotropic molecular polarizability and $\sigma_{1,2}(i\omega)$ is the molecular gyrotropy, i.e., the tensor of the polarizability of the molecule is expressed formally in the form of the following sum:

$$\alpha_{ik}=\alpha_0\delta_{ik}+\delta c_ic_k+\sigma e_{ikl}\frac{\partial}{\partial r_l}. \tag{10}$$

By starting out from Eq. (6), the parameters δ, σ(α_0, of course) can be expressed in terms of the microscopic characteristics

$$\langle d_id_k\rangle=\alpha_0\delta_{ik}+\delta c_ic_k, \quad \langle d_iQ_{kl}\rangle=\sigma e_{ikl}. \tag{11}$$

Or, by choosing a cartesian system of coordinates with the z axis along the long axis of the molecule $\mathbf{c}$,

$$\begin{gathered}\alpha_0=\frac{2}{3}\sum_n\frac{|(d_z)_{0n}|^2+|(d_x)_{0n}|^2+|(d_y)_{0n}|^2}{(\omega_{n0}{}^2-\omega^2)\omega_{n0}{}^{-1}},\\ \delta=\frac{2}{3}\sum_n\frac{|(d_z)_{0n}|^2-{}^1/{}_2|(d_x)_{0n}|^2-{}^1/{}_2|(d_y)_{0n}|^2}{(\omega_{n0}{}^2-\omega^2)\omega_{n0}{}^{-1}},\\ \sigma=\frac{3}{2}\sum_n{}'\frac{(d_x)_{0n}(Q_{yz})_{n0}-(d_y)_{0n}(Q_{zx})_{n0}}{\omega_{n0}-\omega}\\ +\frac{(d_x)_{n0}(Q_{yz})_{0n}-(d_y)_{n0}(Q_{zx})_{0n}}{\omega_{n0}+\omega};\end{gathered} \tag{12}$$

ω_{n0} is the excitation energy of the n-th state of the molecule.

We note that an interaction of the type (7) represents the most general form consistent with the symmetry conditions of the problem. Actually, we can make up from the three vectors $\mathbf{c}_i$, $\mathbf{c}_j$, and $\mathbf{e}_{ij}$ (or $\mathbf{r}_{ij}=r_{ij}\mathbf{e}_{ij}$) five independent scalar variables: $\mathbf{c}_i\cdot\mathbf{c}_j$, $\mathbf{c}_i\cdot\mathbf{r}_{ij}$, $\mathbf{c}_j\cdot\mathbf{r}_{ij}$, r_{ij}, and $[\mathbf{c}_i\times\mathbf{c}_j]\cdot\mathbf{r}_{ij}$.

Moreover, since $([\mathbf{c}_i\times\mathbf{c}_j]\cdot\mathbf{r}_{ij})^2$ (and also higher degrees) is expressed in terms of $\mathbf{c}_i\cdot\mathbf{c}_j$, $\mathbf{c}_i\cdot\mathbf{r}_{ij}$, and $\mathbf{c}_j\cdot\mathbf{r}_{ij}$, then in the most general case we can write

$$U_{ij}=U_{1ij}(r_{ij}, \mathbf{c}_i\mathbf{e}_{ij}, \mathbf{c}_j\mathbf{e}_{ij}, \mathbf{c}_i\mathbf{c}_j)+([\mathbf{c}_i\times\mathbf{c}_j]\mathbf{e}_{ij})U_{2ij}(r_{ij}, \mathbf{c}_i\mathbf{e}_{ij}, \mathbf{c}_j\mathbf{e}_{ij}, \mathbf{c}_i\mathbf{c}_j), \tag{13}$$

which agrees with (7).

FIG. 1.

As is well known,[1] Eq. (7) (see also Sec. 4) leads to the formation of CLC with pitch $\sim I_{12}^{-1}$. Upon formation of CLC in the mixture of NLC and CLC, the quantity I_{12} is proportional to the CLC concentration N. The sign of the helix of the mixture is determined here by the sign of the spiral of the CLC. Thus, upon the addition to CLC of the dextrorotatory CLC, we obtain a right-hand mixture and similarly for the levorotatory CLC.

