

FERROELECTRIC CRYSTALS, FERROELECTRIC INCOMMENSURATE SYSTEMS AND  
FERROELECTRIC LIQUID CRYSTALS

B. Žekš

Institute of Biophysics, Medical Faculty,  
Lipičeva 2, 61105 Ljubljana, Yugoslavia and  
"J.Stefan" Institute, Jamova 39, 61111 Ljubljana, Yugoslavia

Abstract Some of the recent developments in the theory of phase transitions in ferroelectric crystals, ferroelectric incommensurate systems and ferroelectric liquid crystals are reviewed. For  $\text{KH}_2\text{PO}_4$ -type ferroelectrics the expressions for the static and dynamic properties derived by four-cluster analysis are compared with those found from a mean field treatment of the Ising model. The dielectric susceptibility investigation of a sequence of paraelectric-incommensurate-commensurate phase transitions in  $\text{Rb}_2\text{ZnCl}_4$  is presented and a dielectric method for determination of the soliton density and of the intersoliton interaction is described. The model of ferroelectric smectic C\* liquid crystals is reviewed, which includes the bilinear as well as the bi-quadratic coupling between the tilt of molecules from the normal to smectic layers and the spontaneous polarization and which is consistent with the observed anomalous properties of the system.

## I. INTRODUCTION

In this contribution a part of the research of ferroelectric systems performed in Ljubljana in last years will be presented. In Section II the properties of  $\text{KH}_2\text{PO}_4$ -type ferroelectrics will be studied. For these systems /1, 2/ the order parameter of the phase transition between the paraelectric phase and the ferroelectric phase is the ordering of protons (or deuterons for  $\text{KD}_2\text{PO}_4$ ) in hydrogen bonds. The spontaneous polarization originates from the displacements of heavy ions, which are linearly coupled to the ordering of protons. These crystals are therefore proper ferroelectrics and show e.g. a classical Curie-Weiss law behaviour for the dielectric susceptibility.

In Section III some properties of incommensurate crystals of  $\text{Rb}_2\text{ZnCl}_4$  - type will be presented /3/. These systems undergo a sequence of phase

transitions from the high temperature paraelectric (P) phase to the incommensurate (IC) phase and finally to the low temperature commensurate (C) phase, which is ferroelectric. The order parameter of the P - IC phase transition is a frozen-in lattice vibration with a general wave-vector, which is incommensurate to the periodicity of the paraelectric phase. The spontaneous polarization is nonlinearly coupled to the order parameter and forms in the incommensurate phase a modulated structure. This modulation of the spontaneous polarization is sinusoidal close to the P - IC transition and becomes more and more soliton-like at lower temperatures. The soliton density is decreasing with decreasing temperature until at the IC - C transition becomes equal to zero and the homogeneous ferroelectric commensurate phase is formed. Therefore the soliton density can be considered as the order parameter of the IC - C transition. The temperature dependence of the dielectric susceptibility shows at the P - IC transition only a small anomaly, i.e. a discontinuity in the derivative, because the wave vector  $q = 0$ , which corresponds to dielectric measurements, is not the critical wave vector of the transition and because the polarization is nonlinearly coupled to the order parameter and the system could be considered as an improper modulated ferroelectric. At the IC - C transition the dielectric susceptibility shows an asymmetric divergent behaviour. It diverges from the IC side and remains finite in the C phase. This is because the modulation wave-length in the IC phase diverges at the IC - C transition, while the magnitude of the spontaneous polarization in the C phase remains finite at the IC - C transition.

In Section IV some anomalous properties of ferroelectric chiral smectic C\* (SmC\*) liquid crystals will be studied /4/. In these systems the order parameter of the transition from the smectic A phase (SmA) to the smectic C\* phase is the tilt of the molecular director from the normal to smectic layers. The chirality of molecules has two effects: (i) The tilt is not homogeneous but forms a helicoidal structure with the helical axis which is perpendicular to smectic layers. (ii) The chirality allows a linear coupling between the tilt and the spontaneous polarization, which is induced within smectic layers perpendicularly to the direction of the tilt. Because of the helical structure and because of the linear coupling of the spontaneous polarization to the order parameter, these systems are proper helicoidal ferroelectrics. They are expected to show in the dielectric susceptibility an anomaly at the SmA - SmC\* transition, which is not divergent and has a cusp-like behaviour because the critical wave-vector of the transition is different from zero. The experiments confirm the predictions of the model at the transition, but show anomalous effects in the SmC\* phase. These effects can be understood by introducing a nonlinear polarization-tilt coupling, which is of nonchiral character in contrast to the linear coupling /5, 6, 7/.

