Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

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Version of record first published: 24 Sep 2006.

To cite this article: E. I. Kats & V. V. Lebedev (1991): Some Properties of Ferromagnetic Liquid Crystals, Molecular Crystals and Liquid Crystals, 209:1, 329-337

To link to this article: http://dx.doi.org/10.1080/00268949108036208

Mol. Cryst. Liq. Cryst., 1991, Vol. 209, pp. 329–337
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Printed in the United States of America

Some Properties of Ferromagnetic Liquid Crystals

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(Received July 25, 1990)

Keywords: liquid crystals, dynamics, ferromagnetics, eigenmodes

1. It is well known that liquids existing in the nature do not posses any magnetic order and therefore very weakly interact with a magnetic field. On the other hand the possibility to govern the flow and other properties of liquids by means of a magnetic field is fairly attractive for solving various technical problems. This stimulated attempts to synthesize magnetic liquids. Although the existence of such liquids is not in principle prohibited, all attempts to obtain them have so far been unsuccessful.

A hope for experimental realization of such a state is promoted by great success in the synthesis of paramagnetic and metalloorganic liquid crystals. Note, e.g. the work (Eastman *et al.*, 1987) whose authors on the basis of the data on electron spin resonance, concluded that at room temperature there occurs a phase transition from a paramagnetic nematic into a 1d Heisenberg antiferromagnetic discotic. We are optimistic at this subject having in mind the history of discovery of liquid-crystalline ferroelectrics.

From the point of view of applications it would be very important if ferromagnetic liquids or ferromagnetic liquid crystals would exist. The existence of such phases would allow to operate by flow and orientation of the systems through very weak magnetic fields.

As a rule liquid crystals are diamagnetic substances with the anisotropic susceptibility. Usually $\chi_a \sim 10^{-7}$ CGSE. There is the principal possibility to increase χ_a introducing into molecules the paramagnetic ions with the anisotropic g-factor (Chandrasekhar *et al.*, 1986). For such systems the anisotropy of the paramagnetic susceptibility:

$$\chi_{\parallel} - \chi_{\perp} = \frac{n\mu_B S(S+1)}{3T}(g_{\parallel}^2 - g_{\perp}^2)$$

Here $\mu_B = 9.3\ 10^{-21}$ erg/G-the Bohr magneton, n is the concentration of para-

magnetic ions, S is the spin. Unfortunately up to now it is possible to introduce the paramagnetic ions only to the concentration n is smaller than 10^{+20} cm^{-3}. Therefore the paramagnetic susceptibility is also small:

$$\chi_{\parallel} - \chi_{\perp} \sim 10^{-6}$$

If it would be possible to introduce the paramagnetic ions into the molecules up to the concentration 10^{+23} cm^{-3} it would be possible to obtain the value $\chi_{\parallel} - \chi_{\perp} \sim 10^{-3}$. But it is the maximum.

The second way—to introduce into liquids or liquid crystals directly macroscopic ferromagnetic particles [Broshard, de Gennes, 1970; Fabre *et al.*, 1990]. In liquid crystals the orientation of the ferromagnetic particle along the director and in the orthogonal plane requires the different deformation energy. Namely there is the potential barrier:

$$\Delta U_{\text{or}} \approx KL$$

This expression is correct only for $L >> d$ (L is the length of the particle and d-the diameter), K is the Frank module.

If $\Delta U_{\text{or}} \leqslant \text{T}$ the particles will freely rotate and we do not obtain the ordering of the particles. Therefore for the ordering it is necessary to satisfy the condition:

$$KL >> \text{T}$$

In opposite case particles will rotate freely and we do not obtain the ordering of the particles. For typical values: $K \sim 10^{-6}$ erg/cm, $\text{T} \sim 10^{-14}$ erg we obtain $L >> 10^{-8}$–10^{-7} cm. It means for example $L \sim 50$–100 Å, $d \sim 10$–20 Å or $L \sim 1000$ Å, $d \sim 100$ Å.