In the work of Kozawaguchi and Wada,[4] some mixtures of NLC and CLC were studied experimentally. It was established that on mixing of the components of CLC, the rotation (pitch) changes monotonically with concentration, which agrees with (7)–(9). However, in the mixtures of CLC and NLC (at low concentrations of CLC), the sign of the rotation is always left, independent of the sign of the CLC component (in the experiment, two types of NLC were studied; four left and eight right CLC). Therefore, in the mixture NLC+right CLC, the pitch of the helix does not change monotonically with the concentration, but has a maximum at some concentration N_m of right CLC component. At still greater concentrations ($N_0 \approx 2N_m$), an NLC–CLC phase transition is observed. For explanation of the results of this work, we need in the mixture of CLC and NLC an interaction mechanism that guarantees a rotation opposite in sign to that of the CLC component.

It follows from (7)–(9) that $I_{12} > 0$ in the interaction of left molecules ($\sigma > 0$) and $I_{12} < 0$ in the interaction of right ones ($\sigma < 0$). If the signs of the characteristics optical activity of both molecules are opposing ($\sigma_1/\sigma_2 < 0$), then I_{12} is determined by the more active component, but the quantity I_{12} decreases upon addition of the less active component, going to zero at some concentration. In mixtures of CLC and NLC ($\sigma_1 = 0$), the sign of I_{12} is determined by the sign of the optical activity of the CLC molecules. Therefore, for an explanation of the experimental results of Ref. 4, account of the paired van der Waals interaction is not sufficient. It is possible that three-particle non-additive forces are important in this case.

For simplicity, we consider a complex of three molecules: A, B, (NLC), and C(CLC). The energy U of this complex is

$$U = U_{AB} + U_{BC} + U_{CA} + U_{ABC}, \tag{14}$$

where U_{ABC} is the nonadditive three-particle contribution to the energy from the van der Waals forces, and U_{AB}, U_{BC}, and U_{CA} are determined from (7)–(9). The quantity U_{ABC} is determined by the diagram shown in Fig. 2 (and analogous diagrams obtained by permutation of the solid line). The calculations are analogous to those given above for two-particle forces (for atoms, the three-particle forces were also calculated by McLachlan[5]). In the approximation of small distances between the mass centers of the molecules (when the retardation is insignificant), we obtain with account taken of (8) and (10):

$$U_{ABC} = -\frac{1}{\pi} \int_0^\infty d\omega\, \alpha_{ij}(i\omega) D_{jk}{}^E(\mathbf{R}_{AB}) \beta_{km}(i\omega) D_{mn}{}^E(\mathbf{R}_{BC}) \gamma_{np}(i\omega) D_{pi}{}^E(\mathbf{R}_{CA}), \tag{15}$$

FIG. 2.

where $\hat{\alpha}, \hat{\beta}, \hat{\gamma}$ are the polarizabilities of the molecules A, B, C according to Eq. (10).

It is important that both the sign and the magnitude of U_{ABC} depend on the location of the mass centers of the molecules. For the antisymmetric part of interest to us at the arrangement such as in Fig. 3a (the centers of the masses are on one straight line),

$$U_{ABC} = I_1 (\mathbf{c}_A \mathbf{c}_B)(\mathbf{c}_C \mathbf{c}_B)([\mathbf{c}_B \times \mathbf{c}_C] \mathbf{e}_{BC}), \tag{16}$$

where

$$I_1 = -\frac{3}{32\pi R^{10}} \int_0^\infty \delta_A(i\omega) \delta_B(i\omega) \sigma_C(i\omega)\, d\omega. \tag{17}$$

In the arrangement of Fig. 3b (centers of mass at the vertices of an equilateral triangle),

$$I_1 = \frac{33}{8\pi R^{10}} \int_0^\infty \delta_A(i\omega) \delta_B(i\omega) \sigma_C(i\omega)\, d\omega. \tag{18}$$

Thus in a linear arrangement the three-particle forces decrease the effect of the pair forces and in a triangular arrangement they increase them.