## II. MEAN FIELD APPROXIMATION IN $KD_2PO_4$ -TYPE FERROELECTRICS

For deuterated systems, it is generally believed, that the tunnelling of a deuteron between the two positions in a hydrogen bond is negligible /1/ and the energy of the crystal is the sum of the energies of all  $PO_4$ -groups which can have sixteen different configurations. According to the Slater-Takagi model /8, 9/ the energy zero is assigned to the two polar  $D_2PO_4$  groups, the energy  $\epsilon$  to the other four  $D_2PO_4$  configurations, the energy  $w$  to the four  $DPO_4$  configurations, the energy  $w'$  to the four  $D_3PO_4$  configuration and the energies  $w_1$  and  $w_2$  to the groups  $PO_4$  and  $D_4PO_4$ , respectively. The energies  $w$ ,  $w'$ ,  $w_1$  and  $w_2$  are much larger than  $k_B T$  and therefore strong correlations between the deuterons in the four hydrogen bonds surrounding a given  $PO_4$  group exist. The Slater-Takagi model can be also expressed as an Ising model, where a spin-1/2 is associated with a deuteron in a hydrogen bond. Because of strong correlations the mean field treatment of the Ising model is expected to be only of a qualitative value and four-particle cluster calculations /10/ are required for a quantitative analysis. Nevertheless, the mean field expressions are often used for an analysis of experimental data in view of their simplicity. Therefore the question can be asked to what extent can the cluster results be simulated by mean field expressions and what is the meaning of the parameters obtained in this way. By comparing the two models /2, 11/ it is easy to see that the 4-cluster model is equivalent to the mean-field Ising model with an effective, temperature dependent coupling constant  $\tilde{J}_0$  given by

$$\tilde{J}_0 = \frac{6 - 4 \exp(-\beta\epsilon) - \exp(-\beta w_1) - \exp(-\beta w_2)}{2\beta \{2 + \exp(-\beta w) + \exp(-\beta w')\}} + \gamma \quad (1)$$

where  $\beta = 1/k_B T$  and  $\gamma$  represents the contribution of long range forces. For the parameters corresponding to  $KD_2PO_4$ , the temperature dependence of  $\tilde{J}_0$  is presented in Fig. 1. For  $T = T_c$  the temperature dependence is linear  $\tilde{J}_0(T) = k_B T_c + 0.5k_B(T - T_c)$ . For the mean field Ising model susceptibility one therefore obtains

$$\chi = N\mu^2 \frac{1}{k_B T - \tilde{J}_0} = \frac{2N\mu^2}{k_B} \frac{1}{T - T_c} = \frac{(N/2)(2\mu)^2}{k_B} \frac{1}{T - T_c} \quad (2)$$

Here  $N$  is the hydrogen bond density and  $\mu$  the corresponding dipole moment. From Eq. (2) one can see clearly that to one spin in the Ising model corresponds a dipole moment  $2\mu$  and the density is  $N/2$ . As there are two bonds per  $PO_4$  group it can be concluded that a  $PO_4$  group corresponds to a spin and the parameters

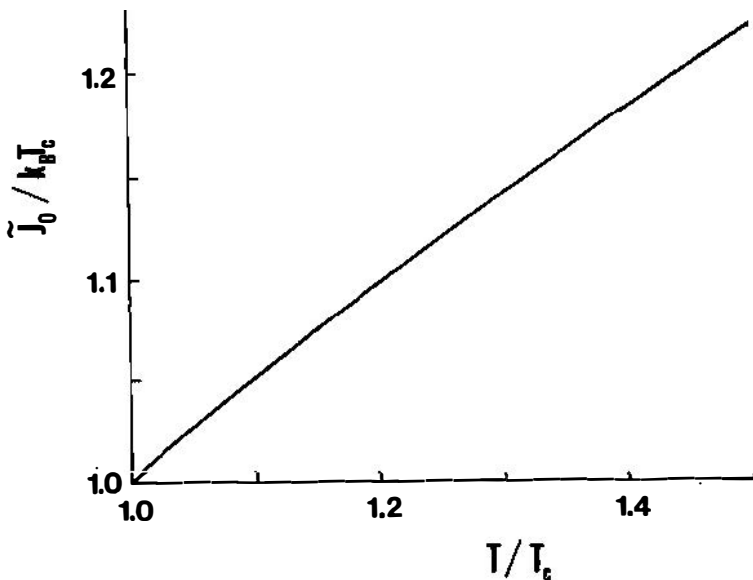


Fig. 1 The temperature dependence of the effective Ising model coupling constant  $J_0$  for  $KD_2PO_4$ .

obtained in such a way from experiments refer to a  $PO_4$  group and not to a hydrogen bond.