This particle has the dipole moment μ:

$$\mu = M_s V$$

Here V is the volume of the particle, M_s is the magnetic moment of the saturation.

Let us consider the case of the easy-axis anisotropy and let us assume that this easy-axis is parallel to the long axis of the particle. There is the energy of the uniaxial anisotropy ΔU_m. We assume $\Delta U_m >> \text{T}$. In opposite case the magnetic moments can be rotated freely and we shall not obtain the magnetic ordering.

There are two possibilities for the reorientation of u. The first possibility is the reorientation of u without mechanical rotations of the particle. For such reorientation it is necessary to apply the magnetic field:

$$H_{\text{mag}} = 2\pi M_s$$

The second possibility is the reorientation of μ through mechanical rotations. For such rotation it is necessary to apply the magnetic field:

$$\mu_B H_{\text{mech}} = KL$$

The ratio:

$$\frac{H_{\text{mech}}}{H_{\text{mag}}} \approx \frac{KL}{2\pi M_s^2 V} = \frac{KL}{2\pi M_s^2 L d^2} = \left(\frac{d_c}{d}\right)^2$$

here $d_c = K/2\pi M_s^2 \sim 50$ Å for Fe_3O_4.
If $d > d_c$ the mechanical rotation is more important.

For such consideration the condition of strong anchoring is very important. The corresponding dimensionless parameter: $\lambda = Wd/K$, where W is the anchoring energy. In real conditions $\lambda \sim 10^{-2}$. So the interaction between n and u is very weak (it means that a spin-orbit interaction is very weak).

2. Some words about the possibility of the observation of the magnetic ordering. In solid crystals as usual the most powerful method is the neutron scattering. As well known the neutron has the magnetic moment and this moment interacts with the spin of the electron. This interaction leads to the appearance some additional (comparison with the same crystal but without magnetic ordering) peaks. But in liquid crystals this method is not very useful because in liquid crystals we have no Bragg reflections.

For ferromagnetic liquid crystals the resonance methods are the most convenient. The fact is that the nucleus feels the fields produced from dipole moments of the neighboring electrons. Therefore it is possible to observe the resonance behavior without external fields. The field which acts on the nucleus is determined by the magnetic ordering.

The third method is related with the measurements of the magnetic susceptibility.

4. The magnetic moments in magnetic materials are constituted from the spin and orbital magnetic moments. The ratio g of the magnetic moment to the mechanical one: $g = 2$ for spin moments (in $e/2mc$ units, where e- is the charge of the electron, m is the mass of the electron and c- is the velocity of the light); for orbital magnetic moments $g = 1$.

It is possible to measure g directly from Einstein-de Haas's effects, Barnet's effect or indirectly from ferromagnetic resonance dates. In all known magnetic materials $g \approx 2$, therefore only the spin moments give contribution to the magnetic moment of the sample.

The exchange interaction is a pure quantum effect. For this energy it is easy to get the following estimation: $I \approx e^2 \exp(-r/a)/r$. Here e is the charge of the electron, r is the interatomic (or intermolecular) distance and a is the parameter $\sim 10^{-8}$ cm. For $r \sim 5\,10^{-8}$ cm, $I \sim 10^{-14}$ erg and therefore I is the same order as the temperature of a nematic-isotropic liquid phase transition. Therefore for such inter molecular distances in principal it is possible to observe some magnetic ordering in liquid crystals. By the way the dipole-dipole interaction give us the energy the order of

$\mu^2/a^3 \sim 10^{-17}$ erg. The corresponding temperature is 0.1 K and is is clear that such transition is not observable in real liquid crystals.

5. I'm not going to discuss further microscopical features of ferromagnetic liquid crystals. I shall suppose only that such systems exist. The analysis of general phenomenological properties of liquid-crystalline ferromagnets has been carried out in the paper (Kats, Lebedev, 1989). It appears that the combination of magnetic and liquid-crystalline order manifests itself most in dynamic properties, above all in eigenmode spectrum. I'm going to consider the general phenomenological dynamic properties of ferromagnetic liquid crystals.