If we assume that in the mixtures investigated experimentally[4] the right CLC are arranged linearly relative to the NLC molecules, and the left have a triangular arrangement, then Eqs. (17) and (18) [together with (7)–(9)] mean that the NLC investigated become levorotatory in the presence of CLC. This effect can be taken into account directly in self-consistent fashion in the macroscopic Frank expansion for the free-energy density of the mixture:

$$f = {}^1\!/_2 (1-N) K_1 (q_m - I_1 N)^2 + {}^1\!/_2 N K_2 (q_m - q_0)^2; \tag{19}$$

here N is the concentration of CLC (left, if $q_0 > 0$, and right if $q_0 < 0$), K_1 and K_2 are the elastic moduli of the nematic and the cholesteric. The equilibrium pitch (or, the value of q_m) is found by minimizing (19):

$$q_m = \frac{(1-N) K_1 I_1 N + q_0 N K_2}{K_1 (1-N) + N K_2}. \tag{20}$$

Equation (20) corresponds to the results of experiment.[4] For right CLC ($q_0 < 0$) we have a certain concentration at which $q_m = 0$ (transition to NLC), and a

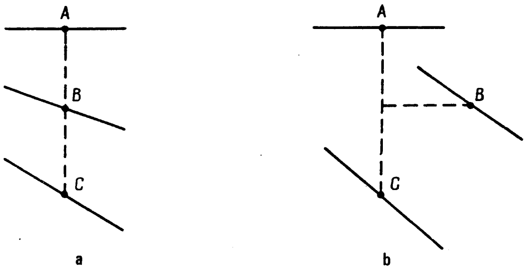

FIG. 3.

maximum at half the concentration N_m, while

$$N_m=(K_1I_1+q_0K_2)/2K_1I_1.$$

Naturally, the reasons for which the mixtures of left molecules studied in the experiment of Ref. 4 group into triangular groups with molecules of NLC, and the right molecules group into linear groups, cannot be understood on the basis of such a macroscopic approach. As has already been mentioned in the Introduction, a complete quantitative account of the induced optical activity is possible only on the basis of a microscopic theory. In simple oscillator models, this calculation is easily carried out to the end. For example, in the helicoidal model of the optical activity,[6] which considers the electron to be moving in a potential (we immediately assume axial symmetry)

$$W={}^1/_2a_1(x^2+y^2)+{}^1/_2b_1z^2+\gamma xyz,$$

everything is determined by the sign of the interaction γ ($\gamma>0$ for left molecules, and $\gamma<0$ for right). If we have a molecule of NLC ($\gamma=0$) interacting with a molecule of CLC, then the energy of such an interaction is

$$V=\frac{e^2}{|\mathbf{R}-\mathbf{r}|},$$

where e is the electron charge, $\mathbf{R}$ is the coordinate of the electron in the CLC molecule, $\mathbf{r}$ that in the NLC.

If we expand V in r/R in the usual fashion taking into account the first nontrivial terms, then

$$V={}^1/_2A_{ij}r_ir_j+{}^1/_6B_{ijk}r_ir_jr_k.$$

The component B_{ijk} leads to induced optical activity, but only the term B_{xyz}. However, the sign of B_{xyz} is determined not only by the sign of γ. The fact is that the quadratic component $\sim A_{ij}$ leads to a rotation of the principal axes in the xy plane (rotation in the planes xz and yz can be disregarded if the values of A_{xz}, A_{yz} are small in comparison with the characteristic anisotropy $|a_1-b_1|$ of the NLC molecule).

With account of what has been said above, we obtain the following for the potential energy in the quadratic approximation:

$$W={}^1/_2(a_1+A_{11})x^2+A_{12}xy+{}^1/_2(a_1+A_{22})y^2+{}^1/_2b_1z^2,$$

i.e., the principal axes in the xy plane are turned through an angle φ:

$$\tan 2\varphi=2A_{12}/(A_{11}-A_{22}),$$

and the sign of the induced optical activity is now determined by the value of the angle φ and the sign of γ. At $\sin 2\varphi>0$, the signs of $B_{x'y'z}$ (x', y' are the new axes in the xy plane) and γ are identical (which corresponds to the triangular arrangement) and at $\sin 2\varphi<0$, the sign of $B_{x'y'z}$ is opposite that of γ (linear arrangement).