By performing the analogous analysis for dynamic properties one obtains /2, 11/ for the single spin, i.e. for the single  $PO_4$  group, the relaxation time

$$\tilde{\tau} = \tau \frac{3}{16} (1 + 2e^{-\beta\epsilon}) e^{\beta w} \quad (3)$$

where  $\tau$  is a single deuteron relaxation time. The  $PO_4$  group relaxation time, which is obtained by analysing experimental data, is much larger than  $\tau$ , because the  $PO_4$  group must go through high energy states to come from one ground state to another.

### III. DIELECTRIC PROPERTIES OF $Rb_2ZnCl_4$

Temperature dependence of the dielectric constant of  $Rb_2ZnCl_4$  in the incommensurate phase is presented in Fig. 2. In the figure the results of model calculations /3/ are shown, which agree perfectly with experimental data. As expected, the dielectric constant diverges when approaching the IC - C transition from the IC side.

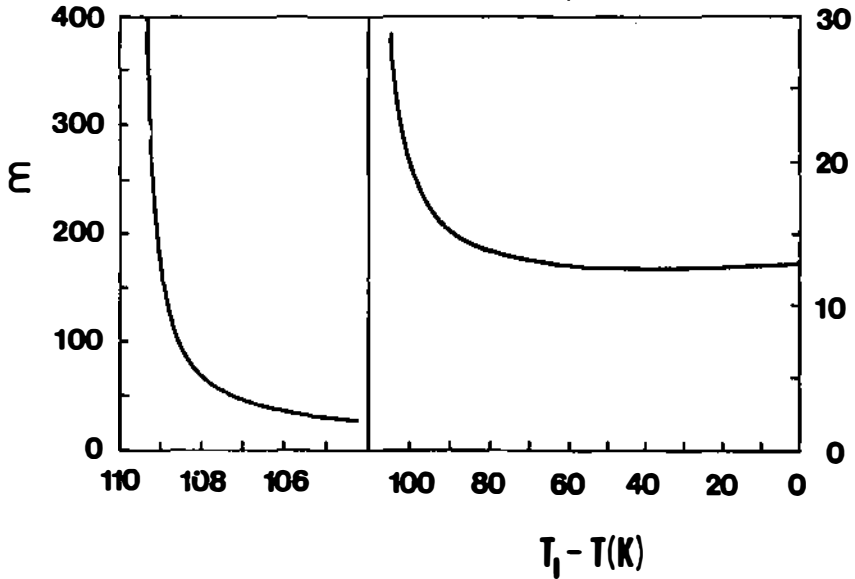


Fig. 2 Dielectric constant  $\epsilon$  versus  $T_I - T$  in the incommensurate phase of  $Rb_2ZnCl_4$ . Here  $T_I$  is the P - IC phase transition temperature.

Below the IC - C transition temperature  $T_c$  one expects a finite and small value of  $\epsilon$ . The measurements /12/ do not show a sharp drop of  $\epsilon$  at  $T_c$ , but an asymmetric divergency is observed which shows large hysteresis below  $T_c$ . The origin of this anomalous contribution to  $\epsilon$  below  $T_c$  is, that even in the commensurate phase a finite number of solitons is present. From dielectric measurements one can estimate the soliton density for  $T < T_c$ , which agrees well with the NMR results /12/.

By measuring the dielectric constant within the commensurate phase in the bias electric field one can estimate the intersoliton interaction potential as a function of the intersoliton distance /13/. Within the constant amplitude approximation, the intersoliton interaction is expected to be exponentially repulsive, but could also have an oscillatory character in the regime, where the constant amplitude approximation is not valid. The dielectric measurements /13/ on  $Rb_2ZnCl_4$  for  $T < T_c$  show that the intersoliton interaction is exponential close to  $T_c$  but becomes oscillatory at low temperatures.

#### IV. FERROELECTRIC LIQUID CRYSTALS

Ferroelectric smectic C\* liquid crystals /4, 14/ are orientationally ordered liquids with a one dimensional density modulation. The smectic C phase is ferroelectric if the molecules are chiral and have a permanent dipole moment transverse to their long molecular axis. In the high temperature smectic A phase the molecules are arranged in smectic layers and their long axes are on the average oriented perpendicular to the layers. They rotate freely around their long axes and there is no transverse ordering. In smectic C phase, the tilt of the long molecular axis from the normal to smectic layers breaks the axial symmetry around the long molecular axis and a transverse ordering is induced resulting in a transverse in-plane polarization perpendicular to the direction of the tilt. Because of the chirality of molecules in chiral smectic C\* systems the molecular tilt as well as the in-plane polarization slowly rotate on going from one smectic plane to another, resulting in a helical structure.