Let me start with considering of the dynamic properties of the ferromagnetic liquids. The dynamic variables, describing the dynamic properties of the ferromagnetic liquids are: the mass density ρ, the momentum density j, specific entropy σ and $\mathbf{m}$—the unit vector along the magnetic moment u. The energy of the system is constituted from the kinetic energy $E_k = j^2/2\rho$, so called an internal energy $\varepsilon(\rho, \sigma)$ and the exchange energy:

$$E_{ex} = \frac{T}{2f}(\nabla \mathbf{m})^2$$

The dynamic equation for $\mathbf{m}$ is called the Landau-Lifshits equation, which has the form:

$$\frac{\partial \mathbf{m}}{\partial t} = -\mathbf{v}\,\nabla \mathbf{m} + \nabla[A\mathbf{m} \times \nabla \mathbf{m}]$$

Here $A = T/fS_o$, S_o- is the module of the spin, and f is some parameter.

In solid ferromagnetics the first term in the r.h.s. of this equation is not important and from this equation one can find the dispersion law for spin wave (ω is a frequency, k is a wave vector):

$$\omega = \pm A\,k^2$$

The attenuation of spin waves in solid ferromagnetics is small (proportional k^4) due to the spin conservation law.

In liquid ferromagnets the interaction between the velocity and $\mathbf{m}$, describing by the first term in the r.h.s. of Landau-Lifshits equation is very important (because the mode associated with components of the velocity transverse to the wave vector is very soft one). It is convenient to use the correlation functions. Let us designate:

$$D_{\mu\nu} = \langle m_\mu m_\nu \rangle = 2\pi A\,\delta_{\mu\nu}\,\delta(\omega - A^2k^4),$$

$$D_{ik}^{(t)} = \langle v_i^{(t)} v_k^{(t)} \rangle = \frac{2\eta T}{\rho^2\omega^2 + \eta^2 k^4}\left(\delta_{ik} - \frac{k_i k_k}{k^2}\right)$$

Here $D_{\mu\nu}$—is the spin-wave correlation function, $D_{ik}^{(t)}$—is the correlation function for transversal components of the velocity, η is the viscosity of the liquid.

The convective term (the first one in the r.h.s. of the Landau-Lifshits equation) describes the interaction between tranverse components of the velocity and spin wave degrees of freedom. Such interaction leads to two effects:

1. This interaction changes the dispersion law for spin wave.
2. This interaction renormalizes the viscosity coefficient.

As result we get for the spin wave dispersion law:

$$\omega = \pm Ak^2 - i\,Yk^3$$

Here $Y = T/16\,\eta$ and η—is the bare viscosity of the liquid. The fluctuation correction to the viscosity (i.e. the correction originating from the interaction term) has the form:

$$\eta_{fl} = \frac{T\,L}{60\,\pi^2 Y}$$

where L is the logarithmic factor.

$$L = \ln\left(\frac{2\pi\,Y^{1/3}}{1\,\omega^{1/3}}\right)$$

(1—is the molecular length). Let me note that the both effects are pure fluctuation effects and therefore they are proportional to the temperature T. Besides in the long wavelength limit this fluctuation attenuation of the spin wave (which is proportional to k^3) is stronger than the regular attenuation of spin wave (which is proportional to k^4). The ratio η_{fl}/η is the universal logarithmic function:

$$\frac{\eta_{fl}}{\eta} = \frac{4}{15\pi^2}\,L$$

Let us consider the ferromagnetic nematics. There are two new features (as compared with the case of ferromagnetic liquids): the anisotropy of the exchange interaction and the spin orbit interaction (so called relativistic effects). I am going to consider the both effects step by step.