3. LANDAU THEORY OF CLC AND NLC MIXTURES

We now consider phenomenologically the phenemena that take place in NLC upon addition of CLC. The experimental data of Ref. 1 indicate that the conditions for the Landau expansion of the free energy are well satisfied in liquid crystals. The order parameter (both in NLC and CLC) is a second rank tensor of the following form:

$$Q_{ik}=s(n_in_k-{}^1/_3\delta_{ik}), \tag{21}$$

where $\mathbf{n}$ is the director, s is the modulus of the order parameter. Since $\operatorname{Sp} Q_{ik}=0$, then the most general form of the expansion of the free energy with accuracy to s^4 will be

$$F_0={}^1/_2A \operatorname{Sp} Q^2-{}^1/_3B \operatorname{Sp} Q^3+{}^1/_4C(\operatorname{Sp} Q^2)^2, \tag{22}$$

where $A=a(T-T_0)$, and $a, B, C>0$.

If, as is the case, for example, in CLC, the equilibrium distribution is inhomogeneous, then it is necessary to take into account terms with gradients of the order parameter also. It is customary to restrict oneself to the expansion

$$F_1=\frac{1}{2}K_1\left(\frac{\partial Q_{\alpha\beta}}{\partial x_\gamma}\right)^2+\frac{1}{2}K_2\left(\frac{\partial Q_{\alpha\beta}}{\partial x_\beta}\right)^2+Pe_{\alpha\beta\gamma}Q_{\alpha j}\nabla_\gamma Q_{\beta j}, \tag{23}$$

where in the NLC phase $P=0$. However, for agreement in accuracy of the expansions (22) and (23), it is necessary to take into account terms in F_1 that are proportional to s^2 and s^4. The general form of such terms can be determined from the considerations of symmetry. For example, for s^2 accuracy, we must calculate all possible convolutions of the form

$$n_in_j\frac{\partial Q_{\alpha\beta}}{\partial x_\gamma}\frac{\partial Q_{\alpha'\beta'}}{\partial x_{\gamma'}}.$$

A similar consideration is easily carried out for the term that is linear in the gradient. Terms of the order s^4 of such a structure are not possible at all. Further simplification is obtained when account is taken of the symmetry of the CLC:

$$n_x=\cos qz,\quad n_y=\sin qz,\quad n_z=0.$$

Denoting the additional coefficients by K_3s and P_1s, respectively, we get, with account of what has been said above,

$$F=F_0+F_1={}^1/_3As^2-{}^2/_{27}Bs^3+{}^1/_9Cs^4+K_1s^2q^2+K_3s^3q^2+Pqs^2+P_1qs^3. \tag{24}$$

Minimization of the expression (24) relative to q gives the equilibrium twist of the CLC helix:

$$q=-(P+P_1s)/2(K_1+K_3s). \tag{25}$$

We note that Eq. (25) gives in natural fashion a pitch value that is temperature dependent. Depending on the relations between the quantities and the signs of the constants P_1 and K_3, we can distinguish different situations. The pitch can increase with decrease in temperature and remain finite at all temperatures in the region of existence of the mesophase (as is usually the case in pure CLC). However, more exotic relations are realizable in principle, for example, a decrease in the pitch with decrease in the temperature, and also the going of the pitch to infinity at some temperature T^* (at which $P=P_1s(T^*)=0$) with subsequent change in the sign of the helicity. Experimental data on mixtures[1] indicate that under some conditions such a situation can exist.