The properties of ferroelectric smectic C\* liquid crystals can be described by a Landau free-energy expansion in two order parameters. These are the primary order parameter, the two component tilt vector  $\vec{\xi} = (\xi_1, \xi_2)$  and the secondary order parameter, the two-component in-plane polarization  $\vec{P} = (P_x, P_y)$ . For chiral systems, the symmetry allows for two types of bilinear coupling between the molecular tilt and the molecular polarization /14, 15/. Namely the piezo-electric coupling

$$P_x \xi_2 - P_y \xi_1 \quad (4)$$

and the flexo-electric coupling

$$P_x \frac{d\xi_1}{dz} + P_y \frac{d\xi_2}{dz} \quad (5)$$

where z-axis is perpendicular to smectic layers. The piezo-electric coupling is of chiral nature and does not exist for achiral systems. The flexo-electric coupling exists for chiral as well as for achiral systems, but for achiral systems the molecules tilt homogeneously ( $d\xi_1/dz = d\xi_2/dz = 0$ ) and the flexo-electric coupling has no effect. Therefore the spontaneous polarization does not exist for achiral systems and is different from zero only for chiral systems. In the helicoidal smectic C\* systems the spontaneous polarization induced by the above two couplings is perpendicular to the direction of the tilt and is proportional to the magnitude of the tilt. Measurements /6, 16/ do not confirm the predicted behaviour of the spontaneous polarization and also the predictions

of the model for other thermodynamic properties of ferroelectric liquid crystals (pitch of the helix, dielectric susceptibility, critical electric and magnetic fields for unwinding the helicoidal structure, etc.) do not agree qualitatively with measured data /17/. It was therefore proposed /5/ that a biquadratic coupling

$$(P_x \xi_2 - P_y \xi_1)^2 \quad (6)$$

between the tilt and the polarization could be relevant in the smectic C\* phase. The meaning of this coupling is, that the tilt induces for chiral as well as for achiral systems a transverse quadrupole ordering in the direction perpendicular to the tilt. This coupling is quadratic in the tilt and has therefore no effect close to the transition from the smectic A to the smectic C\* phase, where only the bilinear couplings (Eqs. 4 and 5) determine the properties of the system. At lower temperature in the smectic C\* phase the quadratic term becomes important and amplifies the effect of the bilinear couplings. The anomalous behaviour of thermodynamic properties of ferroelectric liquid crystals /6, 7, 18/ can be explained as a cross-over behaviour between the two regimes.

The spontaneous polarization is usually measured for helicoidal ferroelectric liquid crystals /6, 16/ in a state unwound by an external electric field. The corresponding Landau free energy density can be expressed as

$$g = -CP\theta - \frac{1}{2}\Omega P^2 \theta^2 + \frac{1}{2\epsilon} P^2 + \frac{1}{4}\eta P^4 \quad (7)$$

Here it was taken that the molecules are tilted homogeneously in the x-direction:  $\vec{\xi} = (\theta, 0)$ , where  $\theta$  is the magnitude of the tilt, and the polarization is induced in the y-direction:  $\vec{P} = (0, P)$ . The first term in the above free energy density is the piezo-electric coupling term. Its coefficient C is small, because it is of chiral nature and all the chiral effects are expected to be small. The piezo-electric coupling is the only bilinear P- $\theta$  coupling because the flexo-electric coupling vanishes in a homogeneously ordered samples. The  $\Omega$ -term in Eq. (7) is the biquadratic P- $\theta$  coupling. We will take here  $\Omega > 0$ . It means that the quadrupole order is induced by tilt in the same direction as the dipole order and therefore the biquadratic coupling amplifies the effect of the bilinear coupling. In Eq. (7)  $\epsilon$ , the coefficient of the harmonic term in P, corresponds to the high temperature dielectric susceptibility and the fourth order term with  $\eta > 0$  is added to stabilize the system.