The exchange interaction in ferromagnetic nematics has the form:

$$E_{ex} = \frac{T}{2f_1}(\nabla\mathbf{m})^2 + \frac{T}{2f_2}(n\,\nabla\mathbf{m})^2.$$

Here f_1, f_2 are two parameters describing the exchange interaction in nematics. This anisotropy leads to the anisotropy of the spin wave dispersion law:

$$\omega = \pm Ak^2 + Yk^3$$

where

$$A = A_1 + A_2 \frac{k_z^2}{k^2}$$

and A_1, A_2 are related with f_1 and f_2 the same manner, as for isotropic liquid ferromagnetics.

In ferromagnetic nematics there is one new (as compared with the isotropic case) soft mode—the mode of the relaxation of the director. The corresponding correlation function has the form:

$$d_{\alpha\beta} = \frac{2\,\mathrm{T}\,\gamma_1}{\gamma_1^2\omega^2 + K_1^2k^4} \frac{k_\alpha k_\beta}{k_\perp^2} + \frac{2\,\mathrm{T}\,\gamma_t}{\gamma_t^2\omega^2 + K_t^2k^4} \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k_\perp^2}\right)$$

Here γ_1 and γ_t are the longitudinal and transversal components of the rotational viscosity, K_1 and K_t—corresponding components of the Frank's modulus. The interaction between the director mode and spin wave mode leads to the attenuation of the last one. As result we get in the spin wave dispersion law:

$$Y = Y_1 + Y_2$$

where:

$$Y_1 = \frac{\mathrm{T}}{16\,\eta} \quad \text{and} \quad Y_2 = \frac{0.1\,\mathrm{T}\,A}{K}$$

First contribution is associated with the interaction between spin waves and the transverse velocity, the second contribution is associated with the interaction between spin waves and director modes.

Let us now to discuss (briefly of course) the role of relativistic effects (or in another words—spin orbit effects). The corresponding contribution to the energy:

$$E_{\mathrm{rel}} = \mp \frac{\mathrm{T}}{2f_1} q_{\mathrm{rel}}^2 (\mathbf{n}\,\mathbf{m})^2$$

Here q_{rel}—is some constant determined by spin orbital interaction, this constant has the dimension of the wave vector. In the case of the upper sign the minimum of this energy takes place when **m** is parallel to the director **n** (so cold the easy axis anisotropy) and for the lower sign—the minimum takes place for **m** is or-

thogonal to **n** (the assay plane anisotropy). Now due to this interaction (unlike to the case of the exchange interaction) equations for **m** and **n** are coupled:

$$\frac{\partial \mathbf{m}}{\partial t} = -(\mathbf{v}\,\nabla\mathbf{m}) + A(\mathbf{m} \times \nabla^2\mathbf{m}) \pm \Xi[\mathbf{m} \times \mathbf{n}](\mathbf{m}\,\mathbf{n}),$$

$$\gamma \frac{\partial n_i}{\partial t} = (\delta_{ik} - n_i n_k)\left[K\,\nabla^2 n_k \pm \frac{\mathrm{T}}{f_1} q_{\mathrm{rel}}^2 m_k(\mathbf{m}\,\mathbf{n})\right]$$

where:

$$\Xi = S_0 \frac{\mathrm{T}}{f_1} q_{\mathrm{rel}}^2$$

From these equations one can find the eigen modes spectrum of our system (the ferromagnetic nematic). For the case of the easy axis anisotropy we have the following modes. There are two gapless modes with dispersion laws:

$$\omega_{1,t} = \frac{i}{\gamma_{1,t}}\left(K_{1,t} + \frac{\mathrm{T}\,A\,q_{\mathrm{rel}}^2}{\Xi f_1}\right) k^2$$

This dispersion law has the same form as the dispersion law for the director mode with the effective Frank's module:

$$K_{\mathrm{eff}} = K_{1,t} + \frac{\mathrm{T}\,A\,q_{\mathrm{rel}}^2}{\Xi f_1}$$