As has already been noted, the coefficients P and P_1

vanish in NLC. Upon addition of CLC, optical activity appears and neither P nor P_1 vanish. Therefore, (in the linear approximation), we can assume that in the mixtures of CLC + NLC (or in mixtures of CLC near the racemic point)

$$P+P_1s=\alpha N \tag{26}$$

(N is the concentration of CLC: for the racemic mixture in (26) we must replace N by $N-N_0$, where N_0 is the concentration of one of the components of CLC at the racemic point). Thus, we can deduce from (26) that

$$q=\beta N. \tag{27}$$

We note that, because of this dependence, there is a shift in the temperature of transition to the isotropic phase:

$$T=T+\frac{3\beta^2N^2}{2a(K_1+K_3s_c)}, \tag{28}$$

where s_c is the modulus of the order parameter at the transition point.

We point out also that external electric and magnetic fields, applied perpendicular to the director, can play a role similar to addition of CLC. Upon imposition of the electric field E, the change in the symmetry of the NLC takes place from $D_{\infty h}$ to $C_{\infty h}$. If a magnetic field H is introduced in the same direction, then the symmetry is lowered to C_∞. The components with the coefficient P in the free energy no longer vanish. Similar to the above, we can set

$$P+P_1s=\alpha EH, \tag{29}$$

and thence

$$q=\beta EH. \tag{30}$$

Actually, the coefficient β can be very small and then the formation of CLC will no longer be observed. In this sense, the racemic mixtures seem to have the greater possibilities. However, there are no reliable experimental data pertaining to this problem at the present time.

4. POSSIBILITY OF THE TRANSITION NLC-CLC AT THE RACEMIC POINT

Zel'dovich[2] called attention to the fact that, in mixtures of right and left stereoisomers, an unusual transition is possible, connected with the fact when concentrations of both components are equal, a center of symmetry appears. For molecules of elongated (or platelike) shape, this corresponds to an NLC-CLC transition. In this Section we shall show that in the simplest CLC model, which is considered in the second section, such a transition can take place.

We write down the interaction (7) in terms of the components of the director:

$$U_{ij}=-J_{ij}(\mathbf{n}_i\mathbf{n}_j)^2-I_{ij}(\mathbf{n}_i\mathbf{n}_j)([\mathbf{n}_i\times\mathbf{n}_j]\mathbf{e}_{ij}), \tag{7a}$$

where J_{ij} and I_{ij} are the induced dipole-dipole and dipole-quadrupole interactions [see Eq. (9)]. In correspondence with what was established in the second section of this paper, if a molecule has a center of inversion, then $I_{ij}=0$. Upon reversal of the sign of the optical activity of the molecules, the parameters of I_{ij} change sign $I_{ij}=0$ in interactions of right and left molecules.

In what follows, we make use of the CLC model: the parallel molecules lie in planes and in the transition from one plane to another the long axes turn through the angle θ. Thus we have the following expressions for the interaction between two right molecules U_{dd}, two left, U_{ll} and a right and a left, U_{dl}:

$$U_{dd}={}^1/_2(J\theta+I)\theta s,\quad U_{ll}={}^1/_2(J\theta-I)\theta s,\quad U_{dl}={}^1/_2J\theta^2s. \tag{31}$$

Here we have assumed that $\theta\ll 1$, J and I are identical for any neighboring pair of molecules with the corresponding sign of rotation, and s (the modulus of the order parameter) is the same in all the phases.

If l left and right molecules are located in the mixture (but transitions $l\rightleftharpoons d$ are possible), then the free energy can be written in the following from (similar to Ref. 2):

$$F={}^1/_2U_{dd}d^2+{}^1/_2U_{ll}l^2+U_{dl}ld+T[l\ln l+d\ln d]. \tag{32}$$

It is convenient to introduce new variables in (32):

$$l+d=N,\quad (l-d)/N=m. \tag{33}$$

We then have

$$F=F_0-{}^1/_2N^2I\theta sm+TNm^2+{}^1/_4N^2J\theta^2s; \tag{34}$$

We have included in F_0 the terms that do not depend on θ, s, and m.