The free energy density g (Eq. 7) represents at given tilt a nonequilibrium free energy density as a function of polarization P. The square of the tilt represents an approximate measure for the temperature T, as it is expected

within the Landau model that the tilt below the transition temperature  $T_c$  in the smectic C\* phase increases monotonously and approximately as  $(T_c - T)^{1/2}$ . The equilibrium value of the polarization is obtained by minimizing the free energy density with respect to P

$$\frac{d\mathcal{G}}{dP} = \eta P^3 + \left(\frac{1}{\epsilon} - \Omega\theta^2\right)P - C\theta = 0 \quad (8)$$

It is appropriate to introduce dimensionless tilt ( $\tilde{\theta}$ ) and dimensionless polarization ( $\tilde{P}$ ) as

$$\tilde{\theta} = (\epsilon\Omega)^{1/2}\theta, \quad \tilde{P} = (\epsilon\eta)^{1/2}P \quad (9)$$

and the equation (8) can be expressed as

$$\tilde{P}^3 + (1 - \tilde{\theta}^2)\tilde{P} - \beta\tilde{\theta} = 0 \quad (10)$$

where the only parameter  $\beta$  is defined as

$$\beta = \frac{\epsilon\eta^{1/2}C}{\Omega^{1/2}} \quad (11)$$

and measures a relative importance of the chiral bilinear coupling coefficient C, which is expected to be small ( $\beta < 1$ ). By solving the Eq. (10) one obtains the dependence of the spontaneous polarization on the tilt and indirectly on the temperature, which agrees with measured dependences /6, 16/. Close to  $T_c$ , i.e. for  $\tilde{\theta} \rightarrow 0$ , the ratio  $\tilde{P}/\tilde{\theta} = \beta$ . By lowering the temperature, i.e. by increasing  $\tilde{\theta}$ , the ratio  $\tilde{P}/\tilde{\theta}$  increases and saturates at  $\tilde{P}/\tilde{\theta} = 1$ . By comparing the predictions of the model with the measured data /7, 18/ one obtains an estimate for the parameters of the model:  $\beta = 0.17$ ,  $(\epsilon\Omega)^{-1/2} = 0.2 \text{ rad}$  and  $(\epsilon\eta)^{-1/2} = 1.3 \times 10^{-5} \text{ Asm}^{-2}$ .

The model describes well also other thermodynamic properties of the smectic C\* phase /7, 18/.

#### References

- /1/ R.Blinc and B.Žekš, "Soft Modes in Ferroelectrics and Antiferroelectrics", North-Holland, Amsterdam (1974).
- /2/ R.Blinc and B.Žekš, *Ferroelectrics* 72, 193 (1987).
- /3/ A.Levstik, P.Prelovšek, C.Filipič, and B.Žekš, *Phys. Rev. B* 25, 3416 (1982).
- /4/ R.B.Meyer, L.Liebert, L.Strzelecki, and P.Keller, *J. Physique Lett.* 36, L69 (1975).

- /5/ B.Žekš, Mol. Cryst. Liq. Cryst. 114, 259 (1984); Ferroelectrics 53, 33 (1984).
- /6/ S.Dumrongrattana and C.C.Huang, Phys.Rev.Lett. 56, 464 (1986).
- /7/ T.Carlsson, B.Žekš, A.Levstik, C.Filipič, I.Levstik, and R.Blinc, Phys. Rev. A 36, 1484 (1987).
- /8/ J.C.Slater, J. Chem. Phys. 9, 16 (1941).
- /9/ Y.Takagi, J. Phys. Soc. Japan 3, 271; 273 (1948).
- /10/ H.B.Silsbee, E.A.Uehling and V.H.Schmidt, Phys. Rev. 133, A165 (1964).
- /11/ A.Levstik, D.R.Tilley and B.Žekš, J. Phys. C: Solid State Phys. 17, 3793 (1984).
- /12/ R.Blinc, P.Prelovšek, A.Levstik, and C.Filipič, Phys. Rev. B 29, 1508 (1984).
- /13/ A.Levstik, H.G.Unruh and P.Prelovšek, Phys. Rev. Letters 58, 1953 (1987).
- /14/ S.A.Pikin and V.L.Indenbom, Usp. Fiz. Nauk 125, 251 (1978).
- /15/ R.Blinc and B.Žekš, Phys. Rev. A 18, 740 (1978).
- /16/ C.Filipič, A.Levstik, I.Levstik, R.Blinc, B.Žekš, M.Glogarova, and T.Carlsson, Ferroelectrics 73, 295 (1987).
- /17/ R.Blinc, B.Žekš, I.Mušević, and A.Levstik, Mol. Cryst. Liq. Cryst. 114, 189 (1984).
- /18/ T.Carlsson, B.Žekš, C.Filipič, A.Levstik, and R.Blinc, Mol. Cryst. Liq. Cryst. 163, 11 (1988).