There are two modes with the gap:

$$\omega = \pm\Xi - i\frac{\mathrm{T}}{f_1\gamma_1} q_{\mathrm{rel}}^2$$

For the case of the easy-plane anisotropy there are three gapless modes:

$$\omega \sim -i\frac{A^2 f_1 \gamma}{\mathrm{T}} k^2$$

And one mode with the gap:

$$\omega = -i\frac{\mathrm{T}}{f_1\gamma} q_{\mathrm{rel}}^2$$

For $k >> q_{\mathrm{rel}}$ the exchange approximation is correct and for spin wave modes the

main contribution to the attenuation is proportional to k^3. The relativistic contribution to the attentuation is important for wave vectors:

$$k << k^* \sim \left(\frac{Tq_{\text{rel}}}{fY\gamma}\right)^{1/5}$$

The same manner it is possible to calculate the eigen modes spectrum for ferromagnetic smectics. For example the dispersion law for the second sound in ferromagnetic smectics:

$$\omega = \pm\left(B\,k_z^2 + \frac{T}{f_1}\,q_{\text{rel}}^2\,k_\perp^2\right)^{1/2}\frac{k_\perp}{k} - \frac{i}{2}\,\eta_{sm}k^2$$

Here η_{sm}—some combination of the viscosity coefficients of a smectic. It is interesting to note that in this dispersion law the velocity of the second sound is not zero for $k_z = 0$. This dispersion law is analogous to the dispersion law for the transversal sound in discotics.

6. Metallorganic liquid crystals. The results of the most thorough texture and calorimetric studies are listed in the paper (Versace *et al.*, 1990). In this paper the authors carried out a comparative study of some mesogenic azobenzennes compounds and their organometallic analogous, obtained in the result of the chemical reaction with the compound $(PdCN)_2PdCl_2$. It proves that although sterically the shape of molecules with the palladium complex and without it differ only slightly many macroscopic properties of the both compounds are different. First of all metallic complexes as a rule render the phase diagram richer, on this phase diagram there appear new (in comparison with the original substance) liquid-crystalline states. The orientation order in nematic phases of metalloorganic liquid crystals becomes biaxial. This leads to anisotropy of correlations in the layers of smectics phases. Therefore formally the structure called in the paper (Versace *et al.*, 1980) a smectic A (since the long axes of the molecules are not tilted with respect to the normal to smectic layers) is not an uniaxial smectic A. It can be called a biaxial smectic A and in terms of the global symmetry is equivalent to a smectic C.

Phase transitions between different structures in metalloorganic liquid crystals as a rule are closer to continuous than in corresponding compounds without metallic complexes. Thus a jump of the order parameter at the transition and the latent heat of the transition decreases, when metallic complexes are added. On the other hand the parameter $\delta = (T_c - T^*)/T_c$ practically the same in the both types of this compounds T_c is the temperature of the first order phase transition under study, T^*—is the temperature of the absolute instability of the high symmetric phase at which this transition would be a second-order phase transition. These three facts (biaxial orientation order parameter, closeness of phase transitions to continuous and invariability of the parameter δ at the formation of metallic complexes) can be related to each other in the framework of the Landau theory.

Acknowledgment

Authors thank the organization committee for kind invitation to participate at 13-th International Conference on Liquid Crystals.

References

1. F. Broshard and P. G. de Gennes, *J. de Phys.*, **31**, 691 (1970).
2. S. Chandrasekhar, B. K. Sadashiva, S. Ramesha and B. S. Srikanta, *Pramana - J. de Phys.*, **27**, 713 (1986).
3. M. P. Eastman, M. L. Horng, B. Freiha and K. W. Shen, *Liquid Crystals*, **2**, 223 (1987).
4. P. Fabre, C. Casagrande, M. Veyssie, V. Cabuil and R. Massart, *Phys. Rev. Lett.*, **64**, 539 (1990).
5. E. I. Kats and V. V. Lebedev, ZhETF (in Russian), **96**, 2045 (1989). Sov. Phys. YETP, **69**, 1155 (1989).
6. C. C. Versace, R. Bartolino, M. Ghedini, F. Neve, S. Armentano, M. Petrov and N. Kirov, *Mol. Cryst. Liq. Cryst.*, (in press) (1990).