Minimization in θ determines the resulting structure:

$$\theta={}^1/_2Im/J,\quad \theta=qz. \tag{35}$$

Substituting (35) in (34), we obtain

$$F=F_0+m^2[TN-{}^3/_{16}I^2N^2s/J]. \tag{36}$$

It then follows that the temperature of the phase transition is determined by the relation

$$T_c={}^3/_{16}I^2Ns(T_c)/J. \tag{37}$$

At $T>T_c$, we have $m=0$ (the number of left and right molecules is the same) and NLC is formed; however, at $T=T_c$, a phase transition to CLC takes place. The period of the structure is determined by Eq. (35). We note that the period of the CLC, formed in such fashion, should always be decreased $\sim(T_c-T)^{1/2}$ with decrease in the temperature. In order to determine the coefficient of proportionality, we must take into account the next term in the expansion (36) in the order parameter.

5. CONCLUSION

The effects considered above are determined by the dependence of the pitch of the CLC on the temperature or concentration. They can all be determined experimentally from the corresponding optical phenomena (for example, from the location of the region of selective reflection of one of the circularly polarized beams). We now give a few qualitative features of the CLC mixture, connected with the dependence of the pitch of the helix on the concentration.

For example, in the propagation of ultrasound in the CLC mixture, additional relaxation damping should be observed. This is connected with the fact that the period of the mixture (or the inverse quantity q_m) is determined by the concentration. Thus, in the propagation of the ultrasound, in addition to the density fluctuations, there is a comparatively slow relaxation (connected with the diffusion) of the pitch of the helix. In the usual fashion,[7] we find the following for the complex wave vector $\varkappa$:

$$\varkappa=\frac{\omega}{c_0}+i\frac{\omega^2\tau}{2c_0^3}(c_\infty^2-c_0^2), \quad \omega\tau<1, \tag{38}$$

$$\varkappa=\frac{\omega}{c_\infty}+i\frac{c_\infty^2-c_0^2}{2\tau c_\infty^3}, \quad \omega\tau>1; \tag{39}$$

here ω is the frequency of the ultrasound, τ is the characteristic diffusion time of establishing the equilibrium, c_0 and c_∞ are the velocities of ultrasound at $\omega\tau \ll 1$ and $\omega\tau \gg 1$, respectively.

We note that the diffusion times τ differ significantly for directions along and transverse to the axis of the helix, while the natural anisotropy of the elastic properties of pure CLC is very small ($\sim 10^{-6}$). In correspondence with this, the dispersion curves for propagation of ultrasound along and transverse to the axis of the CLC helix should also differ.

The presence of an additional (in relation to pure CLC) hydrodynamic variable (concentration) leads to a change in the spectrum of the collective modes. A more detailed consideration of this question goes beyond the framework of this paper. Here we shall only shown the qualitative consequences. Along with ordinary sound and second sound, which is connected with the compressibility along the axis of the CLC (the modulus $K_{22}q^2$) a damped diffusion mode appears. Depending on the relation of the constant of interaction between the components of the mixture, the character of this latter mode can change from purthermodiffusion of the slipping of one component relative to the other. The structure of the modes also depends on the orientation of the wave vector of the mode relative to the axis of the CLC. All these effects can be observed in principle experimentally, for example, by Brillouin scattering. The real estimate depends on the values of the many parameter of elasticity and viscosity, which are unknown at present for most of the CLC mixtures.

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On the possibility of existence of a spin-glass phase in amorphous magnets

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It is shown that in amorphous magnets with "rotating" anisotropy of the easy-axis type of a spin-glass phase can exist. The conditions for the existence of such a phase are discussed. The phase diagram for the ferromagnetic, paramagnetic, and spin-glass phases is derived.

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1. INTRODUCTION

In this paper we consider the properties of one class of amorphous magnets–alloys of rare-earth (Tb, Dy, Ho) and transition (Fe, Co) metals. These alloys possess a number of unusual magnetic properties; e.g., the magnetization at zero temperature does not attain the maximum possible value. To explain these phenomena a model was proposed[1] according to which each magnetic atom is acted upon by a crystal field that is random in direction but constant in magnitude, leading to anisotropy of the easy-axis type. We shall call this anisotropy rotating anisotropy. Subsequently, Mössbauer-effect experiments[2] on these substances